Salicylaldoxime (H$_2$salox) in iron(III) carboxylate chemistry: Synthesis, X-ray crystal structure, spectroscopic characterization and magnetic behavior of trinuclear oxo-centered complexes

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Abstract

Two new neutral trinuclear oxo-centered complexes, [Fe$_3$(μ$_3$-O)(O$_2$CPh)$_5$(salox)L$_1$L$_2$] [L$_1$ = L$_2$ = MeOH (1), L$_1$ = EtOH, L$_2$ = H$_2$O (2)] are reported. In both complexes, the central oxygen atom is bridging the three iron(III) ions, which form a triangle with an average edge of 3.3 Å. The central Fe$_3$(μ$_3$-O)$^{7+}$ core is planar. The benzoato ligands are coordinated through the usual syn$_1$,syn$_2$:g$_1$:g$_1$:$g_1$:$g_1$ mode and the salicylaldoximato ligand shows the common μ$_2$:$η^1$:η$^1$ coordination mode. Two of the iron(III) ions have an O$_6$ coordination environment while the third has an O$_5$N one. The two crystallographically independent trimers in the structure of 1 (a and b, respectively) through intermolecular interactions form polymeric chains of the...a–a–b–b... type, along the ac diagonal of the unit cell. In 2, again through intermolecular interactions, the trimers form layers lying parallel to the [1 0 1] plane. Møssbauer spectra at room temperature from polycrystalline samples of 1 and 2 give rise to two well-resolved doublets with an average isomer shift consistent with high spin iron(III) ions. The two doublets, at 2:1 ratio, are characterized by different quadrupole splitting and are assigned to the nonequivalent iron(III) ions of the clusters. Magnetic measurements of 1 and 2 in the 2–300 K temperature range show antiferromagnetic interactions between the iron(III) ions in the trimers stabilizing a S = 1/2 ground state. The derived values for the exchange interaction constants fall in the range usually found in Fe$_3$(μ$_3$-O)$^{7+}$ clusters. Solid state X-band EPR spectra of 1 and 2 at liquid helium temperatures give rise to broad lines extending several hundred Gauss, indicating weak intermolecular interactions. EPR spectra from 1 and 2 in an acetone glass at 4.2 K exhibit a strong symmetric signal at g ~ 2.0 which is attributed to the S = 1/2 ground state of the clusters.

Keywords: Trinuclear oxo-centered Fe(III) complexes; Salicylaldehyde oxime; Magnetochemistry; Crystal structures; EPR spectroscopy; Mössbauer spectroscopy

1. Introduction

Our interest in the coordination chemistry of phenolic oximes is related to our continuing effort to synthesize polynuclear 3d metal clusters in a quest for new molecule-based magnetic materials. ‘Metal-oximates’ have been attracting the interest of inorganic chemists, since they can be used as ‘building blocks’ for the designed synthesis of polynuclear clusters [1]. According to this synthetic route, the ligands already bound to one metal have free coordination sites and can bind to a second metal of the same or different kind. The major advantages of this method are, the better control of the reaction and of the products formed, factors that cannot be controlled by following the self-assembly route. By using the strategy of ‘metal oximates’ as building blocks, various homo- and hetero-metal complexes have been synthesized [2–8]. The propensity of phenolic oximes to form polynuclear complexes by using both the oxime...
and phenolate groups as chelating and/or bridging units, along with their ability to act in their mono- or di-anionic form, make them interesting candidates for the exploration of their metal coordination chemistry [9].

In their mono-anionic form, phenolic oximes usually act as chelating agents through their oximate nitrogen and phenolate oxygen atoms (mode A in the following scheme) in a variety of mono- and poly-nuclear metal complexes [10–14]. A more interesting coordination mode, includes the use of the phenolate oxygen atom as both chelating and bridging agent (mode B) [10,15].

In their di-anionic form, phenolic oximes usually use their phenolate oxygen and oximate nitrogen atoms to chelate to one metal ion and their oximate oxygen as bridging unit to bind a second metal (mode C). A variety of di- [16–18], tri- [14,19] and tetranuclear [20–22] metal complexes presenting the $\mu_2: \eta^1: \eta^1$ coordination mode have been reported. The oximate oxygen atom can also bind two metal ions, presenting the $\mu_3: \eta^1: \eta^2: \eta^1$ coordination mode (mode D) giving rise to higher nuclearity complexes, such as hexanuclear [23,24], although this coordination mode is also observed in trinuclear [25] and tetranuclear [26] complexes. There is also one example [10] where the dianion of phenolic oximes can act as chelating tridentate ligand according to mode E.

