

Thermal behaviour and characterization of some novel iron(III)-*o*-phthalates

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Received 21 March 1994; accepted 8 April 1994

Abstract

Several polynuclear iron(III)-*o*-phthalates precipitated from acid and alkaline solutions were characterized by chemical and thermogravimetric analysis, and infrared, Mössbauer and magnetic measurements. Compounds prepared in acid solutions contain the trimer unit Fe₃O and, although different in chemical composition and in thermal decomposition behaviour, show very similar IR, Mössbauer and magnetic characteristics. The variable temperature magnetic susceptibility measurements of these compounds were fitted to a theoretical expression derived from a spin Hamiltonian, taking into account two different exchange pathways along inequivalent sides of an isosceles triangle, yielding $J_{12}/\text{cm}^{-1} = -35.4$ and $J_{13}/\text{cm}^{-1} = -21.1$. The Mössbauer spectra of this group of samples could be satisfactorily fitted by considering the superposition of two quadrupole split doublets with different relative areas. Samples prepared in highly alkaline solution show a characteristic band in the infrared spectra at 890 cm^{-1} , assigned to the asymmetric Fe–O–Fe stretch. Their Mössbauer spectra taken in the temperature region 77–300 K reveal superparamagnetic behaviour of small particles or clusters. Magnetic susceptibility measurements of these polynuclear iron(III) species show $T_{\text{max}}/\text{K} = 10$ and 25, respectively. Zero field-cooled, field-cooled and torque measurements were used to prove their spin glass behaviour in the low temperature region.

Keywords: Iron compound; IRS; Magnetic susceptibility; Mössbauer; Novel; Phthalate; TGA

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1. Introduction

It is known that iron(III) forms polymeric complexes, containing an Fe_3O centre, with malonic, succinic, fumaric and phthalic acids, which are insoluble in aqueous solution [1]. For the iron(III) complex with polyimidazole ligand, an asymmetric core was found, which represents a topological isomer of the symmetric Fe_3O unit [2]. The importance of further characterization of larger iron-oxo aggregates has also been emphasized [1].

In the present work, several novel hydrolysed polymeric iron(III) complexes of phthalic acid were prepared. Thermogravimetric, IR, Mössbauer and magnetic measurements were used to characterize these compounds. This work is part of a research program on precipitation reactions of geochemical interest, and is a comparison to the aluminium case [3–6].

2. Materials and methods

2.1. Chemicals

All chemicals used in this work were of analytical grade: phthalic acid ($\text{C}_8\text{H}_6\text{O}_4$) and sodium chloride (NaCl) (Merck, Darmstadt, Germany); iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), iron(III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) (Kemika, Zagreb, Croatia), and tetraphenylphosphonium chloride ($(\text{C}_6\text{H}_5)_4\text{PCl}$) (Fluka AG, Buchs SG, Switzerland).

2.2. Instruments and analysis

A radiometer pH-meter with combined electrode (GK 2322), calibrated with buffers, was used for determination of the pH values in each supernatant prior to filtration.

Sodium, phosphorous and iron were analysed in dissolved samples using an atomic absorption spectrometer (Perkin-Elmer 5000). Carbon and hydrogen were determined by a classical microanalytical technique in the Central Analytical Service of the Rudjer Bošković Institute.

IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer (model 580 B) with KBr pressed pellets.

Thermogravimetric analyses (TGA) were carried out on a Cahn RG electroanalytical balance with a heating rate of 2°C min^{-1} in air.

Mössbauer spectra were taken in the temperature region 77–300 K and analysed by a non-linear least-square computer fit procedure, assuming Voigt or Lorentzian line shapes. The source was ^{57}Co in an Rh matrix, and the velocity scale was calibrated by metallic iron which was also used as a reference for the isomer shift parameter.

Magnetic susceptibility measurements were made in the temperature region 2–390 K, using a Faraday magnetometer [7], in the magnetic field up to 0.94 T.

Magnetization versus field measurements at room temperature do not show ferromagnetic contamination of the samples. Torque measurements were made in the low magnetic field up to 0.04 T, using a home-made sensitive torque magnetometer.

3. Results and discussion

3.1. Preparation of iron(III) *o*-phthalate complexes

The series of precipitates were isolated under the experimental conditions described in detail in Tables 1 and 2.

Samples 1–4 in Table 1, and also samples 1–3 and 6 in Table 2 were prepared at room temperature by mixing the solutions in the following order: sodium chloride was added to the solution of Fe(III) salt and to this mixture phthalic acid containing different amounts of sodium hydroxide was added while stirring constantly. Samples 5 and 7 in Table 2 were prepared in the same way but in the absence of sodium chloride.

Sample 4 in Table 2 was prepared from supernatant of sample 3 (in the same table) which still contained soluble iron after filtration. A few crystals of tetraphenylphosphonium chloride were added to the solution to precipitate the iron complex with the large cation.

Sample 8 in Table 2 was prepared from the polymeric fraction of iron(III) which was previously separated from the monomeric fraction using a Sephadex G-25 column, according to a procedure described earlier [8,9]. Because the polymer was unstable upon dilution with water, other precipitation components were added in solid form.

