Journal of the Serbian Chemical Society
eVersion electronic
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 79 (8) 941–952 (2014)
JSCS–4638

UDC 546.723+547.828+547.44:542.913
Original scientific paper

Synthesis and characterization of μ-hydroxido- and μ-polycarboxylato-bridged iron(III) complexes with 2,2′-bipyridine

NIKOLA TASIĆ[1]*, JELENA ROGAN[2#], DEJAN POLETI[2#], LIDIJA RADOVANOVIĆ[2#] and GORAN BRANKOVIĆ[1#]

[1]Department of Materials Science, Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1, 11030 Belgrade, Serbia and [2]Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

(Received 28 October 2013, revised 10 January, accepted 17 January 2014)

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 $\{[Fe_4(bipy)_2(H_2O)_2(OH)_6(pht)_3]\cdot 2H_2O\}_n$ (**1**), $\{[Fe_4(bipy)_2(Hipht)_2(ipht)_2(OH)_6]\cdot 4H_2O\}_n$ (**2**), $\{[Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2]\cdot 4H_2O\}_n$ (**3**) and $\{[Fe_4(bipy)(H_2O)_8(OH)_4(pyr)_2]\cdot H_2O\}_n$ (**4**). All complexes were red brown and low-spin with a distorted octahedral geometry with FeO_6 or FeN_2O_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; $Fe_2(OH)_2^{4+}$ 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

---

* Corresponding author. E-mail: nikola.tasic@imsi.bg.ac.rs

\# Serbian Chemical Society member.

doi: 10.2298/JSC131028005T

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.[1–7]

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 π–π 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.[8–18]

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.[19] 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,[20] 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,[21–25] and eventually to hydroxido-bridged complexes, such as $[Fe_2(C_4O_4)_2(H_2O)_4(OH)_2]\cdot 2H_2O$,[26] $[Fe_6O_2(C_7H_5O_2)_{10}(hedmp)_2(OH)_2]\cdot 3CH_3CN$, where hedmp is 2-(hydroxyethyl)-3,5-dimethylpyrazole[27] and $[Fe(barbital)(H_2O)_2(OH)]$.[28]

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.[12,13,29] In the present study, four novel Fe(III) complexes with μ-hydroxido and μ-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 $Fe(NO_3)_3\cdot 6H_2O$ (0.01 mol for complexes with pht, ipht and tpht, or 0.02 mol for complex with pyr) in H_2O (200 mL) and a solution of bipy (0.005 mol) in EtOH (15 mL) were first mixed. Then, a dilute solution of Na_2pht/Na_2ipht/Na_2tpht/Na_4pyr (0.015 mol) in H_2O (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_2O, EtOH, and Et_2O 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^{-1}. 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 $BaSO_4$ as an internal standard. The recorded data were transformed using the Kubelka–Munk function in order to obtain absorption spectra.[30-32] 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^{-1} under a nitrogen atmosphere (flow rate: 100 cm^3 min^{-1}). 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: $Fe_4(bipy)_2(OH)_6(pht)_3\cdot 4H_2O$ (**1**), $Fe_4(bipy)_2(Hipht)_2(ipht)_2(OH)_6\cdot 4H_2O$ (**2**), $Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2\cdot 4H_2O$ (**3**) and $Fe_4(bipy)(OH)_4(pyr)_2\cdot 9H_2O$ (**4**). As seen from the formulae, all the obtained compounds were hydrated hydroxido-carboxylato complexes with tetranuclear 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, Hipht 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 μ-hydroxido species typical for Fe(III) compounds.[21–25]

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^{-1}; Anal. Calcd.: C, 43.96; H, 3.52; N, 4.66; H_2O, 5.99 %. Found: C, 44.16; H, 3.35; N, 4.67; H_2O, 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^{-1}; Anal. Calcd.: C, 45.64; H, 3.54; N, 4.09; H_2O, 5.27 %. Found: C, 44.95; H, 3.37; N, 3.90; H_2O, 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^{-1}; Anal. Calcd.: C, 45.64; H, 3.54; N, 4.09; H_2O, 5.27 %. Found: C, 45.24; H, 3.13; N, 4.03; H_2O, 5.27 %.

*$Fe_4(bipy)(OH)_4(pyr)_2\cdot 9H_2O$ (**4**).* Yield: 63.6 %; M.W.: 1109.98 g mol^{-1}; Anal. Calcd.: C, 32.46; H, 3.09; N, 2.52; H_2O, 14.61 %. Found: C, 32.20; H, 2.96; N, 2.74; H_2O, 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 μ_B, due to a considerable orbital contribution.[33] 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.[33,34] Compounds **2** and **3** were insoluble in water, EtOH and acetone, **1** was partially soluble in H_2O but insoluble in EtOH and acetone; **4** was to some extent soluble in EtOH, but insoluble in H_2O and acetone. Considering their solubility, complexes **1**–**4** are probably polymeric.