Further restricting our discussion to polynuclear iron(III) complexes with the simplest member of the phenolic oximes, 2-hydroxy-benzaldehyde (salicylaldoxime, H$_2$salox), only a few examples have been reported. As far as we know, the only example of iron(III) salicylaldoximato complex is the tetranuclear [11] cluster [Fe(Hsalox)(salox)$_2$)$_4$, in which the four Hsalox$^-$ act as chelating agents through their phenolate oxygen and oximate nitrogen atoms (mode A), whilst the four salox$^{2-}$ further use their oximate oxygen atom to bind to two additional metal centers (mode D). In the remaining examples, coligands have been used to complete the coordination spheres of iron(III) centers in polynuclear complexes. In the dinuclear compound [(Me$_3$tacln)Fe(III)(salox)$_2$Fe(III)] [16], as well as in the tetranuclear compound [(Me$_3$tacln)$_2$Fe$_4$(salox)$_2$($\mu_3$-O)$_2$ ($\mu_2$-CH$_2$CO$_2$)$_3$](ClO$_4$) [20] (where Me$_3$taclln = 1,4,7-triazacyclononane) the dianion of salicylaldoxime adopts the $\mu_2: \eta^1: \eta^1: \eta^1$ coordination mode. The only trinuclear iron(III) salicylaldoximato complex known so far is [(C$_2$H$_5$)$_3$NH][Fe$_3$(Osalox)$_2$ (salmp)] [19] (salmp = 2-(bis(salicylideneamino)-methyl) phenol, a new ligand formed during the reaction process), where the Hsalox$^-$ ligands act as chelating units and the salox$^{2-}$ ligands adopt the $\mu_2: \eta^1: \eta^1: \eta^1$ coordination mode.

The aim of our project is to explore the use of salicylaldoxime in iron(III) carboxylate chemistry, encouraged by our previous results on manganese(III) [24]. Herein, we report the first results of our project, in particular the synthesis, X-ray crystal structure, spectroscopic (solid state and frozen solutions EPR, Mössbauer) characterization and magnetic behavior of two neutral trinuclear oxo-centered iron(III) complexes, [Fe$_3$(\mu$_3$-O)- (O$_2$CPh)$_3$)(salox)$_2$] (L$_1$ = L$_2$ = MeOH (1), L$_1$ = EtOH, L$_2$ = H$_2$O (2)). The reported complexes are the first examples of trinuclear carboxylato iron(III) complexes with salicylaldoxime, and can be considered as precursors for the synthesis of higher nuclearity complexes, based on the principle of using ‘metal oximates’ as ‘building blocks’ for polynuclear clusters. In both compounds, the salox$^{2-}$ ligands adopt the $\mu_2: \eta^1: \eta^1: \eta^1$ coordination mode (mode C) thus, the possibility of further using the oximate oxygen atom, under certain reaction conditions, to bind to a second metal is left open.

2. Experimental

2.1. Compound preparations

All manipulations were performed under aerobic conditions using materials as received (Aldrich Co). All chemicals and solvents were of reagent grade.

2.1.1. $[Fe_3(\mu_3-O)(O_2CPh)_3(salox)(MeOH)]_2 \cdot 1.25MeOH \cdot 1.05H_2O$ (1)

A methanolic solution of H$_2$salox (0.069 g, 0.50 mmol) was stirred under reflux, until sodium benzoate (0.216 g, 1.50 mmol) was added. The reflux continued for 30 min and then Fe(NO$_3$)$_3$ · 9H$_2$O
(0.202 g, 0.50 mmol) was added. The color of the solution immediately turned to deep brown. After 24 h of reflux, small amounts of a brown-red solid were filtered, washed with MeOH and identified as compound 1 by FT-IR spectroscopy. The brown filtrate was sealed and after a period of one week X-ray quality brownish-red crystals of 1 were formed (Yield: 0.34 g, ~70%). The crystals of 1 were collected by filtration, washed with cold MeOH and dried in vacuo. The resulting powder analyzed as solvent-free. Anal. Calc. for (C₄₅H₄₆Fe₃NO₁₇.₃): C, 53.47; H, 3.88; N, 1.40%.

2.2. General and physical measurements

Elemental analysis for carbon, hydrogen, and nitrogen was performed on a Perkin Elmer 2400/II automatic analyzer. Infrared spectra were recorded as KBr pellets in the range 400–500 cm⁻¹ on a Bruker Equinox 55/S FT-IR spectrophotometer. EPR spectra were recorded on a Bruker ER 200D-SCC X-band spectrometer equipped with an Oxford ESR 9 cryostat in 4.2–300 K temperature range. Variable temperature magnetic susceptibility measurements were carried out on polycrystalline samples of 1 and 2 in the 2.0–300 K temperature range using a Quantum Design MPMS SQUID susceptometer under a magnetic field of 1000 G. Magnetization measurements were carried out at 2.5 K over the 0–5 T magnetic field range. Diamagnetic corrections for the complexes were estimated from Pascal’s constants. Mössbauer spectra were taken with a constant acceleration spectrometer using a ⁵⁷Co (Rh) source at RT and a variable temperature Oxford cryostat.

