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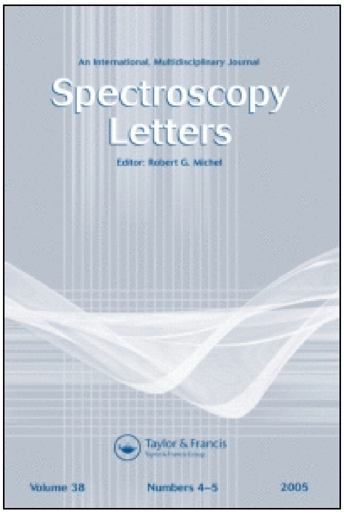

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Preparation and Characterization of Iron-DI- and Poly-Carboxylatepyrocatechol and Pyrogallol Mixed Ligands Chelates

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PREPARATION AND CHARACTERIZATION OF IRON-DI- AND POLY-CARBOXYLATEPYROCATECHOL AND PYROGALLOL MIXED LIGANDS CHELATES

Key Words: Preparation and Characterization, Thermal and Spectroscopic Properties, Iron(III) Mixed Ligand Chelates.

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ABSTRACT

The preparation and structure investigation of six iron-chelates; trioxatoferrate(III),1,trioxalatoferrate(III)-pyrocatechol,2;trioxalatoferrate(III) - pyrogallol 3,Fe(III)-EDTA 4,Fe(III)-EDTA-pyrocatechol 5 and Fe(III)-EDTA-pyrogallol 6, are described in this paper. The prepared compounds were identified by elemental analysis and studied by using infrared spectroscopy and TG and DTA thermal analyses. The possible structures were also suggested and confirmed. The mechanisms of thermal decomposition of these chelates were discussed using the available thermal data. It was concluded that both compounds 1 and 4 had been formed as blue to violet colored thermally stable compounds with pyrocatechol and pyrogallol. Thus, both of them are strongly recommended as analytical chromophoric reagents for the spectrophotometric microdetermination of these di- and trihydric phenols in natural and biological extracts which are the subjects of another paper.

INTRODUCTION

The preparation, structural identification and behavior of many carboxylic, amino carboxylic acids, phenols and their metal compounds have been the subject of studies in this laboratory [1-10]. Some of these aminocarboxylic acids or carboxylic acid salts of iron(II) or (III) form, the phenolic compounds, colored chelates both in solution and in the solid state but most of them were thermally unstable [11]. These reactions were applied to determine some carcinogenic phenols in natural samples, such as biological extracts from tumor patients, which is the subject of other work in this laboratory [11]. Study of the separated solid colored mixed ligand chelates is the ultimate goal of this work. We selected iron(III) compounds of carboxylic and amino carboxylic ligands and their complexes with pyrocatechol(PC) and pyrogallol(PG) as the subject of this paper, because the blood and plasma of tumor patients contain many di- and poly-hydric phenols and their derivatives. The importance of this work stems from the interactions between these chelates and phenols which can be used in many analytical fields.

EXPERIMENTAL

Material and Procedures:

The pyrocatechol (PC) and pyrogallol (PG) ligands were of the Analar grade from Merck. Iron(II) sulfate, H_2O_2 (70%, always kept in the dark and in a refrigerator), and sodium oxalate were used to prepare iron(II) oxalate and consequently trioxalatoferrate(III)(1) by oxidation with H_2O_2 using recommended procedures [11]. The product was green crystals after crystallization from a EtOH : water mixture, of m.p. > 300°C. EDTA (BDH) was used for preparation of Fe(III)-EDTA complex (4) by mixing equal volumes (50 ml of 10^{-2} M) of aqueous solutions of iron(III) sulfate and EDTA at pH = 6.0. The product was left to dry at normal temperature in the reaction vessel for several days, and the product was yellowish white of m.p. > 300°C after crystallization from (1:1) ethanol-water mixture.

In order to prepare mixed ligand complexes of bridged trioxalate ferrate(III) of PC (2) or of PG (3), 2.06×10^{-2} M of (1) was mixed thoroughly with 9.09×10^{-2} M PC or 7.93×10^{-2} M PG at pH 6.0. The pH was adjusted by addition of 0.2 M NaOH (BDH), and left for 5 days in the reaction vessel. The separated solids were washed with acetone and dried. Dark violet mixed ligand chelates (2 and 3) were obtained of melting points >> 300°C, after crystallization from (1:1) ethanol-water mixture.

