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## Synthesis and characterization of $\mu$ -hydroxido- and $\mu$ -polycarboxylato-bridged iron(III) complexes with 2,2'-bipyridine

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**Abstract:** Four novel polymeric iron(III) complexes with 2,2'-bipyridine (bipy) and different aromatic polycarboxylato ligands as anions of phthalic (pht), isophthalic (ipht), terephthalic (tpht) and pyromellitic (pyr) acid were synthesized by ligand exchange reaction. The complexes were characterized by elemental and TG/DSC analysis, FTIR and diffuse reflectance UV–Vis–NIR spectroscopy and magnetic susceptibility measurements. Based on the analytical and spectral data, the formulae of the complexes were  $\{[\text{Fe}_4(\text{bipy})_2(\text{H}_2\text{O})_2(\text{OH})_6(\text{pht})_3] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Hipht})_2(\text{ipht})_2(\text{OH})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Htpht})_2(\text{OH})_6(\text{tpht})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**3**) and  $\{[\text{Fe}_4(\text{bipy})(\text{H}_2\text{O})_8(\text{OH})_4(\text{pyr})_2] \cdot \text{H}_2\text{O}\}_n$  (**4**). All complexes were red brown and low-spin with a distorted octahedral geometry with  $\text{FeO}_6$  or  $\text{FeN}_2\text{O}_4$  chromophores. The polycarboxylato ligands played a bridging role in all cases, whereas monodentate COO groups were present in **2** and **3**, while bridging and chelate COO groups were established in **1** and **4**. The thermal behaviours of **1–4** were investigated in detail and the molar dehydration enthalpies were calculated. According to the all those results, the structural formulae of complexes **1–4** were proposed.

**Keywords:** mixed ligand complexes; iron(III); 2,2'-bipyridine; polycarboxylato ligands;  $\text{Fe}_2(\text{OH})_2^{4+}$  dimer.

### INTRODUCTION

The growing interest in the field of mixed ligand complexes arises from the high structural tunability of these compounds, which directly impacts their magnetic, electrical, optical and catalytic properties. The variety of individual

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building blocks and coordination modes of aromatic polycarboxylates provides a wide range of potentially supramolecular architectures and, consequently, many practical applications. Hitherto, transition metal complexes with polycarboxylato ligands have been utilized in adsorptive hydrogen storage, gas separation, catalysis, and sensitization in dye-solar cells or sensors.<sup>1–7</sup>

In the past few decades, special interest has been developed towards the implementation of aromatic polycarboxylato ligands as building units, which combined with transition metals and *N,N*-ligands, result in one-, two- or three-dimensional complexes based on covalent bonds, as well as on hydrogen bonding and non-covalent  $\pi$ - $\pi$  interactions. The most frequently used aromatic polycarboxylato ligands are the dianions of phthalic ( $H_2pht$ ), isophthalic ( $H_2ipht$ ) and terephthalic ( $H_2tpht$ ) acid, together with the tetra-anion of pyromellitic acid ( $H_4pyr$ ), which usually have a bridging role using numerous donor O atoms from COO groups. A great number of different coordination modes of these polycarboxylates in a variety of transition metal complexes is well understood and explained elsewhere.<sup>8–18</sup>

The iron(III) ion has been rarely utilized as the metal centre within mixed ligand complexes containing aromatic polycarboxylato and diamine ligands. To the best of our knowledge, there are only two reported crystal structures of this kind. One of them,  $[Fe_2(OH)_2(phen)_2(pyr)]_n$ , where phen is 1,10-phenanthroline, is a two-dimensional polymer.<sup>19</sup> The  $pyr^{4-}$  ion bridges two Fe(III) ions and it is coordinated by all four COO groups acting as bis-monodentate and bis-chelate ligands. The distorted octahedral environment of the Fe(III) ion consists of three O atoms from two  $pyr^{4-}$  ligands, two N atoms from phen and one  $OH^-$  group. In the second reported compound,  $[Fe_2(bipy)_2(H_2O)_2(H_2pyr)(pyr)]_n$ , where bipy is 2,2'-bipyridine,<sup>20</sup> the coordination polyhedron of Fe(III) ion is also a distorted octahedron comprising two N atoms from chelate bipy, one O atom from coordinated  $H_2O$ , two O atoms from monodentate COO groups of  $pyr^{4-}$  and one O atom from  $H_2pyr^{2-}$ . The binuclear units built zig-zag chains, which are further connected in layers and finally form a three-dimensional crystal packing governed by numerous hydrogen bonds.