2.2.1. X-ray crystallography and solution of structures

Brownish-red prismatic crystals of 1 (0.05 x 0.25 x 0.75 mm) and 2 (0.05 x 0.15 x 0.25 mm) were mounted in capillary with drops of mother liquid. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Important crystal data and parameters for data collection for 1 are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11° < 2θ < 23°. Intensity data were recorded using a 0–2θ scan. Three standard reflections, monitored every 97 reflections showed less than 3% intensity fluctuation and no decay. Lorentz, polarization and ψ-scan absorption corrections were applied using Crystal Logic software. The structures were solved by direct methods using SHELXS-86 [26] and refined by full matrix least-squares techniques on F² with SHELXL-97 [27]. Further experimental crystallographic details for 1: 2θmax = 40°, scan speed 1.2°/min; scan range 1.7 + 2θ/2 separation; reflections collected/unique/used, 7740/7452 \( | \chi_{int} = 0.0332| / 7452 ; 779 \) parameters refined; (Δ/σ)max = 0.014; (Δ/σ)max = 0.725–0.579 eÅ⁻³; R/Rw (for all data), 0.1223/0.2282. The crystals of 1 were of poor diffraction ability, despite their sufficient size, so the data collection stopped at 20 = 40° because over half of the reflections collected were unobserved. Nevertheless, the quality of the data is adequate to establish the structure. Due to the lack of sufficient number of data only the metal ions and the coordinated atoms as well as the salox⁻² ligands were refined anisotropically. The phenyl rings of the benzoates were refined isotropically and fixed to the geometry of a regular hexagon. Hydrogen atoms on the phenyl rings and on the methyl groups of the coordinated methanol were introduced at calculated positions as riding on bonded atoms. Further experimental crystallographic details for 2: C₄₆H₄₄NO₁₅Fe₃, fw = 1033.93, a = 15.12(2) Å, b = 15.61(2) Å, c = 20.15(2) Å, β = 95.26(3)°, V = 4736(2) Å³, Z = 4, space group P2₁/n, 2θmax = 35° (data collected between 35° and 40° was more than 70% unobserved and it was not used), scan speed 1.2°/min; scan range 1.7 + 2θ/2 separation; reflections collected/unique/used, 3125/2971 \( | \chi_{int} = 0.0401| / 2971 ; 208 \) parameters refined; (Δ/σ)max = 0.013; (Δ/σ)max = 0.96/0.91 eÅ⁻³; R/Rw (for 1797 refs with I > 2σ(I)), 0.2486/0.5077; R/Rw (for all data), 0.3458/0.5897. The crystals of 2 were very small in size.

| Table 1 |
| Crystallographic data for complex 1⋅1.25MeOH⋅1.05H₂O |
| Formula | C₄₅H₄₆Fe₃NO₁₇.₃ |
| Formula weight | 1048.30 |
| Space group | P₂₁/c |
| Unit cell dimensions |
| a (Å) | 19.672 |
| b (Å) | 26.962 |
| c (Å) | 19.702 |
| β (°) | 98.84(3) |
| V (Å³) | 10323(2) |
| Z | 8 |
| T (°C) | 298 |
| Radiation | Mo Kα |
| ρcalc (g/cm³) | 1.348 |
| μ (mm⁻¹) | 0.899 |
| R₁ | 0.0775 |
| wR₁ | 0.1994 |

R₁ = \( \sum |F₁| − |F₁| \sum |F₁| + wR₂ = \{ \sum [w(F₂ − F₂)²]/\sum [w(F₂)²] \}^{1/2} \) for 5082 reflections with I > 2σ(I).

\( \text{a} = 0.1046, b = 0.86, 0.0886. \)
and of very poor diffraction quality. Repeated efforts to grow larger crystals proved unsuccessful. We continued with data collection in order to establish the gross structure of the complex. Since the structure of 2 proved quite similar to that of 1, we felt that complete structural characterization was not crucial. Thus, the refinement was done with anisotropic thermal parameters for the iron(III) ions only, whilst all the rest atoms were refined isotropically. No H-atoms were included in the refinement. The phenyl rings of the salox$^{2-}$ and benzoate ligands were fitted to the geometry of a regular hexagon. The crystallographic analysis revealed the presence of one ethanol of crystallization per trimeric complex.