The preparation of the Fe(III)-EDTA -PC (5) and Fe(III)-EDTA-PG (6) complexes involved the addition of 18.4×10^{-2} M PC or 14.4×10^{-2} M PG to complex 4, of 5.5×10^{-2} M, with continuous agitation and shaking the reactants in the reaction vessel at pH 6.0. The product was left for several days to dry, washed with acetone and dried again. The crystallized chelates from EtOH : water mixture (1:1) had violet colors and mps >> 300°C.

The pH of the solution was measured using Orion pH/mV Ionlyzer digital pH-meter 701 A.

Elemental, Spectral and Thermal Analyses:

Elemental analysis for C, H and metal (M) contents were performed by microanalysis at Cairo University (Table 1). The metal content M was analyzed using a Varian Techtron (model 100) atomic absorption spectrophotometer, after complete digestion of the complexes by recommended procedures [6, 12]. The MW (molecular weights) of the chelates were calculated from these metal contents as usual.

The IR spectra were recorded as KBr discs on a Pye Unicam SP 3-300 IR spectrophotometer over a wavenumber range of 3000-400 cm^{-1}.

Thermogravimetric (TG) and differential thermal analyses (DTA) were done on Shimadzu TG system (Shimaszu 30 series) thermal analyzer. The

Table 1. Elemental Analysis of Compounds I to VI.

	Found (%)			Calcd. (%)		
Chelate	**Fe**	**C**	**H**	**Fe**	**C**	**H**
1	11.3	14.9	2.45	11.78	14.49	2.41
2	9.4	24.3	2.40	9.48	24.54	2.71
3	9.3	23.4	2.60	9.22	23.80	2.60
4	15.0	31.0	4.42	14.43	31.02	4.13
5	11.0	37.66	4.60	10.89	38.44	4.03
6	10.50	36.0	4.00	10.52	36.170	4.52

1: $Na_3[Fe(C_2O_4)_3].6H_2\ O$, M. Wt. = 496.8

2: $Na_3[Fe(C_2O_4)_3(C_6H_6O_2).5H_2O$, M. Wt. = 588.85

3: $Na_3[Fe(C_2O_4)_3(C_6H_6O_3).5H_2O$, M. Wt. = 604.85

4: $NaFe(C_{10}H_{14}O_8N_2].H_2O$, M. Wt. = 386.85

5: $NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_2).H_2O$, M. Wt. = 496.85

6: $NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_3).2H_2O$, M. Wt. = 530.

weight loss and DTA of 5 mg samples were measured in the temperature range 25-600°C using a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Thermogravimetric (TG) and Differential Thermal Analyses (DTA):

The TG and DTA of the compounds 1-6 are illustrated in Figs.(1and 2) and in Table(2). For compound 1, the first stage of decomposition in the range of 90 to 140°C indicates a loss of two molecules of water of crystallization per mole of compound. The mass loss found (estimated=8.0%) and the calculated one (7.6%) were in reasonable agreement. This weight loss can be seen as an endothermic shift at the same temperature (Fig. 2,I). This endothermic peak may also be related to a decrease of heat capacity of the compound during such a