On the other hand, the hydrolytic behaviour of Fe(III) ions in aqueous solution is much more investigated, and represents solid ground for further research and implementation in the synthesis of mixed ligand Fe(III) complexes. Absorption spectroscopy of different Fe(III) salts in aqueous solutions, over a wide range of concentrations and pH values, revealed that the Fe(III) ions are subjected to hydrolysis and polymerization reactions, leading to the formation of compounds with  $Fe(OH)^{2+}$ ,  $Fe(OH)_2^+$  or  $Fe_2(OH)_2^{4+}$  as predominant species,<sup>21–25</sup> and eventually to hydroxido-bridged complexes, such as  $[Fe_2(C_4O_4)_2(H_2O)_4(OH)_2] \cdot 2H_2O$ ,<sup>26</sup>  $[Fe_6O_2(C_7H_5O_2)_{10}(hedmp)_2(OH)_2] \cdot 3CH_3CN$ , where hedmp is 2-(hydroxyethyl)-3,5-dimethylpyrazole<sup>27</sup> and  $[Fe(barbital)(H_2O)_2(OH)]$ .<sup>28</sup>

In this work, the possibilities of implementing Fe(III) ions as metal centres, starting from Fe(III) nitrate, bipy as diamine ligand and different aromatic polycarboxylates: pht, ipht, tpht and pyr, were investigated. Such compounds should be comparable to the already known mixed ligand Co(II), Ni(II) and Cu(II) complexes of similar composition.<sup>12,13,29</sup> In the present study, four novel Fe(III) complexes with  $\mu$ -hydroxido and  $\mu$ -carboxylato bridges were synthesized by ligand exchange reaction and characterized by elemental and TG/DSC analysis, FTIR and diffuse reflectance UV–Vis–NIR spectroscopy and magnetic susceptibility measurements.

## EXPERIMENTAL

### Materials

With the exception of 2,2'-bipyridine, which was of *purum* quality, the other reagents were of analytical grade and were used as purchased.

### Preparation of the complexes

The complexes were prepared according to the following procedure: a solution of Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.01 mol for complexes with pht, ipht and tpht, or 0.02 mol for complex with pyr) in H<sub>2</sub>O (200 mL) and a solution of bipy (0.005 mol) in EtOH (15 mL) were first mixed. Then, a dilute solution of Na<sub>2</sub>pht/Na<sub>2</sub>ipht/Na<sub>2</sub>tpht/Na<sub>4</sub>pyr (0.015 mol) in H<sub>2</sub>O (75 mL) was added dropwise at room temperature over about 1.5 h under vigorous magnetic stirring. During this period, the pH value of the solution increased from 2.0 to 3.0. After standing for several days, the formed precipitates were filtered off, washed several times with H<sub>2</sub>O, EtOH, and Et<sub>2</sub>O and dried at room temperature.

### Characterization of the complexes

Elemental analysis was realised by standard analytical micro-methods. The Fourier-transformed infrared spectra were recorded on a Bomem MB-100, Hartmann Braun FTIR spectrophotometer, using KBr pellets, in the region 4000 – 400 cm<sup>-1</sup>. The diffuse reflectance UV–Vis–NIR spectra, in the region of 200–1400 nm, were taken on a UV-2600 Shimadzu spectrophotometer with an integrating sphere, using BaSO<sub>4</sub> as an internal standard. The recorded data were transformed using the Kubelka–Munk function in order to obtain absorption spectra.<sup>30-32</sup> The thermal behaviour of the complexes was investigated from room temperature up to 1050 °C using an SDT Q600 TGA/DSC instrument (TA instruments), at a heating rate of 20 °C min<sup>-1</sup> under a nitrogen atmosphere (flow rate: 100 cm<sup>3</sup> min<sup>-1</sup>). The magnetic susceptibility measurements were performed at room temperature on an MSB-MK1 magnetic susceptibility balance (Sherwood Scientific Ltd., Cambridge, UK). The data were corrected for diamagnetic susceptibilities.