3. Results and discussion

3.1. Syntheses

As mentioned earlier, our aim was to investigate the use of salicylaldehyde oxime (H$_2$salox) to the iron(III) carboxylate chemistry, extending our previous experience on manganese [24]. The 1:1 molar ratio reaction of Mn(O$_2$CR)$_2$ (R = Me, Ph) and H$_2$salox in EtOH led to the hexanuclear complexes [Mn$_6$O$_{12}$ (O$_2$CR)$_2$ (salox)$_6$ (EtOH)$_4$] (R = Me, Ph). These complexes contain the novel Mn$_6$O$_{12}$ core, whose topology consists of six Mn ions arranged as two {Mn$_3$(salox)} trimers bridged by two oximato oxygen atoms. Both compounds proved to behave as single molecule magnets (SMM) and are the first members of a new class of manganese-based SMMs containing exclusively Mn$^{III}$ ions with blocking temperature greater than 2 K. In order to investigate the possibility of synthesizing the corresponding polynuclear iron(III) complexes and to study their magnetic properties, we have designed the 1:3:1 molar ratio reaction of Fe(O$_2$CPh)$_3$ and H$_2$salox in alcoholic media. The 1:3:1 molar ratio has been chosen so that the M/carboxylate/H$_2$salox ratio remains the same in going from manganese(II) to iron(III) ions. But it turned out that in the iron(III) case, the amount of the carboxylate ions was very high, and the trinuclear oxo-centered complexes 1 and 2 were formed. The salox$^{2-}$ ions are coordinated through the usual $\mu_2$:$\eta_1$:$\eta_1$ mode while the possibility of further use of the oximato oxygen atom to bridge a second metal and to increase the nuclearity of the derived complex has failed. Nevertheless, we still consider compounds 1 and 2 as useful staring materials for polynuclear iron(III) complexes, under different reaction conditions.

The synthesis of 1 and 2 can be summarized in Eqs. (1) and (2), respectively, based on the reasonable assumption that H$_2$O from the starting materials and/or the solvent is the source of the O$^-$ ion.

$$3\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} + 5\text{PhCO}_2\text{Na} + \text{H}_2\text{salox} + 2\text{MeOH} \rightarrow \frac{\text{MeOH}}{\text{EtOH}} \cdot \left[ \text{Fe}_2\text{O}(\text{O}_2\text{CPh})_3(\text{salox})(\text{MeOH})_2 \right] + 5\text{NaNO}_3 + 4\text{HNO}_3 + 26\text{H}_2\text{O} \quad (1)$$

$$3\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 5\text{PhCO}_2\text{Na} + \text{H}_2\text{salox} + \text{EtOH} \rightarrow \frac{\text{EtOH}}{\text{MeOH}} \cdot \left[ \text{Fe}_2\text{O}(\text{O}_2\text{CPh})_3(\text{salox})(\text{EtOH})(\text{H}_2\text{O}) \right] + 5\text{NaCl} + 4\text{HCl} + 16\text{H}_2\text{O} \quad (2)$$

3.2. IR spectroscopy

In the IR spectrum of both 1 and 2, medium-intensity bands at 3451, 3063, 2924 cm$^{-1}$ (for 1) and 3414, 3063, 2980 cm$^{-1}$ (for 2), are assigned to the $\nu$(OH)$_2$O, $\nu$(CH)$_{aromatic}$, $\nu$(CH$_3$), respectively. Strong intensity bands at 1598 cm$^{-1}$ and medium intensity bands at 1286 cm$^{-1}$ observed in the spectrum of both complexes are assigned to the $\nu$(C=O) of the salicylaldoximato ligand [28]. The frequencies of the $\nu$(CO$_2$) bands of PhCO$_2$ coincide in the spectra of 1 (1406 cm$^{-1}$) and 2 (1405 cm$^{-1}$). The bands at 1557 cm$^{-1}$ in 1 and 2, respectively, are assigned to the $\nu$(sal(O$_2$C)) of the benzoato ligands. The difference $\Delta = \nu$(sal(O$_2$C))$\nu$(sal(O$_2$C)$\nu$(CO$_2$)) for 1 is 151 cm$^{-1}$ and for 2 is 152 cm$^{-1}$, less than that for NaO$_2$CPh (184 cm$^{-1}$), as expected for the bridging modes of benzoate ligation [29]. A strong intensity band at 480 cm$^{-1}$ in the spectra of 1 and at 478 cm$^{-1}$ in the spectra of 2 is characteristic of the presence of the [Fe$_3$O] moiety in the structures of 1 and 2.