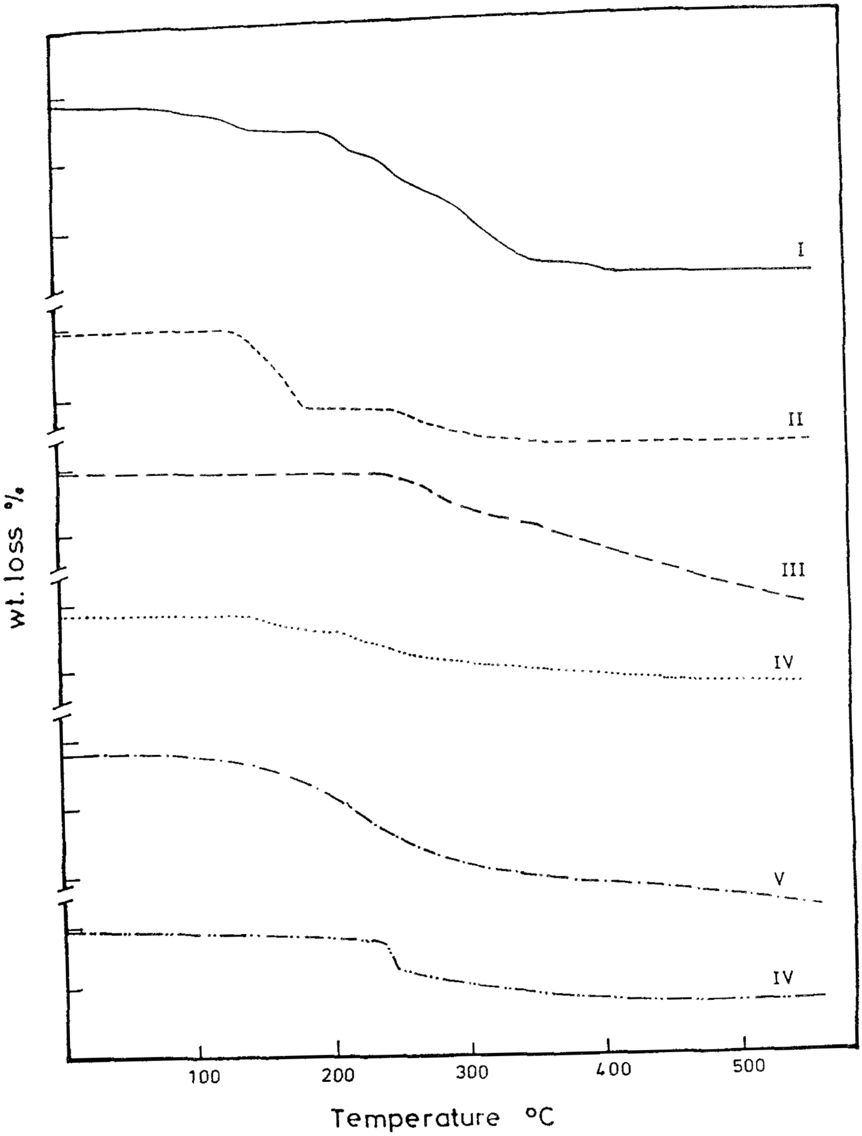

Fig. 1:TG Curves (I-VI)for the Thermal Decomposition of Iron Chelates 1-6.