## RESULTS AND DISCUSSION

All complexes were prepared as microcrystalline products from dilute solutions by ligand exchange reactions. The empirical formulae of the complexes based on analytical and spectral data were: Fe<sub>4</sub>(bipy)<sub>2</sub>(OH)<sub>6</sub>(pht)<sub>3</sub>·4H<sub>2</sub>O (**1**), Fe<sub>4</sub>(bipy)<sub>2</sub>(Hipht)<sub>2</sub>(ipht)<sub>2</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O (**2**), Fe<sub>4</sub>(bipy)<sub>2</sub>(Htpht)<sub>2</sub>(OH)<sub>6</sub>(tpht)<sub>2</sub>·4H<sub>2</sub>O (**3**) and Fe<sub>4</sub>(bipy)(OH)<sub>4</sub>(pyr)<sub>2</sub>·9H<sub>2</sub>O (**4**). As seen from the formulae, all the obtained compounds were hydrated hydroxido-carboxylato complexes with tetra-

nuclear building units. The mole ratio Fe(III):bipy was 2:1 for **1–3**, and 4:1 for **4**, meaning that the initial ratios of reagents were preserved in the products. In addition to the fully deprotonated polycarboxylates present in all cases, protonated dicarboxylates, Hight and Htpht, were found in **2** and **3**. Moreover, complexes **2** and **3** had identical empirical formulae with the only difference being in the polycarboxylato ligand. All complexes contained OH groups, indicating the formation of  $\mu$ -hydroxido species typical for Fe(III) compounds.<sup>21–25</sup>

The analytical data of reported complexes are as follows:

$Fe_4(bipy)_2(OH)_6(pht)_3 \cdot 4H_2O$  (**1**). Yield: 51.6 %; M.W.: 1202.22 g mol<sup>-1</sup>; Anal. Calcd.: C, 43.96; H, 3.52; N, 4.66; H<sub>2</sub>O, 5.99 %. Found: C, 44.16; H, 3.35; N, 4.67; H<sub>2</sub>O, 5.90 %.

$Fe_4(bipy)_2(Hipht)_2(ipht)_2(OH)_6 \cdot 4H_2O$  (**2**). Yield: 54.2 %; M.W.: 1368.35 g mol<sup>-1</sup>; Anal. Calcd.: C, 45.64; H, 3.54; N, 4.09; H<sub>2</sub>O, 5.27 %. Found: C, 44.95; H, 3.37; N, 3.90; H<sub>2</sub>O, 5.90 %.

$Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2 \cdot 4H_2O$  (**3**). Yield: 57.8 %; M.W.: 1368.35 g mol<sup>-1</sup>; Anal. Calcd.: C, 45.64; H, 3.54; N, 4.09; H<sub>2</sub>O, 5.27 %. Found: C, 45.24; H, 3.13; N, 4.03; H<sub>2</sub>O, 5.27 %.

$Fe_4(bipy)(OH)_4(pyr)_2 \cdot 9H_2O$  (**4**). Yield: 63.6 %; M.W.: 1109.98 g mol<sup>-1</sup>; Anal. Calcd.: C, 32.46; H, 3.09; N, 2.52; H<sub>2</sub>O, 14.61 %. Found: C, 32.20; H, 2.96; N, 2.74; H<sub>2</sub>O, 15.14 %.

The total water content was obtained from TG/DSC analysis.

The magnetic moments, calculated from susceptibility measurements at room temperature (Table I), are in accordance with the values reported for low-spin Fe(III) complexes, which are expected to be in the range 2.0–2.5  $\mu_B$ , due to a considerable orbital contribution.<sup>33</sup> Although the complexes exhibited a noticeable difference in shade, all were red–brown coloured, which generally corresponds to other known low-spin Fe(III) complexes with octahedral or distorted octahedral geometry.<sup>33,34</sup> Compounds **2** and **3** were insoluble in water, EtOH and acetone, **1** was partially soluble in H<sub>2</sub>O but insoluble in EtOH and acetone; **4** was to some extent soluble in EtOH, but insoluble in H<sub>2</sub>O and acetone. Considering their solubility, complexes **1–4** are probably polymeric.