3.3. Structural description of $\left[ \text{Fe}_6(\mu_3-O)_{12} \cdot \text{salox}(\text{MeOH})_2 \right] \cdot 1.25\text{MeOH} \cdot 1.05\text{H}_2\text{O}$ (1)

Compound 1 crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent trinuclear complexes in the asymmetric unit (further reported as molecules 1a and 1b). The structure of the molecule 1a is given in Fig. 1. Selected bond distances and angles for both 1a and 1b are listed in Table 2. The structure of 1 consists of a trinuclear iron(III) oxo-centered complex. The three Fe$^{III}$ ions in 1a form an isosceles triangle whilst in 1b the triangle is best described as scalene (see Table 2). The Fe-O$_{oxo}$ bond distances are in the range 1.86–1.94 Å in both molecules 1a and 1b, and the central [Fe$_3$(µ$_3$-O)]$^{12+}$ moiety is planar. Ions Fe(2) and Fe(3) in molecule 1a and the corresponding ions Fe(5) and Fe(6) in molecule 1b have an octahedral oxygen rich coordination environment, while ions Fe(1) and Fe(4) in molecules 1a and 1b, respectively, have a distorted octahedral O$_5$N coordination geometry. The angles within the tetragonal plane of the octahedron range from 82.2° to 97.5° for 1a and from 78.5° to 99.1° for 1b. The angles involving the axial positions of the
octahedron range from 168.5° to 178.5° and from 163.9° to 178.1° in 1a and 1b, respectively.

The salicylaldoximato ligand shows the common \( \mu_2:\eta^1:\eta^1 \) coordination mode with the N–O oximato group and the phenolate oxygen atom lying above and below the \([\text{Fe}_3(\mu_3-O)]^7+\) plane, respectively. The Fe–Ooximato bond distances are 1.982 Å in both molecules 1a and 1b, the Fe–O phenoxy are 1.914 and 1.930 Å in molecules 1a and 1b, respectively. The whole salicylaldoximato ligand is planar and makes an angle of 51.1° and 65.3° with the \([\text{Fe}_3(\mu_3-O)]^7+\) plane in molecules 1a and 1b, respectively.

The benzoato ligands are coordinated in the common \( \text{syn, syn} \mu_2:\eta^1:\eta^1 \) mode. The Fe–O carboxylato bond distances are in the range 1.977–2.029 and 1.990–2.052 Å in molecules 1a and 1b, respectively.

The polymeric lattice structure of 1, shown in Fig. 2, arises from the strong intermolecular interactions between the isolated trimers. More specifically, the oximato oxygen atom O(1) in molecule 1a is strongly interacting (most likely through hydrogen bonding interactions) to a coordinated methanolic oxygen atom Om(1) belonging to a centrosymmetrically related molecule 1a \([O(1)\ldots Om(1) = 2.574 \text{ Å}]\). Thus, a dimer of trimers of the a–a type, is formed through two intermolecular interactions across a center of symmetry. The closest Fe···Fe interatomic distance in the a–a dimer is Fe(2)···Fe(2') = 5.067 Å. The same feature is observed in the case of molecule 1b, where the oximato oxygen atom O(61) is strongly interacting (most likely through H-bonding interactions) to a coordinated methanol Om(3) from a centrosymmetrically related molecule 1b \([O(61)\ldots Om(3') = 2.666 \text{ Å}]\). Thus, a dimer of trimers of the b–b type, is formed due to the double interactions described above. The closest Fe···Fe interatomic distance in the b–b dimer is Fe(5)···Fe(5') = 5.207 Å. Apart from the formation of dimers, another feature is also observed in the lattice structure of 1. The phenoxy oxygen atom O(62) of molecule 1b is

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Table 2

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strongly interacting (most likely through H-bond) to the second coordinated methanolic oxygen Om(2) of molecule 1a [O(62) ⋅ ⋅ ⋅ Om(2′) = 2.693 Å (2 − x, − y, 2 − z)]. Thus, polymeric chains of alternative dimers of the ...a–a–b–b... are formed along the ac diagonal of the unit cell. The closest Fe⋯Fe interatomic distance in the a–b part of the chain is Fe(3) ⋅ ⋅ ⋅ Fe(4′) = 5.518 Å.

3.4. Structural description of [Fe₃(μ₃-O)(O₂CPh)₅(salox)(EtOH)(H₂O)] · EtOH (2)

The structure of 2 (Figure S1) is analogous to that of compound 1, the only difference being in the monodentate ligands completing the octahedral coordination around the iron(III) ions (one ethanol and one water molecules instead of two methanols in 1). The three Fe³⁺ ions form a scalene triangle with edges 3.207, 3.277 and 3.306 Å. The Fe–O oxo bond distances are in the range 1.835–1.923 Å and the central [Fe₃(μ₃-O)]⁺ moiety is planar. Ions Fe(2) and Fe(3) have an octahedral oxygen rich coordination environment, while Fe(1) has a distorted octahedral O₅N coordination geometry.