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

Complex	μ_{eff} / μ_B	ν_{as} / cm^{-1}	ν_s / cm^{-1}	$\Delta\nu$ / cm^{-1}	$\Delta\nu_i$ / cm^{-1}
1	2.59	1566	1410	156	157
2	2.38	1588	1385	203	176
3	2.67	1574	1385	189	173
4	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^{-1} correspond to coordinated or uncoordinated water molecules. A weak shoulder at ~3570 cm^{-1} could be assigned to the bridging OH stretch[22] in the FTIR spectra of all compounds. Since the shape and the position of the ν(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 ~3420 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.[35] Additional confirmation for these conclusions was obtained from the TG analysis (*vide infra*).

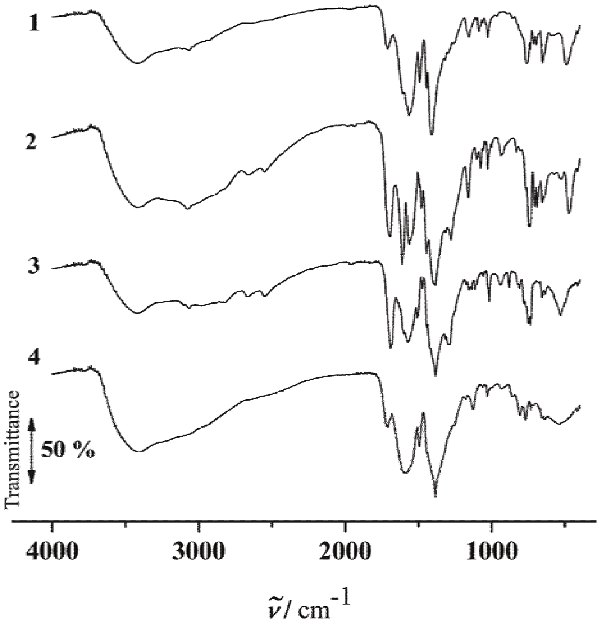

Fig. 1. FTIR spectra of **1**–**4**.

Characteristic vibrations of the aromatic nuclei: ν(C=C), ν(C=N) and ν(C–H), found in the 1610–1600, 1445–1440 and 768–735 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 (ν_{as}) and symmetrical (ν_s) COO vibrations, which are listed in Table I. The difference between these vibrations, Δν, when compared with the "purely ionic" value, $\Delta\nu_i$, for alkaline metal salts Na_2pht (this study), K_2ipht,[36] K_2tpht[37] and Na_4pyr (this study), predicts the coordination mode of COO groups.[38] The significant difference between Δν and $\Delta\nu_i$ for **2** and **3** suggests a monodentate coordination mode of the COO groups. On the other hand, the small difference between Δν and $\Delta\nu_i$

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

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

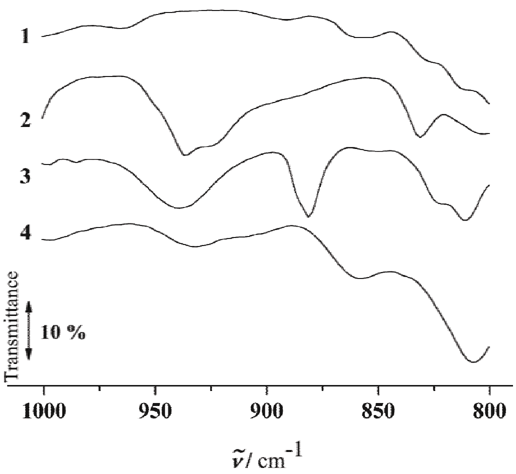

Fig. 2. FTIR spectra of **1**–**4** in the region 1000–800 cm^{-1}.

Flynn[21] conducted extensive research regarding the hydrolysis of inorganic Fe(III) salts and established a correlation between the found OH$^-$/Fe^{3+} mole ratio and the pH value of aqueous Fe(NO$_3$)$_3$ solutions. For the mole ratio OH$^-$/Fe^{3+} between 0.5 and 2.5, the pH values of fresh 0.1 and 0.01 mol dm^{-3} solutions were 1.9–2.4 and 2.3–2.8, respectively. Since the initial pH values were ~2.0 in the present case, it could be concluded that the corresponding OH$^-$/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 μ-hydroxido species might be Fe$_2$(OH)$_2^{4+}$, *i.e.*, hydroxido-bridged Fe(OH)$^{2+}$ 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 ~235 and ~294 nm and several shoulders at higher wavelengths, which could be attributed to the presence of Fe(III), Fe(OH)$^{2+}$ and Fe$_2$(OH)$_2^{4+}$ species.[25,39] In addition, $^4T_{1g} \rightarrow {}^6A_{1g}$ energy transitions characteristic for a distorted octahedral environment of low-spin Fe(III) complexes[40] and the FeO$_6$ or FeN$_2$O$_4$ chromophore[41] were found as weak maxima in the range 956–999 nm (inset in Fig. 3).