TABLE I. Magnetic moments and selected FTIR spectral data for **1–4**

Complex	$\mu_{\text{eff}} / \mu_B$	$\nu_{\text{as}} / \text{cm}^{-1}$	$\nu_s / \text{cm}^{-1}$	$\Delta\nu / \text{cm}^{-1}$	$\Delta\nu_1 / \text{cm}^{-1}$
<b>1</b>	2.59	1566	1410	156	157
<b>2</b>	2.38	1588	1385	203	176
<b>3</b>	2.67	1574	1385	189	173
<b>4</b>	2.21	1583	1385	198	193

The presence of OH groups, water molecules, diamine and benzenepolycarboxylato ligands were confirmed in detail from the FTIR spectra (Fig. 1). Broad O–H stretching vibrations in the region of 3420–3060 cm<sup>-1</sup> correspond to

coordinated or uncoordinated water molecules. A weak shoulder at  $\sim 3570\text{ cm}^{-1}$  could be assigned to the bridging OH stretch<sup>22</sup> in the FTIR spectra of all compounds. Since the shape and the position of the  $\nu(\text{OH})$  bands are similar in the spectra of **1–3**, it can be concluded that the number of water molecules in these complexes was the same or very similar. The extremely broad band centred at  $\sim 3420\text{ cm}^{-1}$  in spectrum of **4** indicates a larger number of water molecules. Such bands are characteristic for pyr-containing compounds with numerous and short hydrogen bonds.<sup>35</sup> Additional confirmation for these conclusions was obtained from the TG analysis (*vide infra*).

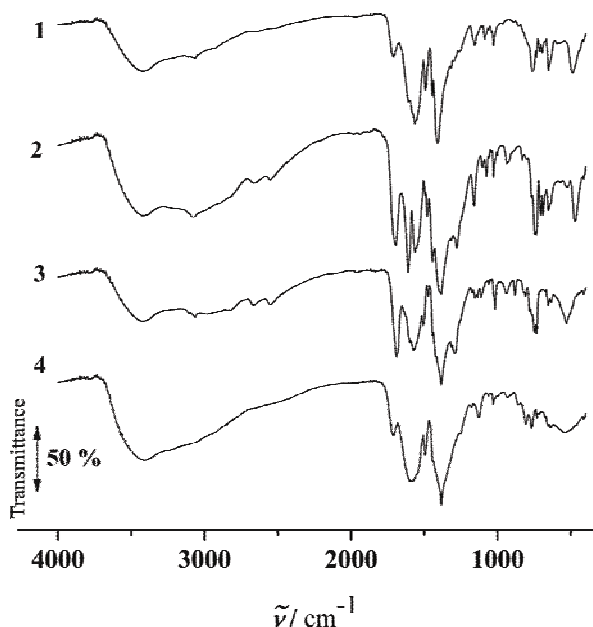


Fig. 1. FTIR spectra of **1–4**.

Characteristic vibrations of the aromatic nuclei:  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{H})$ , found in the  $1610\text{--}1600$ ,  $1445\text{--}1440$  and  $768\text{--}735\text{ cm}^{-1}$  regions, respectively, verify the coordination of the bipy ligand in all the synthesized complexes. The presence of coordinated aromatic polycarboxylato ligands caused the appearance of two very intense bands, due to the asymmetrical ( $\nu_{\text{as}}$ ) and symmetrical ( $\nu_{\text{s}}$ ) COO vibrations, which are listed in Table I. The difference between these vibrations,  $\Delta\nu$ , when compared with the “purely ionic” value,  $\Delta\nu_{\text{i}}$ , for alkaline metal salts  $\text{Na}_2\text{pht}$  (this study),  $\text{K}_2\text{ipht}$ ,<sup>36</sup>  $\text{K}_2\text{tpht}$ <sup>37</sup> and  $\text{Na}_4\text{pyr}$  (this study), predicts the coordination mode of COO groups.<sup>38</sup> The significant difference between  $\Delta\nu$  and  $\Delta\nu_{\text{i}}$  for **2** and **3** suggests a monodentate coordination mode of the COO groups. On the other hand, the small difference between  $\Delta\nu$  and  $\Delta\nu_{\text{i}}$

indicates a combination of chelate and/or bridging COO groups, such as in **1** and **4**. Besides the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  vibrations in the FTIR spectra of **2** and **3**, additional pairs of intense bands at 1697 and 1281  $\text{cm}^{-1}$  for **2**, and 1690 and 1288  $\text{cm}^{-1}$  for **3** confirm the presence of the protonated species  $\text{Hipht}^-$  and  $\text{Htpht}^-$ .<sup>38</sup>

