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Polynuclear coordination compounds as precursors for $CuFe_2O_4$

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The possibility of obtaining copper ferrite through the thermal decomposition of the two polynuclear coordination compounds: $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ (**I**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$ (**II**) was considered. The polynuclear compounds were characterized by various physical chemical techniques, *e.g.*, IR, UV-VIS, EPR, Mössbauer spectra, thermal analysis and magnetic measurements. The final products obtained after thermal decomposition of the complex compounds were analysed by X-ray diffraction. A mixture of tetragonal $CuFe_2O_4$, α-Fe_2O_3 and CuO is generated from the thermolysis of compound **I**, while a clean tetragonal $CuFe_2O_4$ with saturation magnetization of 26.89 emu g^{-1} is obtained from compound **II**.

1. Introduction

In the last decade, the pollution by diesel-engine exhausts has become more and more serious. NO_x and soot are main components to be removed from diesel exhausts. Among bimetallic spinel-type oxides, $CuFe_2O_4$ a useful catalyst, which shows intermediate activity and exceptionally high and low selectivity, respectively, to N_2 and N_2O formation.[1]

Copper ferrite, $CuFe_2O_4$, exhibits two polymorphic varieties. A tetragonally distorted spinel is obtained at room temperature. However, higher temperatures (350–400 °C) favour the formation of a cubic spinel structure.[2,3] Tetragonal $CuFe_2O_4$ is an inverse spinel in which Cu^{2+} ions occupy mainly octahedral B-sites, whereas Fe^{3+} ions are found on B-sites and tetrahedral A-sites with approximately equal occupancy. It is known that the two crystalline forms of $CuFe_2O_4$ have different catalytic activity.[1] The tetragonal $CuFe_2O_4$ is more active than the cubic one.[4,5]

For several years, our laboratory has been engaged in the synthesis of ferrites. Considerable efforts have been made to develop synthesis methods that yield precursors with two or more metallic ions included in the same molecular entity. Polynuclear coordination compounds precursors with two or more metallic ions are capable of forming mixed oxides through their thermal decomposition.[6–8]

In this paper, our recent studies concerning the synthesis of polynuclear coordination compounds as precursors for $CuFe_2O_4$ are described.

2. Experimental

All chemicals were of reagent quality (Merck) and all manipulations were performed using materials as received. An oxalic acid solution was added to an aqueous or ethanolic solution that contained the ions in the ratio $Fe^{3+} : Cu^{2+} = 2 : 1$. In order to establish the optimal conditions of polynuclear coordination compounds isolation, the following systems were studied:

$$2FeX_3 : 1CuX_2 : mC_2O_4^{2-}$$

where $X = Cl^-$, NO_3^-, and $m = 2$ and 10.

A solution of $NH_4OH : H_2O$ (1 : 1) was carefully added for a complete precipitation (pH ~4.5–6). The slurries were filtered, washed with water (or ethanol) and dried on P_4O_{10}. The resulting coordination compounds with colors from green to brown–green, were crystalline powders. The metal content was determined by atomic absorption spectrophotometry. Elemental analysis was consistent with the formula $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ (**I**) and $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$ (**II**). Anal.: Calcd. for $Fe_2CuN_8C_{16}H_{32}O_{32}$ (**I**): Fe, 10.94; Cu, 6.20; C, 18.75; N, 10.93. Found: Fe, 11.20; Cu, 6.06; C, 20.02; N, 10.58%; Anal.: Calcd. for $Fe_2CuC_4O_{16}H_{12}$ (**II**): Fe, 22.76; Cu, 13.00; C, 9.75. Found: Fe, 23.11; Cu, 12.91; C, 10.25%.

In order to obtain information about the function of the oxalate anions, the IR spectra (KBr pellets) of the polynuclear coordination compounds were recorded on a Bio-Rad FTS-135 spectrophotometer in the 4000–400 cm^{-1} region.

Data about the stereochemistry of the metal ions were obtained from UV–VIS spectra (diffuse reflectance technique) recorded with a Specord M 40 spectrophotometer, in the range 10000–5000 cm^{-1}.

EPR spectra were registered on an ART-S IFIN–Bucharest spectrometer, in X-Band, with a klystron frequency of 9060 MHz, and field modulation of 100 KHz. Mn^{2+} was used as internal standard.