Immediate precipitation occurred in all experiments. Samples were aged as described in Tables 1 and 2, filtered, washed with ethanol to remove traces of NaCl, and dried in a desiccator over silica gel.

3.2. Thermogravimetric measurements and analyses

The different thermal transformation sequences for the studied compounds are shown by the TGA curves in Fig. 1a and b. TGA measurements for samples 1–4 in Table 1 and for sample 1 in Table 2 could not be made because sublimation took place. The total weight losses, determined by ignition in an oven at 1173 K in separate experiments, are presented in Table 2 with other analytical data (the Fe, Na, C, H, N, and P contents), from which the simplest chemical composition was deduced.

3.3. IR spectral characteristics

Samples 1–4 in Table 1 have IR spectra identical to that of $[\text{Fe}_3(\text{o-phthalate})_3(\text{H}_2\text{O})_3](\text{o-phthalate})_{0.5} \cdot 2\text{H}_2\text{O}$, as described by Dziobkowski et al. [1].

Table 1
Initial concentration of precipitation components in mmol dm^{-3} , chemical composition of precipitates and analytical data for reference compound

Sample no.	[Fe] _{lot}	[L] _{lot}	[NaOH]	[NaCl] _{lot}	Days aged	pH	Chemical composition of precipitates	M	Average values (1–4)			
									Fe/%	C/%	H/%	
1	10	5	5	0.6	22	1.8						
2	10	10	10	0.6	22	1.8	[Fe ₃ O(L) ₃](L) _{0.5} · 6H ₂ O	866.05	19.30 (19.35)	38.84 (38.83)	3.43 (3.03)	
3	10	30	30	0.6	22	1.8						
4	10	50	50	0.6	22	2.5						

Key: [Fe]_{lot} = FeCl₃; [L]_{lot} = phthalic acid; L = phthalate²⁻; () calculated.

Table 2
Initial concentration of precipitation components in mmol dm^{-3} , chemical composition of precipitates and analytical data for novel polynuclear iron(III) *o*-phthalates

Sample no.	[Fe] _{lot}	[L] _{lot}	[NaOH] _{lot}	[NaCl] _{lot}	Days aged	pH	Chemical composition of precipitates	M	Fe/%	Na/%	C/%	H/%	N/%	P/%	% of L.O.I. at 1173 K		
																1	10
2	10	10	30	0.06	18	3.1	Na[(Fe ₃ O)(L) ₃](OH)NO ₃ · 6H ₂ O	885.99 (18.91)	18.40 (2.59)	2.73 (32.54)	31.94 (2.84)	3.46 (1.58)	0.81 (1.58)	0	0	67.43 (69.47)	
3	10	30	60	0.06	30	4.8	Na ₂ [(Fe ₃ O)(L) ₃](OH) ₃ · 9H ₂ O	935.04 (17.92)	17.74 (4.92)	4.49 (30.93)	31.05 (3.56)	3.47 (3.56)	–	–	0 (67.75)	67.34 (67.75)	
4	Supernatant of sample 3				1	4.8	Na[(C ₆ H ₃) ₃ Pl] ₃ [(Fe ₃ O)(L) ₃](OH) ₂ (NO ₃) ₂ · 6H ₂ O	1643.80 (10.19)	11.00 (1.40)	1.70 (1.40)	52.14 (52.61)	4.08 (4.05)	1.46 (1.70)	1.46 (3.77)	–	–	73.79 (74.91)
5	50	50	120	0	2	5.6	Na ₂ Fe ₁₃ O ₁₃ (L) ₂ (OH) ₆ (NO ₃) ₂ · 3H ₂ O	1639.34 (44.29)	45.00 (2.80)	2.50 (2.80)	11.89 (11.72)	1.80 (1.41)	1.22 (1.71)	0	0	33.39 (32.90)	
6	10	30	90	0.06	18	6.5	Na ₃ Fe ₉ O ₈ (L) ₂ (OH) ₇ NO ₃ · 8H ₂ O	1369.00 (36.71)	37.00 (5.04)	4.80 (14.04)	14.29 (2.28)	2.71 (2.28)	0.97 (1.02)	0	0	40.86 (40.72)	
7	50	50	360	0	2	12.5	Na ₉ Fe ₃ O ₃₁ (L) ₂ (OH) ₃ (NO ₃) ₃ · 15H ₂ O	3869.87 (44.74)	45.00 (5.35)	5.30 (4.97)	4.98 (1.80)	1.85 (1.81)	1.88 (1.81)	0	0	29.81 (28.83)	
8*	50	30	118	0.06	1	12.46	Na ₃ Fe ₃₀ O ₃₀ (L) ₂ (OH) ₂₆ (NO ₃) ₃ · 3H ₂ O	3793.33 (44.17)	44.00 (1.82)	1.75 (1.82)	5.04 (2.71)	2.17 (2.71)	1.13 (1.11)	0	0	30.36 (34.40)	

Key: [Fe]_{lot} = Fe(NO₃)₃; [L]_{lot} = phthalic acid; L = phthalate²⁻; L.O.I. = loss on ignition; () calculated; –, not determined. * Sample 8 was prepared from polymer fraction separated by Sephadex G-25 whose fractional range was 1000–5000 molecular weight units. It was ignited to 982 K only.