Despite its similarities in the molecular structure with that of 1, compound 2 presents a different lattice structure originated by the existence of intermolecular interactions between the isolated trimers. Strong intermolecular interactions (possibly through H-bonds) between the oximato oxygen atom O(1) and the coordinated ethanolic oxygen atom Oe(1) of a centrosymmetrically related trimer [O(1) ⋅ ⋅ ⋅ Oe(1′) = 2.674 Å (− x, − y, 1 − z)], and between the phenolate oxygen atom O(2) and the coordinated water molecule Ow(1) of a neighboring trimer [O(2) ⋅ ⋅ ⋅ Ow(1″) = 2.967 Å (0.5 − x, − 0.5 + y, 0.5 − z)], are responsible for the 2D polymeric network (parallel to the [1 0 1] crystallographic plane) in 2 (Figure S2). The closest Fe⋯Fe interatomic distances due to the H-bonding interactions are Fe(2) ⋅ ⋅ ⋅ Fe(2′) = 5.075 Å, and Fe(1) ⋅ ⋅ ⋅ Fe(3″) = 5.913 Å.

Compounds 1 and 2 can be considered as part of the large ‘basic carboxylates’ family of trivalent oxo-centered trinuclear compounds with the general formula [M₃(μ₃-O)(O₂CR)L₃] (L = terminal monodentate ligand). The only difference between the ‘basic carboxylates’ and compounds 1 and 2 is that, one of the carboxylates and one of the terminal ligands have been replaced by the oximato and phenoxy group of the salicylaldoxime, respectively. In that sense, bond distances and angles in the coordination sphere are in the ranges found for several iron(III) ‘basic carboxylates’ [30–37].

3.5. Mössbauer spectra

Fig. 3 shows Mössbauer spectra from powder samples of 1 and 2 recorded at room temperature in the absence of an external magnetic field. The spectra for both compounds consist of two well resolved doublets. Solid lines above the spectra are theoretical simulations assuming two iron sites at 2:1 ratio with the parameters quoted in Table 3. For both compounds the isomer shifts for sites I and II are typical for high spin Fe³⁺ in an octahedral environment comprising O/N atoms.

From the crystal structure of complex 1, site I which represents the majority species is readily assigned to the iron sites with O₆ environment whereas site II, the minority species, is assigned to the iron site with O₅N coordination. Site II is characterized by a significantly larger ΔE₀ relatively to site I. The ΔE₀ parameter reflects the degree of asymmetry around the Fe ion. This can be asymmetry of Fe–L bond lengths and coordination geometry, or asymmetry in the nature of donor atoms (N or O). In terms of coordination geometry, significant trans effects are experienced by Fe(2), Fe(3) in
molecule 1a, and by Fe(5), Fe(6) in molecule 1b, with the shortest bond being the Fe–(μ-3-O2/C0) in each case. The corresponding 
trans effect experienced by atoms Fe(1) and Fe(4) is insignificant (see Table 2). In terms of donor atoms, there are two iron atoms with asymmetric O₅N chromophores [Fe(1) and Fe(4)] and four atoms with more symmetric O₆ chromophores [Fe(2), Fe(3), Fe(5) and Fe(6)]. The Mössbauer spectra, therefore, indicate that the O₅N coordination should be considered responsible for the larger ΔE_Q value of site II.

The resolution of the spectrum of complex 1 does not allow us to distinguish the two crystallographically different molecules 1a and 1b, with two rather different geometries; isosceles (for 1a) and scalene (for 1b, see description of structures). Due to the different geometries it is expected that

3.6. Magnetic behaviour

For complex 1, the ²M∕T product at 300 K is 3.94 cm² mol⁻¹ K (Fig. 4), significantly lower than the theoretically expected value for three non-interacting S = 5/2 spins (13.14 cm² mol⁻¹ K), suggesting antiferromagnetic interactions. Upon cooling, the ²M∕T product decreases to 0.31 cm² mol⁻¹ K at 2 K, without extrapolating to zero as the temperatures tends to zero, which agrees with the interplay of antiferromagnetic interactions, and a magnetic ground state.

As analyzed in the description of the structures, complex 1 actually consists of two independent molecules (1a and 1b), with two rather different geometries; isosceles (for 1a) and scalene (for 1b, see description of structures). Due to the different geometries it is expected that

Table 3

<table>
<thead>
<tr>
<th>Complex</th>
<th>Site</th>
<th>Temperature (K)</th>
<th>ΔE/Qᵃ,c</th>
<th>I/2ᵃ,d</th>
<th>Area (%)[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>300</td>
<td>0.42(1)</td>
<td>0.56(1)</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>0.54(1)</td>
<td>0.61(1)</td>
<td>0.19</td>
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<tr>
<td></td>
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<td>300</td>
<td>0.41(1)</td>
<td>1.24(1)</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>0.53(1)</td>
<td>1.15(1)</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>300</td>
<td>0.42(1)</td>
<td>0.70(1)</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>0.55(1)</td>
<td>0.79(1)</td>
<td>0.19</td>
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<tr>
<td></td>
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<td>1.29(1)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>4.2</td>
<td>0.54(1)</td>
<td>1.31(1)</td>
<td>0.19</td>
</tr>
</tbody>
</table>

[^a]: In mm s⁻¹.
[^b]: Isomer shifts are reported relative to iron metal at room temperature.
[^c]: Number in parentheses represent errors in the last digit.
[^d]: Fixed.
**1a** and **1b** have different magnetic properties. However, consideration of two different magnetic entities for the analysis of the bulk magnetic susceptibility data would lead to a large number of parameters with a small degree of reliability. Therefore, we have analyzed the data assuming one single trinuclear species.