Mössbauer spectra were obtained at room temperature with a constant acceleration spectrometer (PROMEDA type equipment) with a 10 mCi ^{57}Co (Rh) source. The α-Fe foil (Amersham, England) was used to calibrate the Mössbauer spectrometer in a velocity range of ± 10 mm s^{-1}. The Mössbauer spectra obtained were least square fitted to the hypothesis of Lorentzian line shape.

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Thermal decomposition curves were obtained with a Q-1500 D Paulik–Paulik–Erdey derivatograph in a static air atmosphere at a heating rate of 5 K min^{-1}, in the temperature range 1000–20 °C, with α-Al_2O_3 as the inert reference compound. The isolable decomposition intermediates were characterized by elemental and IR analysis.

The magnetization curves of the encapsulated polynuclear compounds samples were measured as function of temperature at decreasing applied field from 5 T using a SQUID magnetomer (MPMS-5S, Quantum Design). The magnetic susceptibilities of the oxides were determined at room temperature using a Faraday balance, with Ni as calibrant.

The magnetic susceptibilities of the complex compound were calculated from the spin-coupled wave functions by using a simplified form of the van Vlek equation:[9]

$$\chi T = N_A k \frac{\sum_{i=1,n} |< \Psi_i | \hat{\mu} | \Psi_i >|^2 \exp(-E_i/kT)}{\sum_{i=1,n} \exp(-E_i/kT)}$$

where E_i is the energy level with wave function ψ_i and $\hat{\mu}$ is the moment operator given by

$$\hat{\mu} = \mu_B \sum_{i=1,5} g_i \hat{S}_{Zi}.$$

To fit the temperature dependent magnetic susceptibilities, the least-squares fitting computer program FDHM, full diagonalisation of the Heisenberg matrix, was employed.[10]

The crystalline phases in the calcined powders were identified by XRD powder methods using a DRON X-ray diffractometer, with Co K$_\alpha$ radiation. For quantitative analysis a step scanning technique was applied in the 2θ range 20–75° with a step of 0.01° for 20 s at each step. SiO_2–α-quartz was used as internal standard. Diffraction peaks were fitted assuming Voight-function for the peak profile. A simplified least squares procedure (Savitsky–Golay)[11] was applied in order to smooth the primary XRD data collected. The background was treated as a linear function. For the determination of the average crystallite size the Scherrer formula $D = 0.91\lambda/(\beta\cos\theta)$ was used, where D is the crystallite size, λ the wavelength (Co Kα), β the corrected half-width obtained using α-quartz as reference and the Warren formula, and θ the diffraction angle of 311 diffraction peaks.[12]

3. Results and discussion

3.1. Pattern polynuclear coordination compounds

Independent of the nature of the starting materials, and depending only on the reaction conditions (the nature of the solvent, pH reaction medium, oxalic content parameter m), the polynuclear compounds obtained were characterized by their molecular formula.

For $m = 10$

I $(NH_4)_8[Fe_2Cu(C_2O_4)_8]\cdot x(NH_4)_2C_2O_4$

When the reaction solvent was ethanol, pH ~4–4.5, $x = 0$.

When the reaction solvent was H_2O, pH ~5–6, $x = 2$.

For $m = 2$

II $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$

Reaction solvent, H_2O/C_2H_5OH, pH ~5–6.

The IR spectra of carboxylate complex compounds are usually dominated by two strong bands in the 1650–1550 cm^{-1} and 1400–1300 cm^{-1} ranges, arising from C–O stretching vibrations. In the case of $C_2O_4^{2-}$ anion, the attribution is more complicated because $C_2O_4^{2-}$ can act as mono-, bi-, tri- or tetradentate ligand. The spectra of the studied coordination compounds are a proof in this way (Fig. 1).