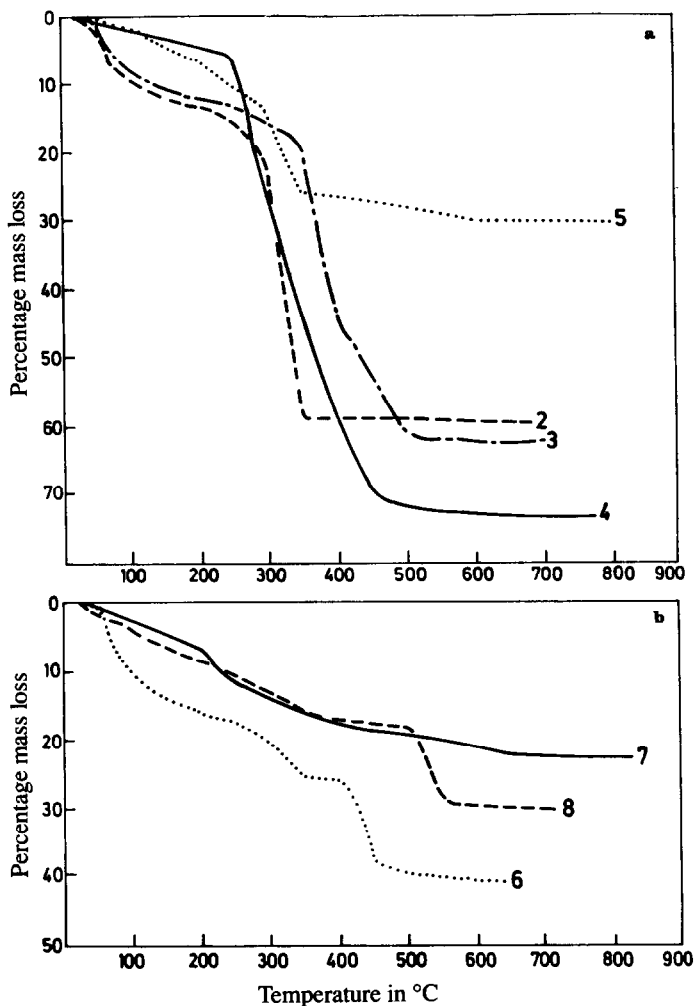
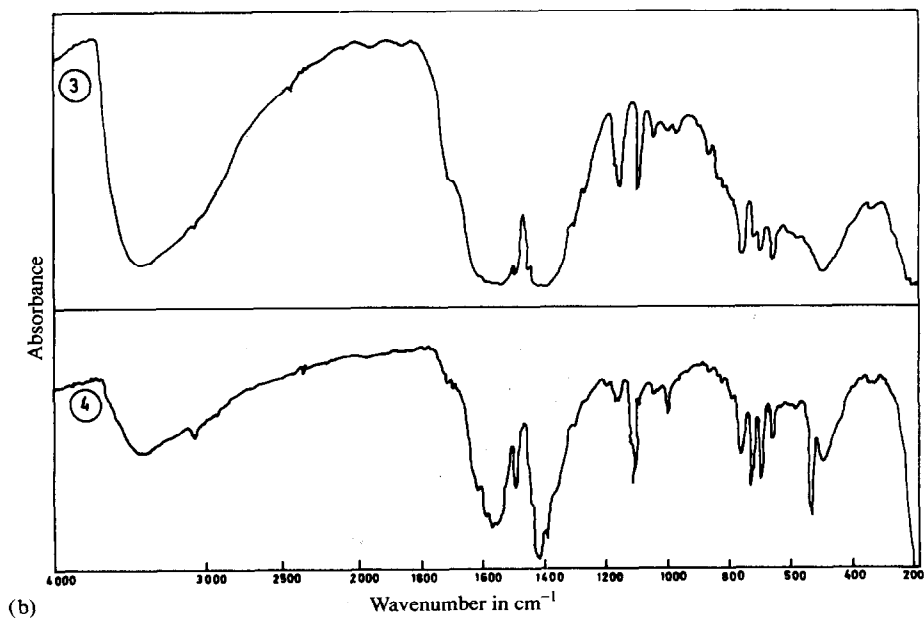
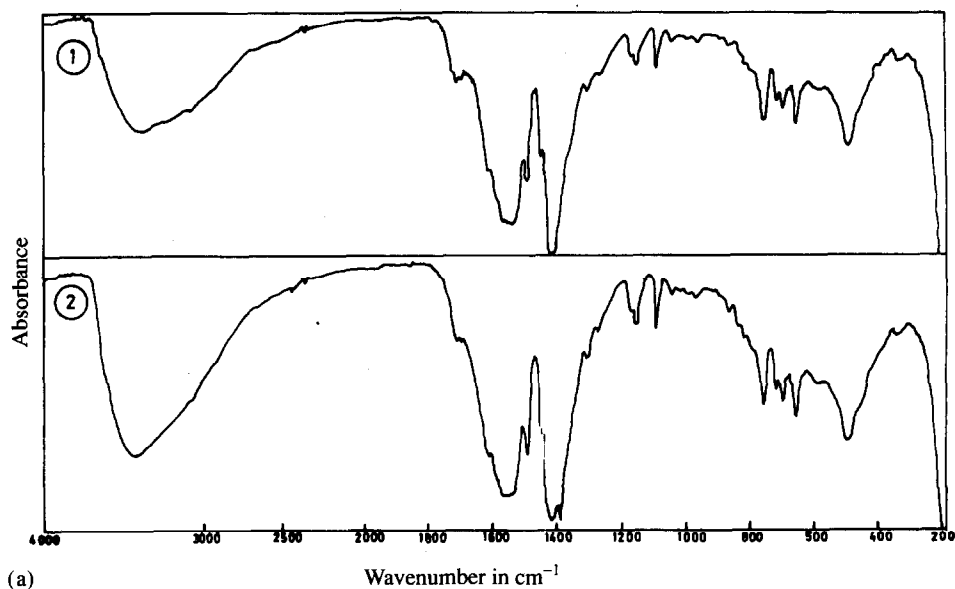
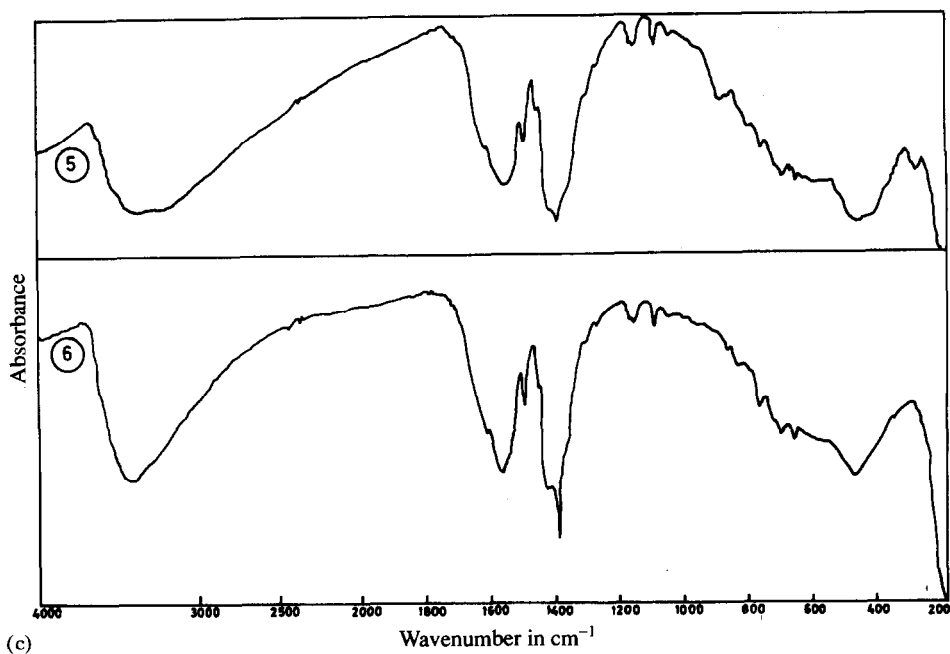