Close observation of the region between 1000 and 800  $\text{cm}^{-1}$ , shown in Fig. 2, provided information about hydrolysis and polymerization tendency of the Fe(III) ions. The asymmetric bands at 858–831  $\text{cm}^{-1}$  could be attributed to the Fe–O–Fe unit, while the bands at 962–932  $\text{cm}^{-1}$  refer to OH bridging deformation in an  $[\text{Fe}-(\text{OH})_2-\text{Fe}]^{4+}$  entity.<sup>22</sup>

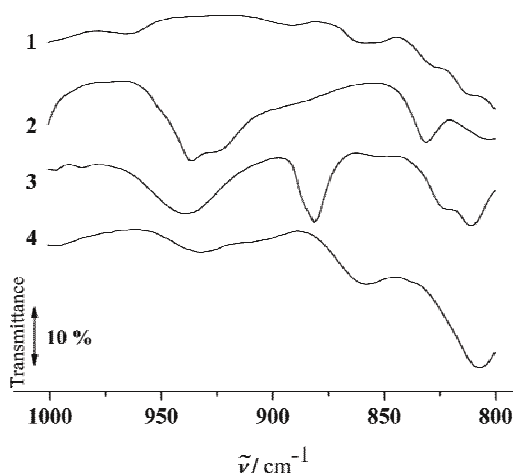


Fig. 2. FTIR spectra of **1–4** in the region 1000–800  $\text{cm}^{-1}$ .

Flynn<sup>21</sup> conducted extensive research regarding the hydrolysis of inorganic Fe(III) salts and established a correlation between the found  $\text{OH}^-/\text{Fe}^{3+}$  mole ratio and the pH value of aqueous  $\text{Fe}(\text{NO}_3)_3$  solutions. For the mole ratio  $\text{OH}^-/\text{Fe}^{3+}$  between 0.5 and 2.5, the pH values of fresh 0.1 and 0.01  $\text{mol dm}^{-3}$  solutions were 1.9–2.4 and 2.3–2.8, respectively. Since the initial pH values were  $\sim 2.0$  in the present case, it could be concluded that the corresponding  $\text{OH}^-/\text{Fe}^{3+}$  ratio was within the reported interval 0.5–2.5. This leads to the assumption that during the synthesis of **1–4**, the dominant  $\mu$ -hydroxido species might be  $\text{Fe}_2(\text{OH})_2^{4+}$ , *i.e.*, hydroxido-bridged  $\text{Fe}(\text{OH})_2^{2+}$  dimers. The confirmation was obtained by the results of UV–Vis–NIR spectroscopic measurements, shown in Fig. 3. All spectra exhibited very prominent peaks at  $\sim 235$  and  $\sim 294$  nm and several shoulders at higher wavelengths, which could be attributed to the presence of Fe(III),  $\text{Fe}(\text{OH})_2^{2+}$  and  $\text{Fe}_2(\text{OH})_2^{4+}$  species.<sup>25,39</sup> In addition,  ${}^4\text{T}_{1\text{g}} \rightarrow {}^6\text{A}_{1\text{g}}$  energy transitions characteristic for a distorted octahedral environment of low-spin Fe(III) complexes<sup>40</sup> and the  $\text{FeO}_6$  or  $\text{FeN}_2\text{O}_4$  chromophore<sup>41</sup> were found as weak maxima in the range 956–999 nm (inset in Fig. 3).

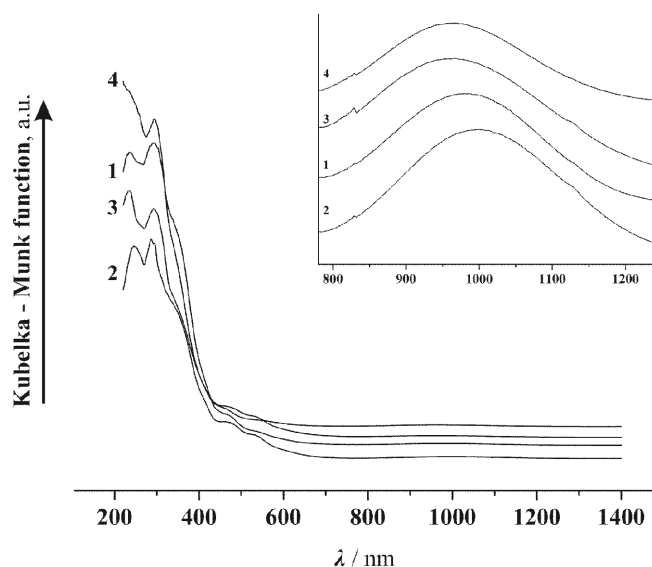


Fig. 3. UV-Vis-NIR spectra of **1-4**.