Thus, the splitting of $\nu_{asim(OCO)}$ and $\nu_{sim(OCO)}$ vibrations detected in the spectra of compound **I** suggest two different coordination modes for $C_2O_4^{2-}$ anions: as tetradentate bridges ($\nu_{asim(OCO)}$ ~1680 cm^{-1}; $\nu_{sim(OCO)}$ ~1400–1360 cm^{-1}) and as chelate ($\nu_{asim(OCO)}$ ~1715 cm^{-1}; $\nu_{sim(OCO)}$ ~1300–1270 cm^{-1}). For compound **II** only a tetradentate bonding is evidenced. The coordination of the ligand through oxygen is supported also by a medium band at ~500 cm^{-1} characteristic of an M–O bond. Besides these bands, the IR spectrum of the first compound exhibits bands characteristic of NH_4^+ ion (~2850 cm^{-1} and ~1400 cm^{-1}). A band characteristic of OH^- ion at ~3500 cm^{-1} is present in the second one.

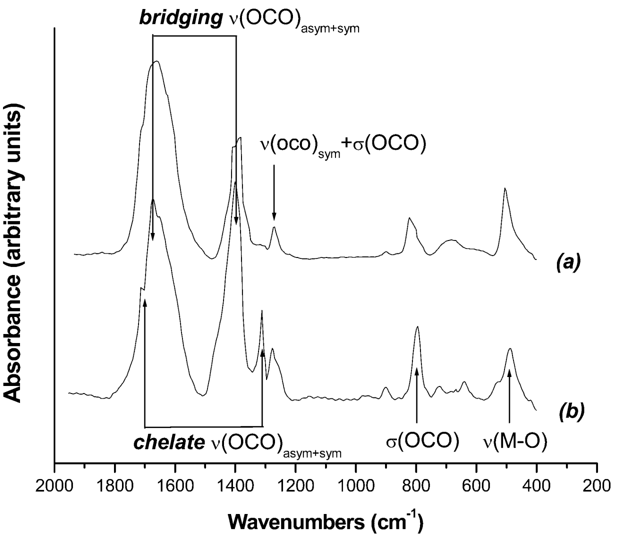

Fig. 1 IR spectra of the compounds: (a) $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ and (b) $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$.

The reflectance spectra reveal the presence of the forbidden spin transition bands in an octahedral high spin configuration of the $Fe^{3+}(d^5)$ ions and the characteristic bands of a pseudo-tetrahedral environment of Cu^{2+} (d^9) ions (Table 1).

The above mentioned stereochemistry of the Cu^{2+} and Fe^{3+} ions are sustained by the EPR and Mössbauer investigations, respectively.

The EPR spectrum for compound **I** (Fig. 2) is specific for Cu^{2+} ions as paramagnetic species in a tetrahedral surrounding ($g_\parallel = 2.1237$; $g_\perp = 2.0633$). The line arising from Fe^{3+} ion

Table 1 Absorption bands in the electronic spectra of the compounds **I** and **II**

Transition	I/nm	II/nm
$^6A_{1g} \to {}^4E_g$	~480	~400
CT (O → Cu)	~300	~300
$D_z^2 \to d_x^2$–d_y^2	690–700	690–700

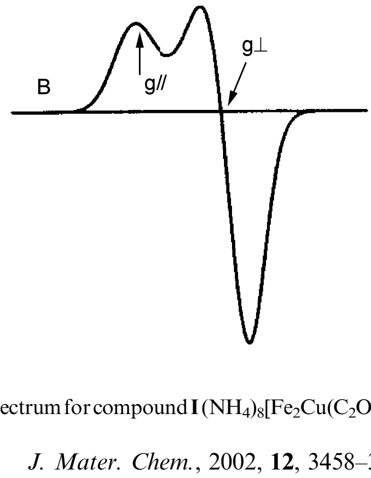

Fig. 2 EPR spectrum for compound **I** $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ at 25 ± 1 °C.

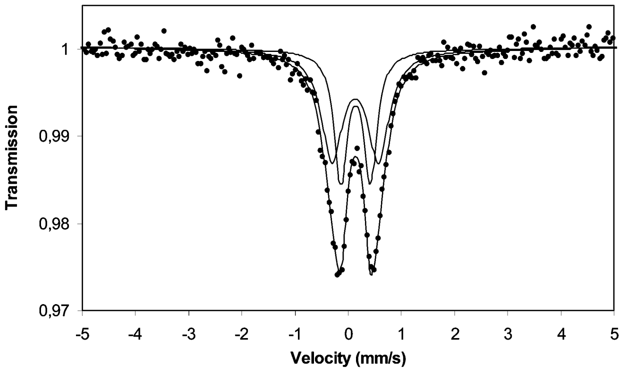

Fig. 3 Mössbauer spectrum of compound **II** [$Fe_2Cu(C_2O_4)_2(OH)_4$]·$4H_2O$ at 25 ± 1 °C.