Fig. 1. TGA curves for Fe(III)-*o*-phthalates from Table 2: (a) samples 2–5; (b) samples 6–8.

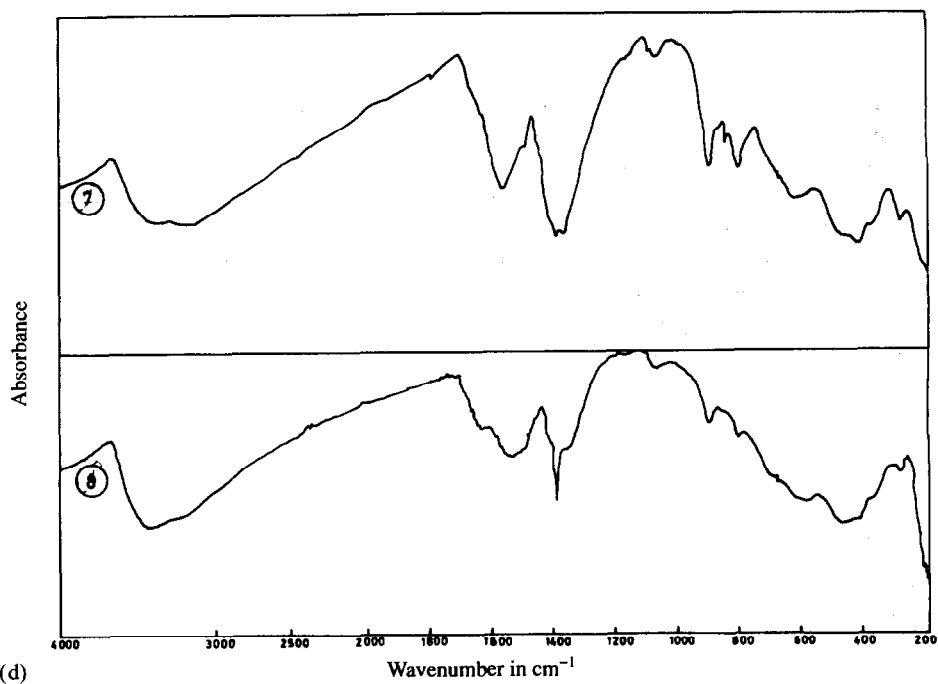
The infrared spectra of compounds 1–8 from Table 2 are presented in Fig. 2a–2d. Only the most characteristic features of the IR spectra will be discussed, using the conventions of Nakamoto [10] and table XV in the Supplementary material of Dziobkowski et al. [1]. The IR spectra were taken over the range $4000\text{--}200\text{ cm}^{-1}$. They all have in common a broad and strong band centred at 3400 cm^{-1} indicating hydrogen bonding. The weak band at 1710 cm^{-1} assigned [1] to $\nu_{\text{asymm}}(\text{COO})$ anionic, exists in samples 1–4 in Table 1 and in samples 1–4 in Table 2. It is not present in samples 5–8. The strong, broad band at 1560 cm^{-1} is similar in all samples, except sample 8 (Table 2). This can be assigned [1] to $\nu_{\text{asymm}}(\text{COO}) + \nu(\text{C}=\text{C})$. Sample 8 shows a broad band at 1530 cm^{-1} and a shoulder