Thermal properties of synthesized complexes were investigated by TG/DSC analysis (Fig. 4). The first significant weight loss corresponded to the dehydration (the  $\text{H}_2\text{O}$  content is listed above), which is a single step process in all four cases, and it was not possible to distinguish between coordinated and uncoordinated water molecules. As seen from the initial,  $T_{\text{deh,i}}$ , and final,  $T_{\text{deh,f}}$ , dehydration temperatures (Table II), complexes **1-3** were easily dehydrated with  $T_{\text{deh,f}}$  not exceeding  $144\text{ }^\circ\text{C}$ . In the case of **4**, DSC peak maximum,  $T_{\text{max}}$ , corresponding to dehydration, as well as  $T_{\text{deh,f}}$  were higher in comparison to those for **1-3**, very likely due to the nine  $\text{H}_2\text{O}$  molecules within the formula. According to the DSC curves, the molar dehydration enthalpies,  $\Delta_{\text{deh}}H^\circ_{\text{m}}$ , for **1-4** were calculated by measuring the area under the peaks. The values  $\Delta_{\text{deh}}H^\circ_{\text{m}}$ , listed in Table II, varied from  $143$  to  $441\text{ kJ mol}^{-1}$ , as a consequence of the different number of  $\text{H}_2\text{O}$  molecules in the complexes.

Further decomposition of the anhydrous compounds occurred in several not well-separated steps. In the case of **1**, the removal of water was followed by three overlapped steps, with an overall mass loss of  $65.9\%$ , ending at  $519\text{ }^\circ\text{C}$ , and one additional loss of  $12.0\%$ , ending at  $661\text{ }^\circ\text{C}$ . These steps could be attributed to the consecutive removal of bipy, pht and OH groups, respectively. In the cases of **2-4**, the thermal decomposition had similar pattern. After the dehydration, the next mass loss corresponded to the elimination of bipy followed by the removal of the polycarboxylato ligand, ending at  $524\text{--}565\text{ }^\circ\text{C}$ , and a final step of about  $13\%$ , after which OH groups were assumed to have been removed. The only noticeable difference between **1** and **2-4** was that the TG curve for **1** dropped suddenly at about

620 °C, which was accompanied by a sharp endothermic DSC maximum, while the analogous processes for 2–4 were slower with broader DSC peaks (Fig. 4).