Table 2 Mössbauer hyperfine parameters of the parent compounds **I** and **II**

Compund	Mössbauer pattern	Isomer shift/mm s^{-1}	Quadrupolar shift/mm s^{-1}	Relative intensity (%)
I	Doublet (1)	0.216	0.237	67.80
	Doublet (2)	0.280	0.186	32.20
II	Doublet (1)	0.249	0.437	57.33
	Doublet (2)	0.256	0.279	42.67
Error		±0.045	±0.050	±0.95

having a lower intensity is overlapped by the line of Cu^{2+}. For compound **II**, the EPR spectrum, at room temperature, has a lower intensity and resolution, the signal being assigned only to iron ions. The absence of a spectrum characteristic of Cu^{2+} suggests the possibility of intermolecular coupling similar to dimer structures.

The Mössbauer spectra can be resolved in two quadrupole doublets. Fig. 3 shows, for example, the Mössbauer spectrum of compound **II**. The Mössbauer parameters (Table 2) reveal the presence of Fe^{3+} ions in a coordination close to the octahedral one for both compounds.[13] The quadrupolar shift of the doublet (1) is greater than the corresponding parameter of the doublet (2) suggesting a more distorted octahedral symmetry of Fe^{3+} ions that provide the more abundant doublets of the parent compounds. Accordingly, the Mössbauer analyses evidence the crystallographic inequivalence of the Fe^{3+} ions, in the parent compounds studied.

From a magnetic point of view both compounds are paramagnetic. The magnetic moments at room temperature of 7.47 and 4.84 BM for compounds **I** and **II**, respectively, are lower than the theoretical one of 8.51 BM. While the difference evidenced for compound **I** can be assigned to antiferromagnetic interactions between the odd electrons of two or more paramagnetic metal ions, the unexpectedly small value registered for the second one has another cause.

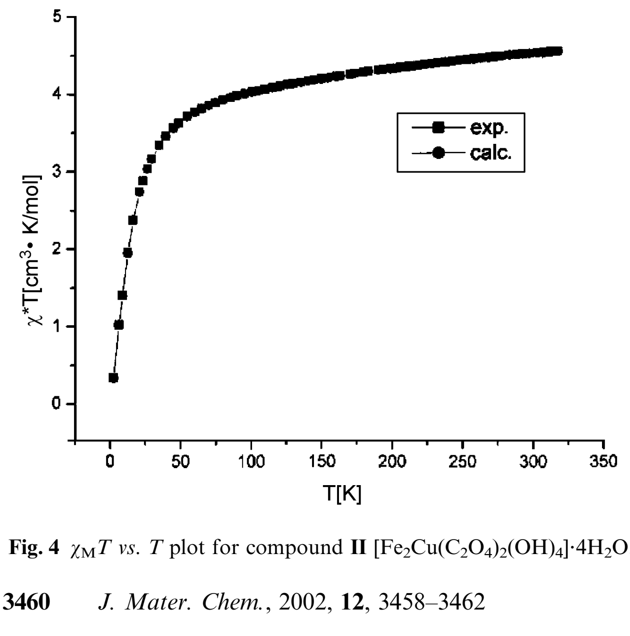

Fig. 4 $\chi_M T$ *vs.* T plot for compound **II** [$Fe_2Cu(C_2O_4)_2(OH)_4$]·$4H_2O$.