Initial attempts to simulate the magnetic properties of the complex by considering a single exchange constant, \( J \), did not yield satisfactory results. It was, therefore, concluded that a model taking into account a second exchange constant, \( J' \), should be considered. The Hamiltonian used was

\[
\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3) - 2J'(\hat{S}_1 \cdot \hat{S}_2).
\]

The fitting process yielded two solutions of comparable quality (with \( g \) fixed to 2.0), as is usually the case for complexes containing the \([\text{Fe}_3\text{O}]^{7+}\) core, with a \( S = 1/2 \) ground state [39,40]. The best-fit parameters were, **A**: \( J = -27.3 \text{ cm}^{-1}, \ J' = -42.7 \text{ cm}^{-1}, \ g = 2.0 \ (R = 1.2 \times 10^{-3}) \) and **B**: \( J = -34.7 \text{ cm}^{-1}, \ J' = -24.6 \text{ cm}^{-1}, \ g = 2.0 \ (R = 1.7 \times 10^{-3}) \). This is better depicted by an error surface plot of \( J \) versus \( J' \), which reveals the existence of two minima (Figure S4). Both these solutions imply a \( S = 1/2 \) ground state.

In order to verify the validity of these results, a simulation of the \( M \) versus \( H \) curve at 2.5 K was carried out with the MAGPACK program package [41,42], using the best-fit parameters of solutions **A** and **B**. These reproduced the experimental curves very nicely, producing practically superimposable curves, without the use of a paramagnetic impurity fraction (Fig. 5).

The situation is similar in the case of complex **2**, with the \( \chi_M T \) product decreasing smoothly from 3.65 cm\(^3\)mol\(^{-1}\)K at 300 K down to 0.28 cm\(^3\)mol\(^{-1}\)K at 2 K, without extrapolating to zero (Fig. 6). For the analysis of the data we assumed the same model as above. The fit shown in Fig. 6 was carried out over the 8–300 K temperature region. Two solutions of comparable quality were determined, their parameters being, **A**: \( J = -35.9 \text{ cm}^{-1}, \ J' = -29.8 \text{ cm}^{-1}, \ g = 2.0 \ (R = 3.7 \times 10^{-3}) \) and **B**: \( J = -31.3 \text{ cm}^{-1}, \ J' = -41.2 \text{ cm}^{-1}, \ g = 2.0 \ (R = 4.3 \times 10^{-4}) \). Fitting over the 2–300 K temperature range yielded small discrepancies at low temperatures. These discrepancies are attributed to the presence of weak intermolecular interactions.

The existence of two minima in the fitting procedure of the magnetic susceptibility data is an inherent property of trinuclear complexes [40]. It would be reasonable to correlate the value of the exchange coupling constants with the magnetic characteristics of the complexes. This approach however may not be realistic in the present case. First, complex **1** consists of two different molecules and the unambiguous determination of the individual magnetic properties is not feasible from the present bulk magnetic susceptibility measurements. Second, even in the simpler case of equilateral complexes the necessity of at least two different exchange coupling constants for the reproduction of the magnetic susceptibility measurements indicate that magnetostructural correlations are not straightforward and other factors have to be taken into account. We observe however that on average, the derived values for the exchange constants for solutions **A** and **B** for both complexes fall within the range of values usually found in trinuclear complexes [43–47].

**3.7. EPR spectroscopy**

EPR spectra from powder samples for both complexes at 4.2 K are shown in Fig. 7. For compound **1** the spectra reveal a feature at \( g \approx 2.0 \) accompanied by broad features at lower magnetic fields. For compound **2** an additional broad feature is observed at higher magnetic fields. The magnetic susceptibility data indicate that the clusters are characterized by a \( S = 1/2 \) ground state, however the EPR signals cannot be attributed to
isolated $S = 1/2$ systems. We attribute this behaviour to intermolecular interactions present in the solid state. This is supported by the crystal structure revealing intermolecular interactions between neighbouring trimers. We note that the low temperature magnetic susceptibility data for complex 2 cannot be reproduced with isolated trimers and the EPR spectra support weak intermolecular interactions. For compound 1 the intermolecular interactions appear to be weak enough, so they do not affect the magnetic susceptibility data. However, weak dipolar interactions may substantially affect the EPR spectra. For instance a weak dipolar interaction between two $S = 1/2$ systems of the order of $\sim 0.05\text{ cm}^{-1}$ can be hardly discernible in bulk magnetic susceptibility measurements, but it will critically affect the EPR measurements leading to spectra extending in a large magnetic field region.