at 1630 cm^{-1} . The shoulder corresponds to $\nu(\text{H}_2\text{O})$. The strongest band in most samples is that at 1410 cm^{-1} (samples 1–4 in Table 1 and samples 1, 2, 4 and 5 in Table 2). In sample 3 it is of equal intensity to that at 1560 cm^{-1} . It can be assigned [1] to $\nu_{\text{symm}}(\text{COO})$. IR spectra of samples 5–8 in Table 2 show an additional sharp peak at 1390 cm^{-1} corresponding to NO_3^- frequency [11].





(c)



(d)

Fig. 2. IR spectra of Fe(III)-*o*-phthalates from Table 2: (a) samples 1, 2; (b) samples 3, 4; (c) samples 5, 6; (d) samples 7, 8.

Weak unassigned frequencies at 1300, 1270 and 1040 cm^{-1} are present in all samples except samples 7 and 8.

A weak band in the range 1150–1070 cm^{-1} , assigned [1] to $\delta(\text{CH})$, is present in all samples except sample 8.

Samples 7 and 8 show a band at 890 cm^{-1} assigned to the asymmetric Fe–O–Fe stretch [12]. The frequency at 760 cm^{-1} of medium intensity assigned [1] to $\pi(\text{C–C})$ in samples 1–4 in Tables 1 and 2, is not pronounced in samples 5 and 6 and is absent in samples 7 and 8.

Weak bands at 660 and 700 cm^{-1} assigned [1] to $\delta(\text{COO}) + \pi(\text{COO or CH})$ are also present in all samples except samples 7 and 8.

The medium band at 490 cm^{-1} assigned [1] to $\nu(\text{FeO})$ is present in samples 1–4 in Table 1 and samples 1–4 in Table 2. In samples 5–8, there is a broader band shifted to slightly lower frequency, with several shoulders in the last two samples.

The weak unassigned [1] frequency at 340 cm^{-1} is absent in samples 5–8, Table 2. Samples 5, 7 and 8 show an additional unassigned weak band at 275 cm^{-1} .

From the IR spectra it can be concluded that samples 1–4 in Table 2 show a similarity in structure with the reference compound [1]; that samples 7 and 8 in Table 2 are oxo-bridged Fe(III) polymers; and that samples 5 and 6 probably have a different type of bridging mode, not yet identified.

3.4. Mössbauer effect study

In the temperature region 77–300 K, the Mössbauer spectra of the samples given in Table 1, as well as samples 1–6 in Table 2 are very similar. The spectra appeared as slightly asymmetric quadrupole split doublets with rather broad resonance lines, as shown in Fig. 3. It was found that these spectra could not be satisfactorily fitted by considering only one iron environment. Improved fitting [13] of these spectra was possible by assuming two quadrupole split doublets with different relative areas. Table 3 shows the corresponding hyperfine parameters which give evidence that in all the studied complexes iron ions occur in the high-spin ferric form. The additional broadening of the resonance lines can be explained by some distribution of the quadrupole splitting parameters at the two main iron sites due to slightly different iron environments, caused by bound water and some replacement of various ligands, such as NO_3^- , OH^- and phthalate. The relative intensities of the two quadrupole split doublets depend strongly on precipitation conditions and indicate that these trinuclear oxo-iron complexes contain bondings which do not resemble the equatorial iron triangle found in basic iron acetates and their analogues [14]. The appearance in some samples of two quadrupole split subspectra with relative intensities of 1:2 can be explained by the existence of some isosceles triangles [13] with two nearly equivalent iron sites and one unique iron site. Samples 7 and 8 in Table 2 (which were prepared at significantly higher pH values) reveal interesting Mössbauer spectra below room temperature, consisting of a magnetic hyperfine sextet and quadrupole split doublet patterns (Fig. 4). These spectra suggest that the nucleation of these phases occurred in a manner different from those in the other samples. For simplicity, the obtained spectra were fitted by