To understand this behaviour, the magnetic susceptibility *vs.* temperature was performed for this compound (Fig. 4). A theoretical analysis of the magnetic data performed using the Heisenberg–Dirac–van Vleck (HDvV) model,[9] support the existence of a dimer structure (estimated by EPR spectra), with a bimolecular unit in which iron ions are linked *via* HO bridges:

$$\mathrm{Fe}^{(1)}_{\mathrm{hs}}(\mathrm{III}) \underset{J_{\mathrm{ff}}}{\cdots} \mathrm{Fe}^{(2)}_{\mathrm{hs}}(\mathrm{III}) \underset{J_{\mathrm{fc}}}{—} \mathrm{Cu}^{(3)}(\mathrm{II}) \underset{J_{\mathrm{cc}}}{—}$$

$$\mathrm{Cu}^{(4)}(\mathrm{II}) \underset{J_{\mathrm{fc}}}{—} \mathrm{Fe}^{(5)}_{\mathrm{hs}}(\mathrm{III}) \underset{J_{\mathrm{ff}}}{\cdots} \mathrm{Fe}^{(6)}_{\mathrm{hs}}(\mathrm{III})$$

where J_{ff}, J_{fc}, J_{cc} are the exchange parameters.

The results of the least-squares fit of the $(\chi_M T)_{obs}$ give very strong antiferromagnetic interactions, ($J_{fc} = -2539\ cm^{-1}$; $J_{cc} = -8490\ cm^{-1}$). This means that the sequence:

$$\mathrm{Fe}^{(2)}_{\mathrm{hs}}(\mathrm{III}) — \mathrm{Cu}^{(3)}(\mathrm{II}) — \mathrm{Cu}^{(4)}(\mathrm{II}) — \mathrm{Fe}^{(2)}_{\mathrm{hs}}(\mathrm{III})$$

could be a diamagnetic unit which intermediates only a weak antiferromagnetic interaction ($J = -5\ cm^{-1}$) between $Fe^{(1)}_{hs}$(III) and $Fe^{(6)}_{hs}$(III). So, for the magnetic behaviour at room temperature it is necessary to consider only a 5/2 spin per molecular unit [$(\chi_M T)^{obs}_{HT}$ ~4.4 $cm^3 mol^{-1} K$ corresponding to

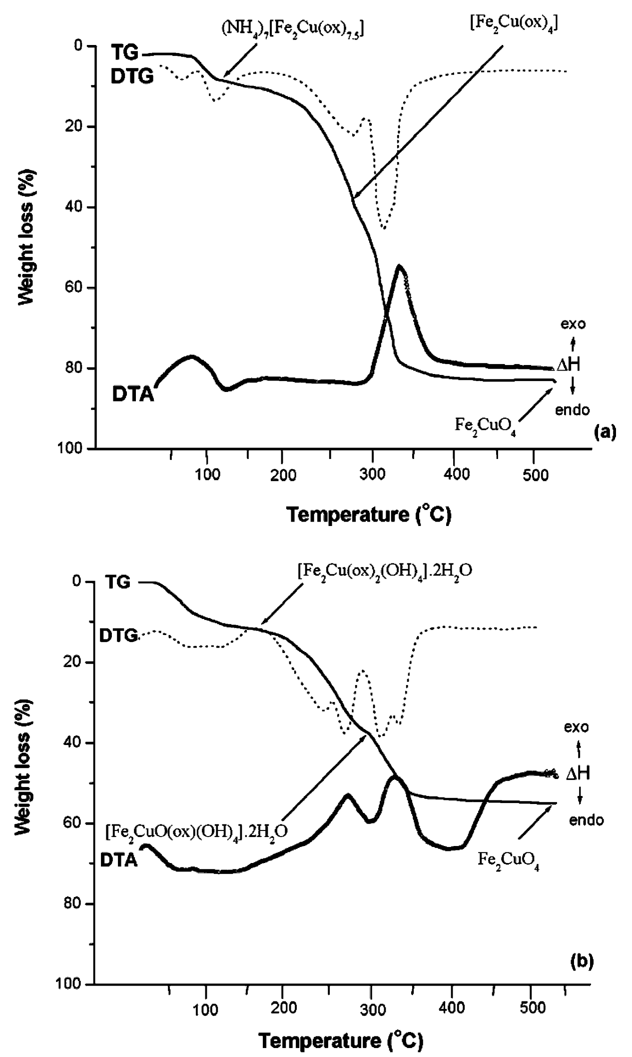

Fig. 5 Thermal behaviour of the complex compounds: (a) $(NH_4)_8$-[$Fe_2Cu(C_2O_4)_8$] and (b) [$Fe_2Cu(C_2O_4)_2(OH)_4$]·$4H_2O$.