In order to eliminate the solid-state effects, we studied by EPR both compounds in an acetone glass, a weakly coordinating solvent. The 4.2 K spectra are shown in Fig. 8. A strong signal is observed at $g \sim 2.0$ for both compounds. The signal is characterized by a symmetric derivative feature with a line-shape which is better described by a Lorentzian curve. The temperature dependence of this signal indicates that it arises from a ground state. The dependence of the signal on microwave power and the line-shape argues against a free radical species. Further, it is improbable that this signal arises from monomeric Fe$^{III}$ ($S = 5/2$) species resulting from decomposition of the compound upon solvation in acetone. Usually such species gives rise to signals at higher $g$-values (for instance at $g \sim 4.3$) as a result of zero-field splitting effects. No such signals are observed in the present case. A monomeric Fe$^{III}$ ($S = 1/2$) low spin species can be also excluded because in this case fairly anisotropic signals are expected.

On the other hand, it is reasonable to assume that the EPR signals of Fig. 8 arise from the $S = 1/2$ ground state of isolated trimers in both compounds. The symmetric line-shape of the signals suggests an isotropic system. This is indeed expected from a trimer comprising Fe$^{III}$ ($S = 5/2$) sites antiferromagnetically coupled with the isotropic Heisenberg–Dirac–van Vleck Hamiltonian as the main interaction. Although symmetric EPR lines are expected this is rarely met in trinuclear complexes of Fe$^{III}$ ($S = 5/2$) or Cr$^{III}$ ($S = 3/2$) [39,48–53]. Usually, in such systems, non-Heisenberg interactions such as antisymmetric exchange and/or single-ion zero-field splitting terms result in an anisotropic $S = 1/2$ ground state. Due to the anisotropy, broad EPR signals are observed extending to high field values with $g \ll 2.0$. In the present case the signal is symmetric and confined at the $g \sim 2.0$ region indicating that the contribution of these terms is negligible. From this point of view compounds 1 and 2 are rare cases of triferric complexes where the anticipated $S = 1/2$ EPR signals are indeed observed.

4. Conclusions

As part of our continuing efforts to synthesize polynuclear iron(III) complexes with novel magnetic properties, we have reacted H$_3$salox with iron(III) in the presence of carboxylates. The two new neutral iron(III) complexes, [Fe$_3$(µ-O)(O$_2$CPh)$_3$(salox)L$_1$L$_2$] (L$_1$ = L$_2$ = MeOH (1), L$_1$ = EtOH, L$_2$ = H$_2$O (2)) derived, contain the [Fe$_3$O]$^{7+}$ core found in ‘basic iron carboxylates’. In complexes 1 and 2 however two iron atoms are in an O$_6$ coordination environment whereas the third is found in an O$_3$N one. A detailed characterization of complexes 1 and 2 including spectroscopic and magnetic studies has been carried out. The nonequivalence of the
iron(III) ions is depicted in the Mössbauer spectra. The magnetic properties are interpreted within the context of a trimer with exchange constants typical for complexes with the \( [\text{Fe}_3(\mu_3-\text{O})]^{7+} \) core and a \( S = 1/2 \) ground state. The crystal structure analysis of 1 reveals intermolecular interactions between the trimers forming 1D polymeric chains. In 2 the intermolecular interactions lead to the formation of a 2D network. These interactions give rise to broad EPR spectra in the solid state. The salox\( ^{2-} \) formation of a 2D network. These interactions give rise to broad EPR spectra in the solid state. The salox\( ^{2-} \) formation of a 2D network. These interactions give rise to broad EPR spectra in the solid state.

**Acknowledgements**

The Greek General Secretariat of Research and Technology is acknowledged for supporting the present work within the frame of the Competitiveness EPAN 2000–2006, Centers of Excellence # 25. We also thank Dr. D. Stamopoulos for the magnetic measurements.

**Appendix A. Supplementary data**

Full crystallographic details have been deposited in CIF format with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336408, e-mail: deposit@ccdc.cam.ac.uk or www. at http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 261079 (1), and CCDC 261080 (2). Four figures showing the molecular and lattice structure of 2, the Mössbauer spectra from powder samples of 1 and 2 at 4.2 K, and the surface error plot of \( J \) versus \( J' \) (with \( g = 2.00 \)), as well as a table of the bond distances and angles around the coordination sphere of the three iron(III) ions in 1, are also given as supplementary material. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.02.002.

**References**