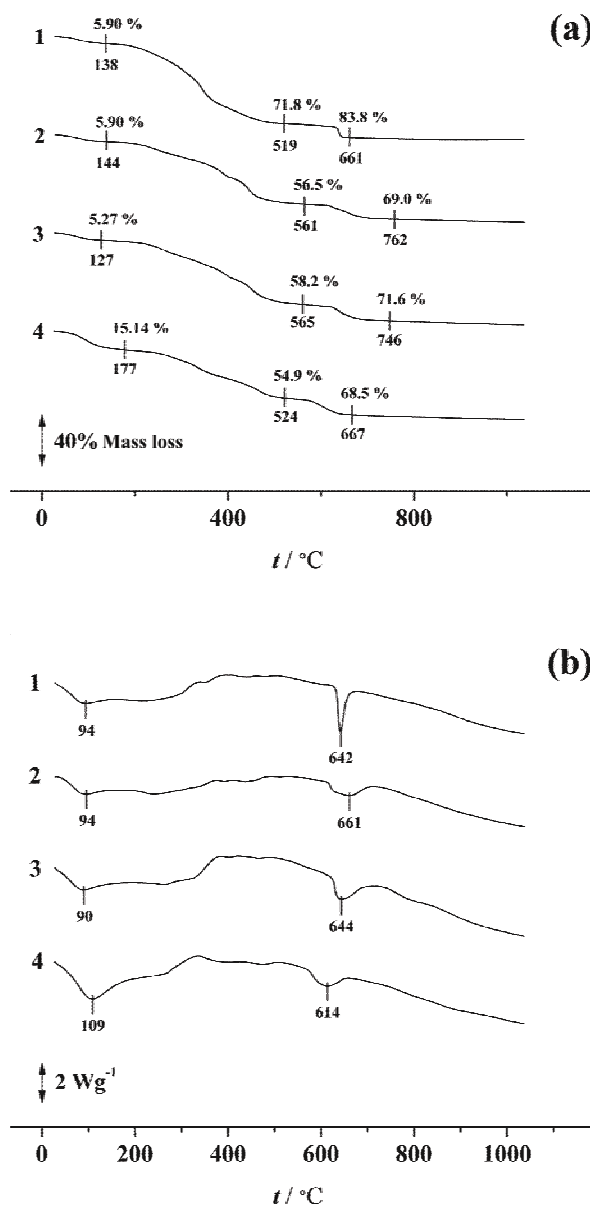


Fig. 4. TG (a) and DSC (b) curves of 1–4.

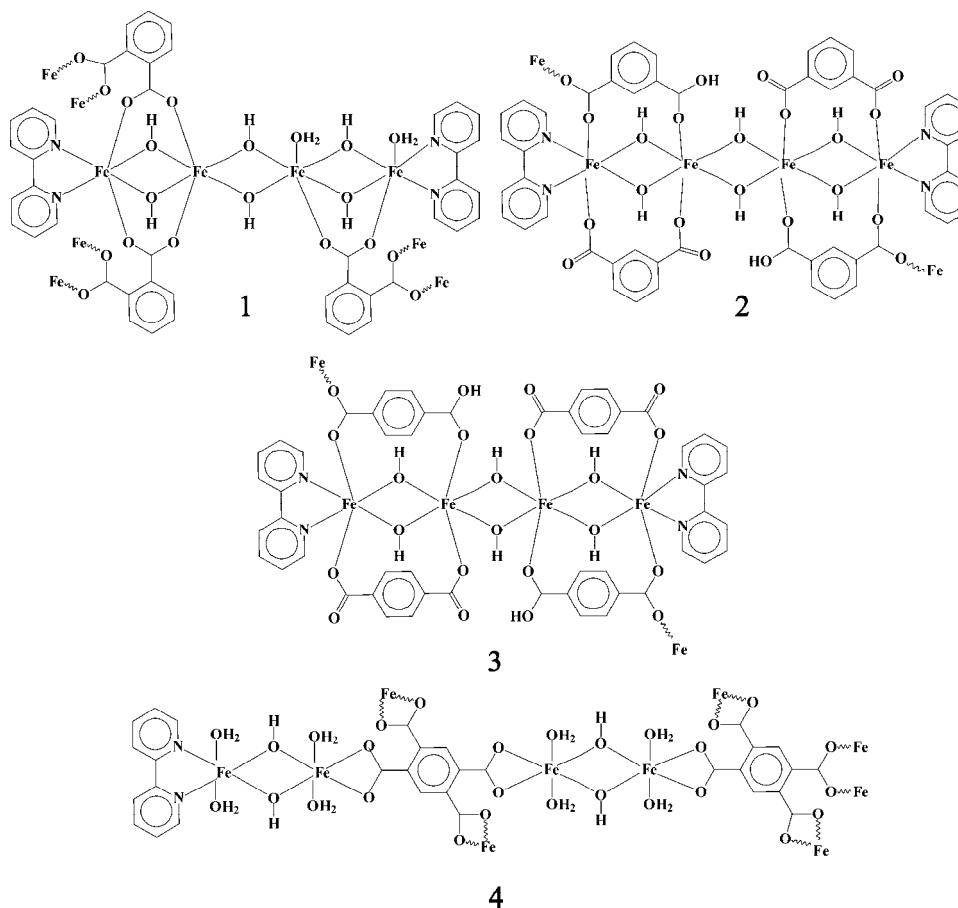
Although the final temperature of the decomposition process was insufficient to form pure ferrimagnetic  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ,<sup>42</sup> the black residue exhibited magnetic interactions at room temperature.



TABLE II. Extracted data from the TG and DSC curves

Complex	$T_{\text{deh},i} / ^\circ\text{C}$	$T_{\text{deh},f} / ^\circ\text{C}$	$T_{\text{max}} / ^\circ\text{C}$	$\Delta_{\text{deh}}H_m^\circ / \text{kJ mol}^{-1}$
<b>1</b>	37	138	94	143
<b>2</b>	45	144	94	167
<b>3</b>	35	127	90	170
<b>4</b>	47	177	109	441

Based on the above described analytical and spectral data, and the results of TG/DSC analysis and magnetic measurements, the following structural formulae for complexes **1–4** were proposed:  $\{[\text{Fe}_4(\text{bipy})_2(\text{H}_2\text{O})_2(\text{OH})_6(\text{pht})_3] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Hipt})_2(\text{ipht})_2(\text{OH})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Htpht})_2(\text{OH})_6(\text{tpht})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**3**) and  $\{[\text{Fe}_4(\text{bipy})(\text{H}_2\text{O})_8(\text{OH})_4(\text{pyr})_2] \cdot \text{H}_2\text{O}\}_n$  (**4**), which are shown in Fig. 5.