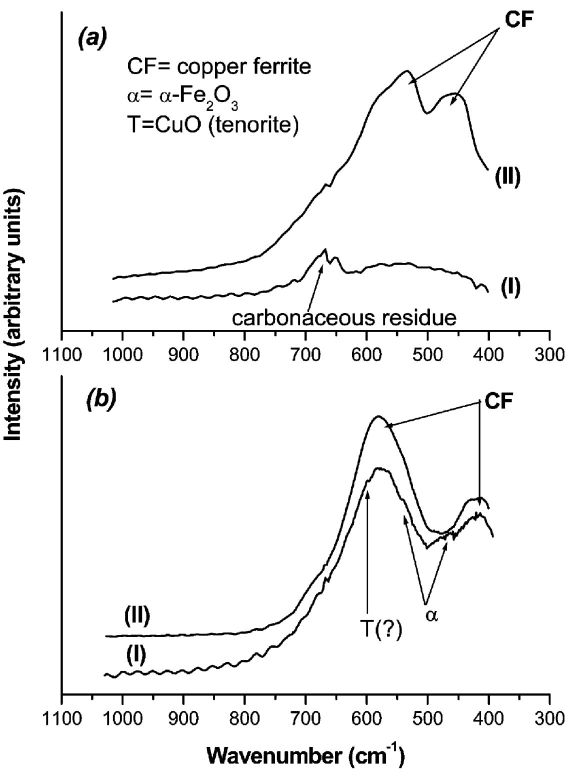

Fig. 6 IR spectra of the oxides obtained from the two precursors at: (a) 375 °C (heating rate 5 °C min^{-1}, without annealing plateau with quenching) and (b) 400 °C for 4 h (heating rate 5 °C min^{-1}).

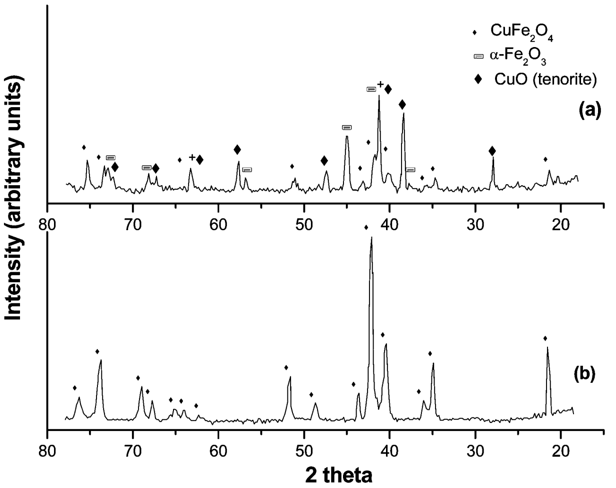

Fig. 7 Powder XRD patterns of the final thermolysis products of: (a) $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ and (b) $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$ (400 °C for 4 h, heating rate 5 °C min^{-1})

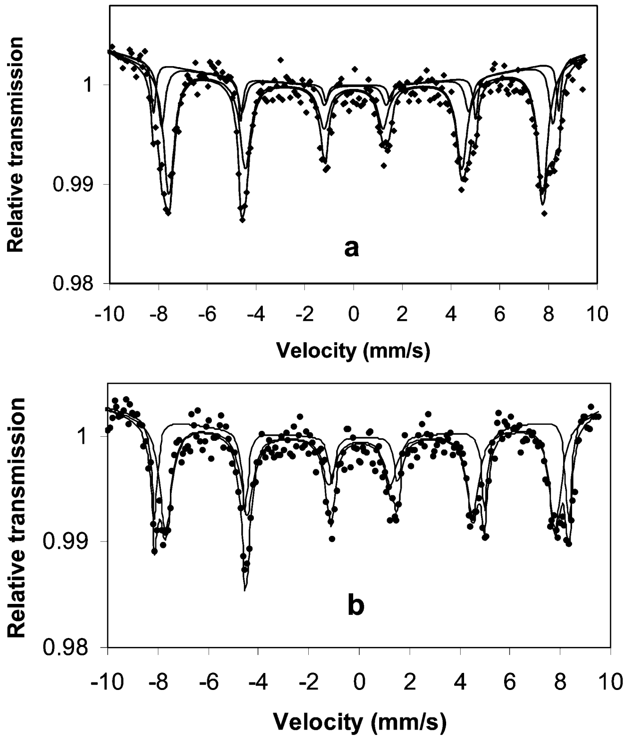

Fig. 8 Mössbauer spectra of the final thermolysis products of: (a) $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ and (b) $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$ at 25 ± 1 °C

the value expected for a Fe(III)-high spin per molecular unit, a value which leads to $g_{\text{average}} = 2$].