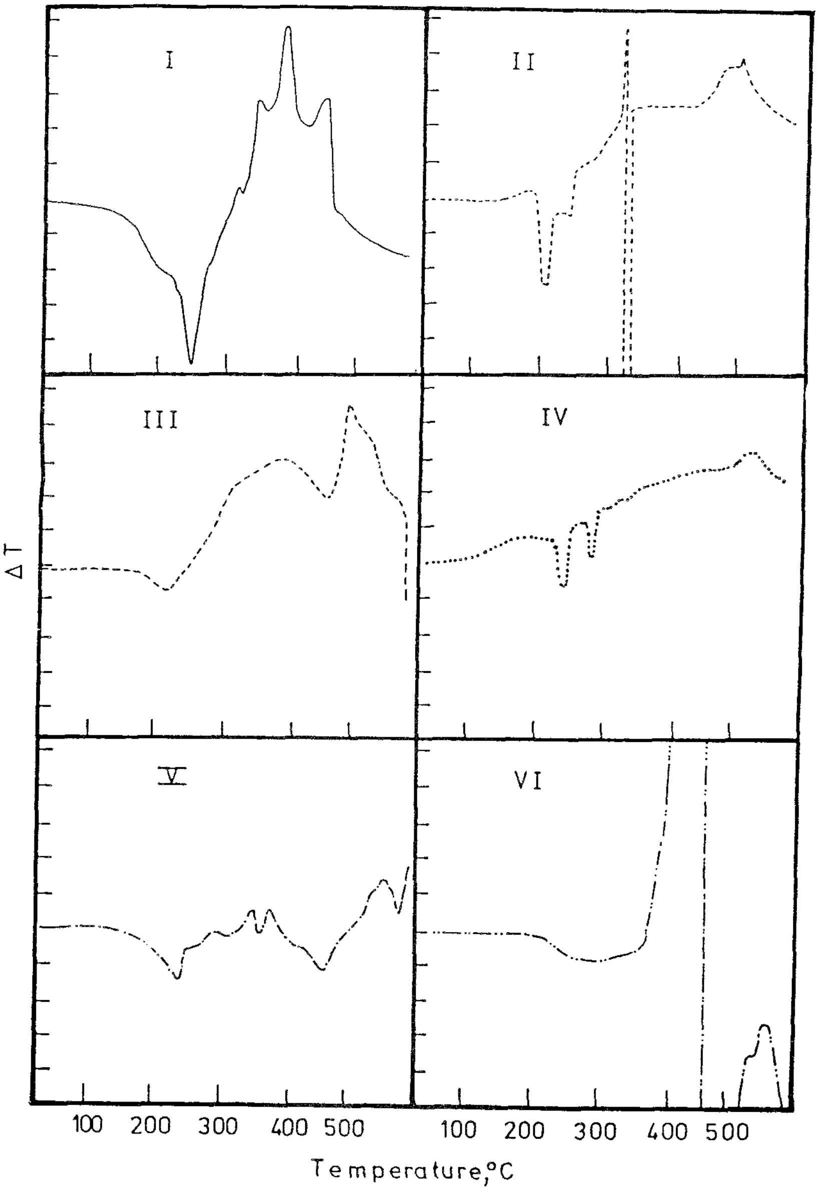

Fig. 2:DTA (I-VI)Curves of Iron Chelates 1-6.

Table 2. Mass Loss of Compounds 1 to 6

Chelate	Temp. Range (°C)	Decomposition Products Lost	Weight loss (%)	
			Found	Calcd.
1	40-200	$2H_2O$ cryst.	8.0	7.60
	200-280	3CO	18.0	17.72
	280-450	$3CO_2$	27.0	27.86
2	100-180	P.G. + H_2O cryst.	25.0	24.77
	180-460	$2CO_2$	15.0	14.94
3	110-190	P.G. + H_2O cryst.	23.0	23.80
	190-550	$3CO + 3CO_2$	36.0	35.71
4	150-320	CO_2	12.0	11.36
	320-550	CO_2	12.0	11.36
5	100-500	P.G. + H_2O cryst.	42.0	42.12
		$2CO_2$		
6	200-360	$2H_2O$	7.0	6.81
		$2CO_2$	17.0	16.64

1: $Na_3[Fe(C_2O_4)_3].6H_2O$, M. Wt. = 496.8

2: $Na_3[Fe(C_2O_4)_3(C_6H_6O_2).5H_2O$, M. Wt. = 588.85

3: $Na_3[Fe(C_2O_4)_3(C_6H_6O_3).5H_2O$, M. Wt. = 604.85

4: $NaFe(C_{10}H_{14}O_8N_2].H_2O$, M. Wt. = 386.85

5: $NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_2).H_2O$, M. Wt. = 496.85

6: $NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_3).2H_2O$, M. Wt. = 530.85

loss. The sharp endothermic peak appears at 200-280°C (Fig. 2) centered at 250°C may be explained by the loss of three CO groups (estimated mass loss 18.0% and calcd. 17.72%), which react with oxygen in the furnace to give three molecules of CO_2 in the temperature range 280 to 450°C (estimated 27.0%, calcd. 27.86%).

This explanation agrees well with the appearance of the three sharp exothermic peaks at 280-480°C, centered at 320, 380 and 440°C (cf. Fig. 2, I). Therefore, we can suggest scheme 1 for the decomposition of compound 1, as:

$$Na_3[Fe(C_2O_4)_3].6H_2O \longrightarrow Na_3[Fe(C_2O_4)_3].4H_2O + 2H_2O$$

$$Na_3[Fe(C_2O_4)_3].4H_2O \longrightarrow 1\tfrac{1}{2}\,Na_2O + \tfrac{1}{2}Fe_2O_3.3H_2O + 3CO + 3CO_2 + H_2O$$