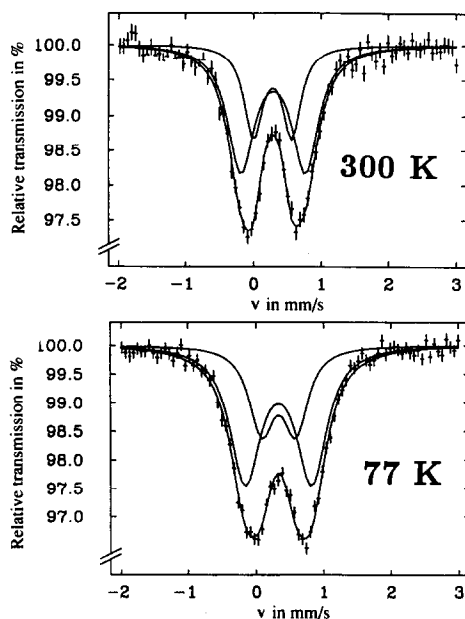


Fig. 3. Mössbauer spectra of ^{57}Fe in sample 3 (Table 2) measured at 300 and 77 K using a $^{57}\text{Co}/\text{Rh}$ source.

Table 3

Parameters of Mössbauer spectra (recorded at temperature T) of the samples with the composition given in Table 2

Sample no. (Table 2)	T / K	Sub spec.	IS/ (mm s $^{-1}$)	QS/ (mm s $^{-1}$)	Γ / (mm s $^{-1}$)	$H_{\text{eff}}/(\text{kG})$	Rel. areas
1	300	D1	0.39 (1)	0.57 (2)	0.32 (1)		0.33
		D2	0.40 (1)	0.95 (1)	0.46 (4)		0.67
2	300	D1	0.39 (1)	0.62 (1)	0.34 (2)		0.33
		D2	0.40 (1)	1.00 (1)	0.47 (2)		0.67
3	300	D1	0.39 (1)	0.60 (1)	0.32 (2)		0.33
		D2	0.40 (1)	1.00 (1)	0.47 (1)		0.67
4	300	D1	0.38 (1)	0.64 (1)	0.41 (2)		0.41
		D2	0.37 (1)	1.12 (1)	0.40 (1)		0.59
5	300	D1	0.35 (1)	0.59 (1)	0.35 (1)		0.67
		D2	0.35 (1)	0.99 (1)	0.39 (2)		0.33
6	300	D1	0.34 (1)	0.55 (1)	0.36 (2)		0.53
		D2	0.33 (1)	0.98 (1)	0.42 (2)		0.47
7	300	D1	0.34 (1)	0.55 (1)	0.36 (2)		0.72
		D2	0.33 (1)	1.05 (1)	0.43 (2)		0.28
7	77	D	0.46 (2)	0.63 (1)	0.45 (1)		0.47
		Sextet	0.48 (1)	0.56 (2)	0.42 (1)		457 (2)
8	300	D1	0.40 (1)	0.52 (1)	0.63 (2)		0.69
		D2	0.38 (1)	0.84 (1)	0.40 (2)		0.31

Key: IS, isomer shift relative to $\alpha\text{-Fe}$ at RT; QS, quadrupole splitting parameter; Γ , full width at half maximum of resonance line; H_{eff} , effective magnetic hyperfine field at nuclei ^{57}Fe .

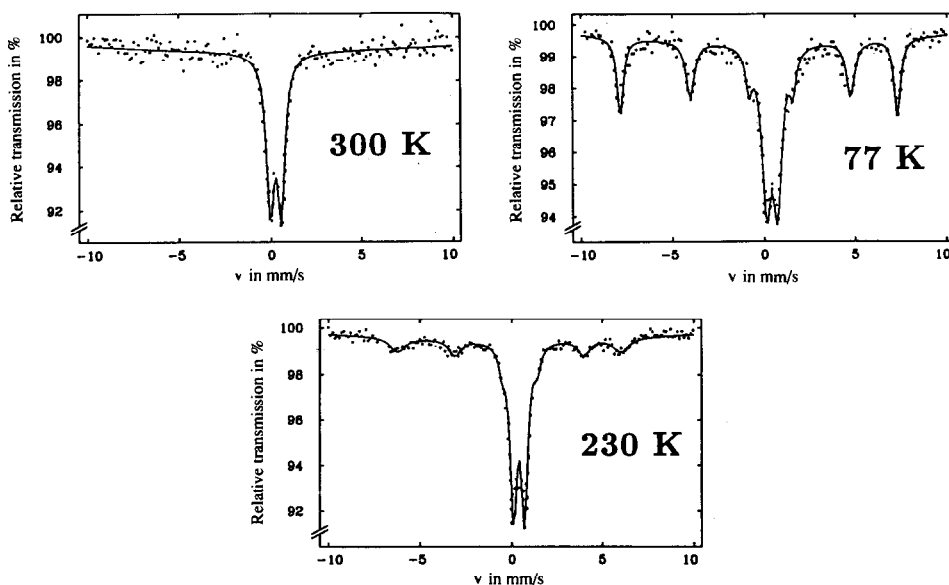


Fig. 4. Mössbauer spectra of ^{57}Fe in sample 7 (Table 2) measured at various temperatures using a $^{57}\text{Co}/\text{Rh}$ source.