The coordination compounds decompose in the temperature range 80–375 °C (Fig. 5). The experimental losses recorded by TG measurements were 77.3% and 51.3% for compounds **I** and **II**, respectively, in comparison with the theoretical values of 76.62% and 51.21% when it is assumed that the solid residue is $CuFe_2O_4$. A first endothermic step corresponding to partial water and $(NH_4)_2C_2O_4$ evolution (~80–120 °C) is followed by two exothermic processes corresponding to an oxidative ligand breakdown process.

Only the IR spectrum of the decomposition residue generated from compound **II** presents the absorption bands (~400 and ~600 cm^{-1}) characteristic to the intrinsic vibrations of the tetrahedral and respective octahedral groups[14] (Fig. 6(a)). This finding led to the outcome that the spinel lattice is available when the thermal decomposition of compound **II** is accomplished.

3.2. Oxide products

The IR and X-ray analysis of the thermolysis products (Figs. 6(b) and 7) evidenced that the thermal decomposition of compound **I** led to the formation of not only tetragonal $CuFe_2O_4$ (as the main product) but also to single metal oxides, α-Fe_2O_3 (haematite) and CuO (tenorite). Clean tetragonal $CuFe_2O_4$ is identified in the final thermolysis product of compound **II**. Mean crystallite sizes of 105 and 185 Å were obtained for copper ferrite generated from compounds **I** and **II**, respectively. The low value of the first may be directly connected with the larger amount of gases evolved during the thermal decomposition of the pattern compounds.

The formation of an inverse spinel, where the ferric ions populate either tetrahedral sites (A sites) or octahedral sites (B sites) in about equal amounts is also indicated by Mössbauer investigations. In the case of compound **I**, the Mössbauer spectrum (Fig. 8a) exhibits, besides the two characteristic sextets[15] of $CuFe_2O_4$, a sextet that belongs to a residual α-Fe_2O_3 (Table 3). The Mössbauer spectrum of the oxide derived from compound **II** exhibits only the two magnetic sextets characteristic of the $CuFe_2O_4$ tetragonal phase (Fig. 8b).

Table 3 Mössbauer hyperfine parameters of the final thermolysis products of the compounds **I** and **II**

Sample	H_{hf}/ kOe	IS/ mm s^{-1}	QS/ mm s^{-1}	Relative area (%)	Site assignment
Compound **I**	478	0.16	0.08	67.4	A (tetra)
	501	0.23	0.07	20.8	B (octa)
	518	0.27	−0.09	11.8	α-Fe_2O_3
Compound **II**	483	0.15	0.03	67.5	A (tetra)
	513	0.27	0.12	32.5	B (octa)
Error	±2	±0.01	±0.02	±0.7	

The values for the saturation magnetization of 16.60 and 26.89 emu g^{-1}, respectively, for compounds **I** and **II** sustain these results. The value obtained for the pure $CuFe_2O_4$ tetragonal phase is in accord with the literature data.[16]

Conclusion

The presented data reveal the importance of the precursor nature on the accessibility and characteristics of the final product.

The two polynuclear coordination compounds were selected as precursors for $CuFe_2O_4$ due to their special features. Compound **I** $(NH_4)_8[Fe_2Cu(C_2O_4)_8]$ contains in its molecular composition a large amount of gas generators $(8(NH_4)^+$ and $8(C_2O_4)^{2-})$, whose fast and energetic decomposition makes possible a lowering of the temperature of decomposition and the formation of nanosized oxide particles. The specific molecular architecture of compound **II** $[Fe_2Cu(C_2O_4)_2(OH)_4]\cdot 4H_2O$, namely the Fe–Fe–Cu succession with iron ions linked *via* HO bridges, shorter in length compared with oxalate ones, favors solid-state ferritization simultaneously with the thermal decomposition.

Acknowledgements

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