Scheme 1

The IR spectra [13] of compound 1, show ν_{OH} at 3000-3500 cm^{-1}, which is an intense broad band referring to the water of crystallization, ν_{CO} at 1670 cm^{-1} due to CO of bonded carbonyl groups, ν_{COOH} as a sharp intense band at 1600-1730 cm^{-1} due to the coordinated COOH groups. The Fe-O bond with some carboxylic groups appeared as $\nu_{M\text{-}O}$ at 350 cm^{-1}. The chelate 2 in TG (Fig. 1, II and Table 2)shows two mass losses; one at 130-180°C due to the loss of one mole of PC ligand, followed immediately by the loss of one molecule of water of crystallization (estimated 25.0%, calcd. 24.77%). The loss of the volatile PC molecule appears in DTA (Fig. 2, II) as an exothermic base shift starting at 170 to 200°C, which attributed to expansion of PC and its loss from the entity of compound 2. This loss appears as a sharp endothermic peak at 205°C. The loss of further water of crystallization appears immediately as another small endothermic peak at 230°C. This compound starts to expand as indicated by the abrupt exothermic base shift (Fig. 2, II) in the range 240-280°C. This is attributed to the loss of two carboxylic groups as CO_2 from the compound 2 (estimated 15.0%, calcd. 14.94%), in the temperature range 280-460°C. It is believed that these groups are lost firsty, as two CO molecules which then react with oxygen to give two CO_2. This suggestion is confirmed by the appearance of very vigorous sharp exo- and endothermic peaks at 320-330°C (Fig. 2, II). The broad exotherm at 420 to 530°C, may be attributed to the start of decomposition of the remaining oxalate group to leave hydrated iron oxide or may be due to the sublimation of pyrocatechol molecules.

The IR spectra of compound 2, which is actually PC mixed ligand chelate of1, show ν_{OH} 3300-3500 cm^{-1}, ν_{CO} and ν_{COOH} at 1680 and 1625-1730 cm^{-1}, respectively, and ν_{ring} vibrations at 1200-1400 cm^{-1}, and $\nu_{M\text{-}O}$ at 300-360 cm^{-1}. These bands appear at higher ν values in comparison with their counterparts in compound 1; which refers to the stability of compound 2 > 1. This is also in good agreement with the fact that trioxalatoferrate(III),1 as a part of compound 2, starts to decompose at 40°C (Table 2). The trioxalatoferrate(III)-PG mixed ligand chelate 3 starts to decompose, with a first step (Fig. I, III) at 110 to 190°C (estimated 23.0%, calcd. 23.8%). It loses the molecule of PG together with a H_2O molecule of crystallization (cf. Fig. I, III). In DTA of compound 3 (Fig. 2, III), the decomposition step appears as a broad endotherm starting from 130 to 230°C. The nonappearance of an exothermic base shift as in the case of the PC chelate 2 in this temperature range may be attributed to the lower volatility of PG molecule rather than PC. Therefore, it is followed immediately by a broad exothermic peak at 250-450°C (Fig. 2, III). The remaining part of compound 3 decomposed in a second step at 190-550°C when 3 CO and 3 CO_2 gas molecules were liberated (estimated 36.0%, calcd. 35.71%). This step appeared in the DTA (Fig. 2, III) as an endothermic broad peak at 380-450°C; followed by another broad exothermic peak at 450-570°C. The appearance of the last two broad endo- and exothermic peaks at this very high temperature range than 2 may be attributed first, to the decomposition of oxalate groups into CO and CO_2 gases and secondly due to the stability of mixed ligand chelate 3 > 2 > 1.

The thermal stability of the iron(II)-EDTA monohydrate complex 4, was studied by both TG (Fig. 1, IV) and DTA (Fig. 2, IV). The TG of compound 4 showed the first loss at 150 to 320°C (estimated 12.0% and calcd. 11.36%) due to the loss of one molecule of CO_2 by decomposition of one carboxylic acid group of EDTA, that does not attach to Fe(III) ions in five membered rings. This was followed by decomposition of the other group at 320 to 550°C (estimated 12.0%, and calcd. 11.36%). These two decomposition steps are represented by a broad endotherm in the temperature range 220 to 345°C followed by very vigorous exothermic and endothermic peaks in the temperature range 345 to 560°C, which may be explained by the loss of CO gas which oxidized to CO_2.