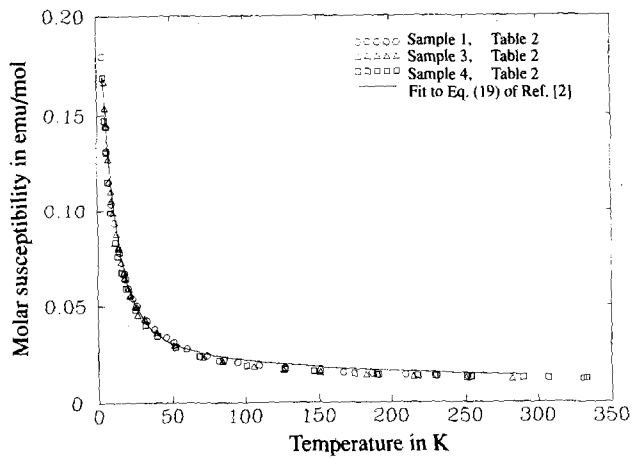
assuming only one doublet and one magnetic sextet pattern with broadened resonance lines. It was found that the relative area of the doublet pattern increases at the expense of the magnetic sextet pattern with increasing temperature. From such a temperature behaviour of spectra, it can be predicted that these samples reveal superparamagnetism [9] of small particles or clusters. According to the hyperfine parameters obtained at 77 K, it might follow that these small particles are goethite-like in their structural character with sizes of 15–20 nm for sample 7, and 10 nm for sample 8.

3.5. Magnetic studies

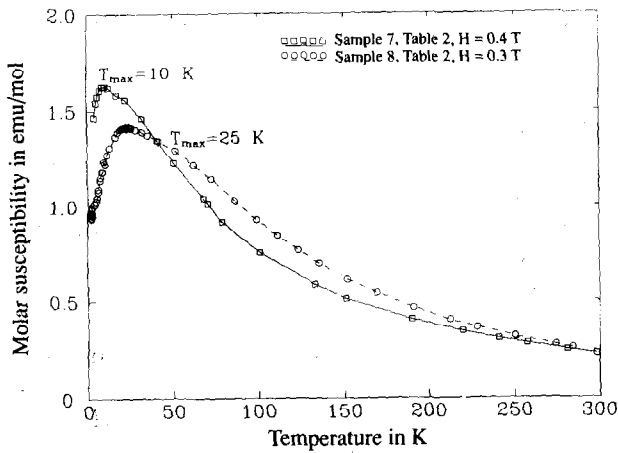
Selected samples were used for magnetic susceptibility and torque measurements. Two different types of behaviour were obtained. The magnetic susceptibilities induced by warming the samples from the lowest temperature are presented as a function of temperature in Fig. 5a and 5b. Analysis of the susceptibility results for samples 1, 3 and 4 in Table 2 are presented in Fig. 5a. The solid line displays the fit of the data to expression (19) of Ref. [2], applicable for the isosceles triangle. For the exchange integrals, the data give $J_{12}/\text{cm}^{-1} = -35.4$ and $J_{13}/\text{cm}^{-1} = -21.1$. There was no need to introduce temperature-independent paramagnetism.

Fig. 5b presents the susceptibility results for samples 7 and 8, Table 2, which show maximum susceptibility at $T_{\text{max}}/\text{K} = 10$ and 25, respectively.

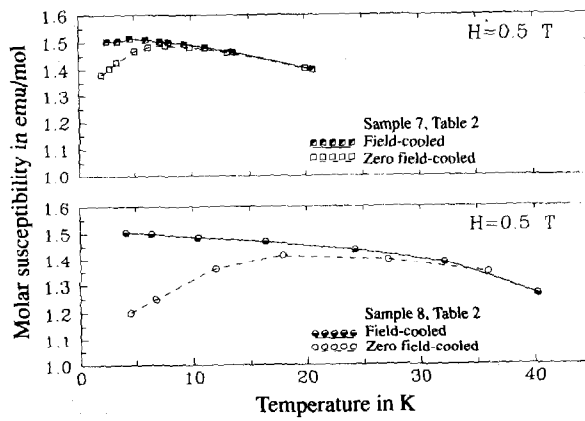
In order to resolve between antiferromagnetic and spin glass behaviour, additional experiments were performed. The results of zero field-cooled and field-cooled



(a)

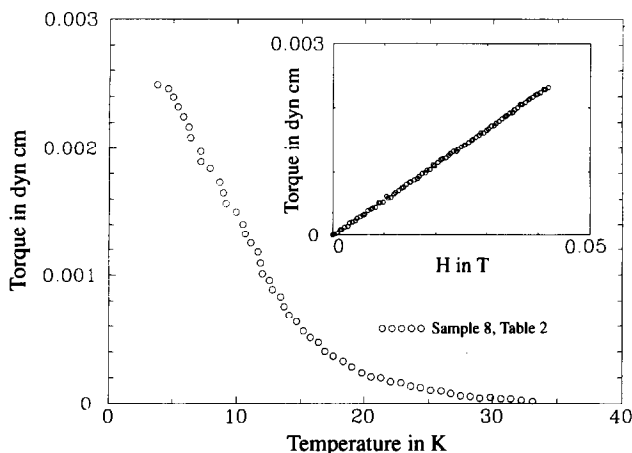


(b)



(c)

Fig. 5. (a)–(c).