Fig. 5. Structural formulae of **1–4** (uncoordinated water molecules are not shown).

## CONCLUSIONS

Four  $\mu$ -hydroxido and  $\mu$ -carboxylato mixed ligand iron(III) complexes, *i.e.*,  $\{[\text{Fe}_4(\text{bipy})_2(\text{H}_2\text{O})_2(\text{OH})_6(\text{pht})_3] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Hipht})_2(\text{ipht})_2(\text{OH})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Htpht})_2(\text{OH})_6(\text{tpht})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**3**) and  $\{[\text{Fe}_4(\text{bipy})(\text{H}_2\text{O})_8(\text{OH})_4(\text{pyr})_2] \cdot \text{H}_2\text{O}\}_n$  (**4**), were synthesized and characterized. All complexes are polymeric with tetranuclear units, red–brown coloured and low-spin, without noticeable magnetic interactions at room temperature. A distorted octahedral geometry was proposed in all cases. The polycarboxylato ligands play a bridging role in all compounds; while monodentate COO groups were present in **2** and **3**, bridging and chelate COO groups were found in **1** and **4**. The presence of  $\text{Fe}_2(\text{OH})_2^{4+}$  dimers in **1–4** was confirmed by UV–Vis–NIR spectroscopic measurements. The dehydration and decomposition of the anhydrous compounds were discussed in detail and the calculated molar dehydration enthalpies were in the range of 143–441 kJ mol<sup>-1</sup>. Furthermore, the structural formulae of the complexes **1–4** were proposed. Attempts to obtain the compounds **1–4** in the single crystal form suitable for X-ray structure analysis are in progress; this could confirm the supposed structural formulae of the complexes.

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## ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ГВОЖЂЕ(III)-КОМПЛЕКСА СА  
 $\mu$ -ХИДРОКСИДО И  $\mu$ -ПОЛИКАРБОКСИЛАТО МОСТОВИМА И 2,2'-БИПИРИДИНОМ

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Реакцијом измене лиганда синтетисана су четири нова полимерна комплекса гвожђа(III) са 2,2'-бипиридином (bipy) и различитим ароматичним поликарбоксилатним лигандима, као што су анјони фталне (pht), изофталне (ipht), терефталне (tpht) и пиромелитне (pyr) киселине. Комплекси су окарактерисани елементарном и TG/DSC анализом, FTIR и дифузионо-рефлексионом UV–Vis–NIR спектроскопијом, као и магнетним мерењима. На основу аналитичких и спектралних података, утврђене су следеће формуле комплекса:  $\{[\text{Fe}_4(\text{bipy})_2(\text{H}_2\text{O})_2(\text{OH})_6(\text{pht})_3] \cdot 2\text{H}_2\text{O}\}_n$  (**1**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Hipht})_2(\text{ipht})_2(\text{OH})_6] \cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Fe}_4(\text{bipy})_2(\text{Htpht})_2(\text{OH})_6(\text{tpht})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**3**) и  $\{[\text{Fe}_4(\text{bipy})(\text{H}_2\text{O})_8(\text{OH})_4(\text{pyr})_2] \cdot \text{H}_2\text{O}\}_n$  (**4**). Сви комплекси су црвеномрке боје и нискоспински са деформисаном октаедарском геометријом и хромофором типа  $\text{FeO}_6$  или  $\text{FeN}_2\text{O}_4$ . Поликарбоксилато лиганди имају мостовну улогу код свих једињења, међутим, док код **2** и **3** постоје монодентатне  $\text{COO}^-$  групе, код **1** и **4** нађене су мостовне или хелатне  $\text{COO}^-$  групе. Детаљно је испитано термичко понашање комплекса **1–4** и израчунате су моларне енталпије дехидратације. На основу свих добијених резултата, предложене су структурне формуле комплекса **1–4**.

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