The IR spectra of compound 4 show ν_{OH} at 3400 cm^{-1}, ν_{NH} at 3260 cm^{-1}, ν_{CO} at 1690-1740 cm^{-1}, ν_{COOH} at 1590-1620 cm^{-1}, and ν_{M-O} at 490 cm^{-1}. This spectra may refer to the presence of free carboxylic groups weakly bonded to iron(III) in compound 4, and consequently are decomposed during heating. The Fe(III)-EDTA-PC mixed ligand chelate 5 decomposed in one step at 100-500°C to give one mole PC, one H_2O molecule and two moles CO_2 (Fig.1,V). This loss appears as one endothermic peak at 270°C. This endothermic peak followed by many endo- and exothermic peaks starting from 290 to 600°C. These endo- and exotherms may arise from the decomposition of the eliminated PC volatile molecule from the moiety of the chelate 5. The IR spectra of compound 5 show ν_{OH} at 3500 cm^{-1}, ν_{NH} at 2960 cm^{-1}, ν_{COOH} at 1570-1650 cm^{-1}, ν_{ring} at 1000 to 1200 cm^{-1}, ν_{M-O} at 300 to 360 cm^{-1}. These are the same for Fe(III)-EDTA 4, except some slight shifts to higher or to lower frequency values. These shifts are attributed to the introduction of PC molecule into the moiety of chelate 4 to give compound 5.

The TG of the mixed ligand chelate 6 (Fig. 1, VI) shows an estimated mass loss of 7.0% (calcd. 6.81%) due to the loss of one molecule of water of

Table 3. IR Spectra of Iron Chelates I, II, IV, V.

	Compound			
Mode	I	II	IV	V
ν_{OH}	3000-3500	3300-3500	3420	3500
	bi	lbi	s-sh	i-sh
ν_{NH}	---	---	2360	2960
			s-sh	s-sh
ν_{CO}	1670	1680	1690-1740	---
	i-sh	i-sh	s-sh	
ν_{COOH}	1600-1730	1680-17	1590-1620	1570-1650
	i-sh	i-sh	s-sh	i-sh
ν_{ring}	---	1200-1450	---	1000-1300
		sev-sh		sev-sh
$\nu_{M\text{-}O}$	350	300-360	490	300-360
	i-sh	b-s	s-sh	b-s

b: broad, sh: sharp, s: small, i: intense, l: less, sev: several peaks.

crystallization, followed immediately by another estimated mass loss of 17.0% (calcd. 16.65%) which is due to the decomposition of COOH groups of EDTA as two CO_2 molecules at 200 to 360°C. The DTA of compound 6 (Fig. 2, VI) gives one broad endotherm at 200 to 360°C which confirm such a loss of H_2O and CO_2. There is also a vigorous exothermic process at 360 to 460°C followed by another vigorous endothermic process at 460 to 520°C and finally an exothermic one at 520 to 600°C . These endo- and exothermic peaks may be explained by vigorous decomposition of unbonded carboxylic groups of EDTA as CO which reacted with the oxygen of the furnace to give CO_2 and also to the vigorous elimination of PG from the stem of compound 6 at this very high temperature (360-600°C) rather than the elimination of PC from the compound

5 (290-600°C). This means that PG is strongly bonded to the Fe(III)-EDTA complex rather than the PC ligand. Thus, the compound 6 is more stable than 5.

CONCLUSION

Finally we can conclude that iron trioxalatoferrate(III), 1 or iron(III)-EDTA, 4 hold PG more strongly than PC, although they can bond with both of them. This criteria makes the complexes 1and 4 act as good chromophoric analytical reagents, forming thermally stable mixed ligand chelates with PC or PG in aqueous; nonaqueous and biological extracts which is the target of this work.

The aim of the present work is to study the thermal stability of iron-carboxylate complexes (1 and 4) and iron-carboxylate-phenolate mixed ligand chelates (2, 3,5 and 6). The suggested molecular formula of these complexes and chelates from elemental analysis (Table 1), thermal analyses TG (Table 2 and Fig. 1), and DTA (Fig. 2), and IR (Table 3) are:

$Na_3[Fe_2(C_2O_4)_3].6H_2O$, 1;$Na_3[Fe(C_2O_4)_3(C_6H_6O_2).5H_2O$, 2;
$Na_3[Fe(C_2O_4)_3(C_6H_6O_3).5H_2O$, 3;$NaFe(C_{10}H_{14}O_8N_2).H_2O$, 4;
$NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_2).H_2O$, 5; $NaFe(C_{10}H_{14}O_8N_2)(C_6H_6O_3).2H_2O$, 6

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