(d)

Fig. 5. Magnetic susceptibility data vs. temperature for selected samples from Table 2: (a) samples 1, 3 and 4 by warming up; (b) samples 7 and 8 by warming up; (c) samples 7 and 8 in field-cooled and zero field-cooled; (d) torque measurements for sample 8.

susceptibility measurements, shown in Fig. 5c, rule out antiferromagnetic behaviour. The most direct evidence of the spin glass behaviour comes from the torque measurements displayed in Fig. 5d.

Sample 8 was cooled through the T_{\max} in a magnetic field of 0.5 T down to 4.2 K and the torque, i.e. the “frozen” magnetization, was measured on warming up. The magnetization vanishes at 30 K, which is in accordance with the susceptibility results (Fig. 5b, sample 8). We note that there was no torque signal in zero field-cooled measurements. The torque versus magnetic field (inserted in Fig. 5d) shows a linear dependence. This fact, together with the vanishing magnetization at temperatures close to T_{\max} , is characteristic of spin glass behaviour [15,16].

Fig. 6 presents the calculated magnetic moments $\mu_{\text{eff}}/\text{Fe}$ (in B.M.) vs. temperature for samples 1, 3, 4, 7 and 8, Table 2. The broken curve presents the values obtained by Dziobkowski et al. [1] for the reference compound. From Fig. 6 it can be concluded that samples 1, 3 and 4, Table 2, have structures similar to that of the reported compound [1] and that samples 7 and 8 show significantly higher $\mu_{\text{eff}}/\text{Fe}$, up to 4.49 and 5 B.M., respectively.

4. Conclusions

Several different polynuclear Fe(III)-*o*-phthalates have been prepared and characterized by comparative techniques. By changing the concentrations of the precipitation components, compounds with different ions balancing the charge (OH^- , NO_3^- , Na^+ , or $(\text{C}_6\text{H}_5)_4\text{P}^+$) have been obtained. Samples 1–8 in Table 2, although different in chemical composition, show very similar IR and Mössbauer spectra and magnetic properties to the reference compound described in detail by Dziobkowski

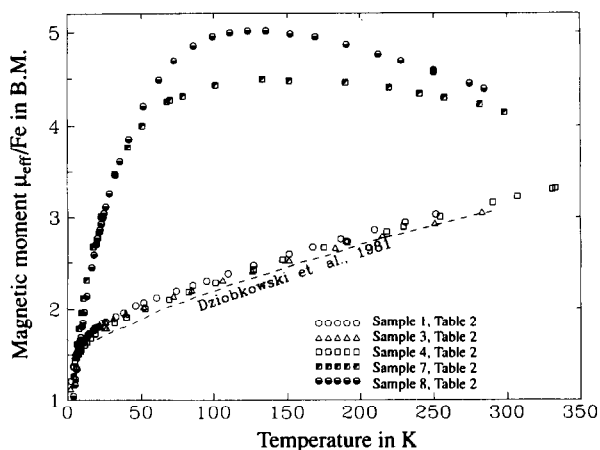


Fig. 6. Calculated magnetic moments $\mu_{\text{eff}}/\text{Fe}$ (in B.M.) vs. temperature for selected samples 1, 3, 4, 7 and 8, Table 2, in comparison with the reference compound $[\text{Fe}_3(o\text{-phthalate})_3(\text{H}_2\text{O})_3](o\text{-phthalate})_{0.5} \cdot 2\text{H}_2\text{O}$, presented by the broken line.

et al. [1]. It can be concluded that the trimer unit Fe_3O is present in these samples. The IR spectrum of sample 4 in Table 2 also confirms the presence of the Fe_3O unit and additional unassigned bands from the $(\text{C}_6\text{H}_5)_4\text{P}^+$ ion. Mössbauer spectra could be satisfactorily fitted by assuming two quadrupole split doublets, which indicate the existence of two main iron environments in these compounds. The magnetic moment of this sample is comparable to other samples containing the Fe_3O unit. Samples 5–8 do not show the presence of Fe_3O units in their IR spectra. Samples 7 and 8 show a band at 890 cm^{-1} which has been assigned to the asymmetric Fe–O–Fe stretch [12]. Their Mössbauer spectra show a combination of magnetic sextet and paramagnetic doublet patterns below room temperature. The intensity ratio of both patterns is temperature dependent, which is typical for superparamagnetic behaviour of small particles.

The analysis of the susceptibility results for samples 1, 3 and 4 reveals the exchange integrals $J_{12}/\text{cm}^{-1} = -35.4$ and $J_{13}/\text{cm}^{-1} = -21.1$. The susceptibility and torque measurements show that samples 7 and 8 have characteristics of spin glass in the temperature range 10–30 K. The calculated magnetic moments $\mu_{\text{eff}}/\text{Fe}$ for these samples are the highest in the studied series.

Acknowledgements

This work was supported by the Ministry of Science of Croatia and Slovenia. Additional support by U.S. Geological Survey is appreciated. We also acknowledge Mr. A. Dürriegl, "Pliva", Zagreb for the AAS determination of iron.

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