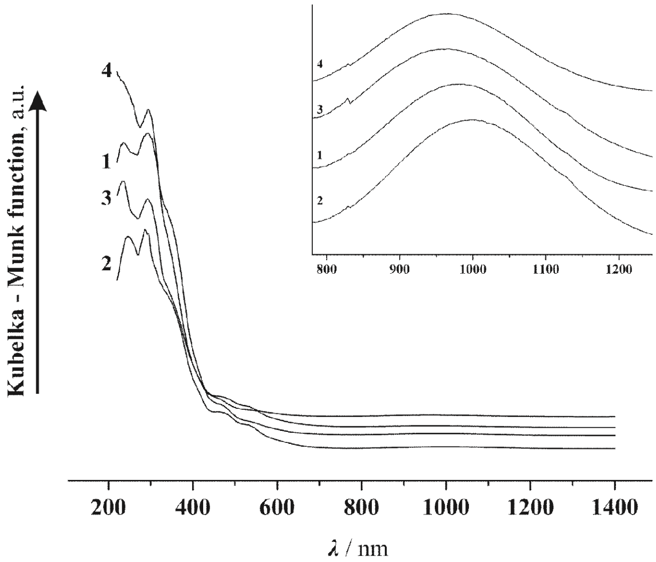

Fig. 3. UV–Vis–NIR spectra of **1**–**4**.

Thermal properties of synthesized complexes were investigated by TG/DSC analysis (Fig. 4). The first significant weight loss corresponded to the dehydration (the H_2O 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 °C. In the case of **4**, DSC peak maximum, T_{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 H_2O 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 kJ mol^{-1}, as a consequence of the different number of H_2O 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 °C, and one additional loss of 12.0 %, ending at 661 °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 524–565 °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).

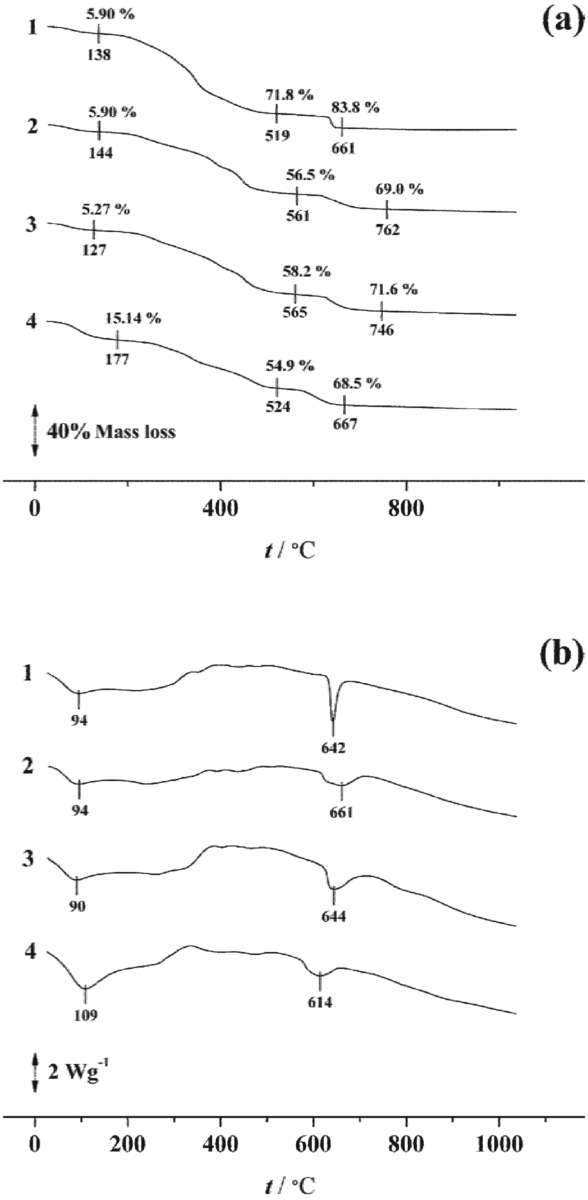

Fig. 4. TG (a) and DSC (b) curves of **1**–**4**.

Although the final temperature of the decomposition process was insufficient to form pure ferrimagnetic Fe_2O_3 or Fe_3O_4,[42] the black residue exhibited magnetic interactions at room temperature.

TABLE II. Extracted data from the TG and DSC curves

Complex	$T_{\mathrm{deh,i}}$ / °C	$T_{\mathrm{deh},f}$ / °C	$T_{\max}$ / °C	$\Delta_{\mathrm{deh}}H°_{\mathrm{m}}$ / kJ mol^{-1}
1	37	138	94	143
2	45	144	94	167
3	35	127	90	170
4	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: $\{[Fe_4(bipy)_2(H_2O)_2(OH)_6(pht)_3]\cdot 2H_2O\}_n$ (**1**), $\{[Fe_4(bipy)_2(Hipht)_2(ipht)_2(OH)_6]\cdot 4H_2O\}_n$ (**2**), $\{[Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2]\cdot 4H_2O\}_n$ (**3**) and $\{[Fe_4(bipy)(H_2O)_8(OH)_4(pyr)_2]\cdot H_2O\}_n$ (**4**), which are shown in Fig. 5.

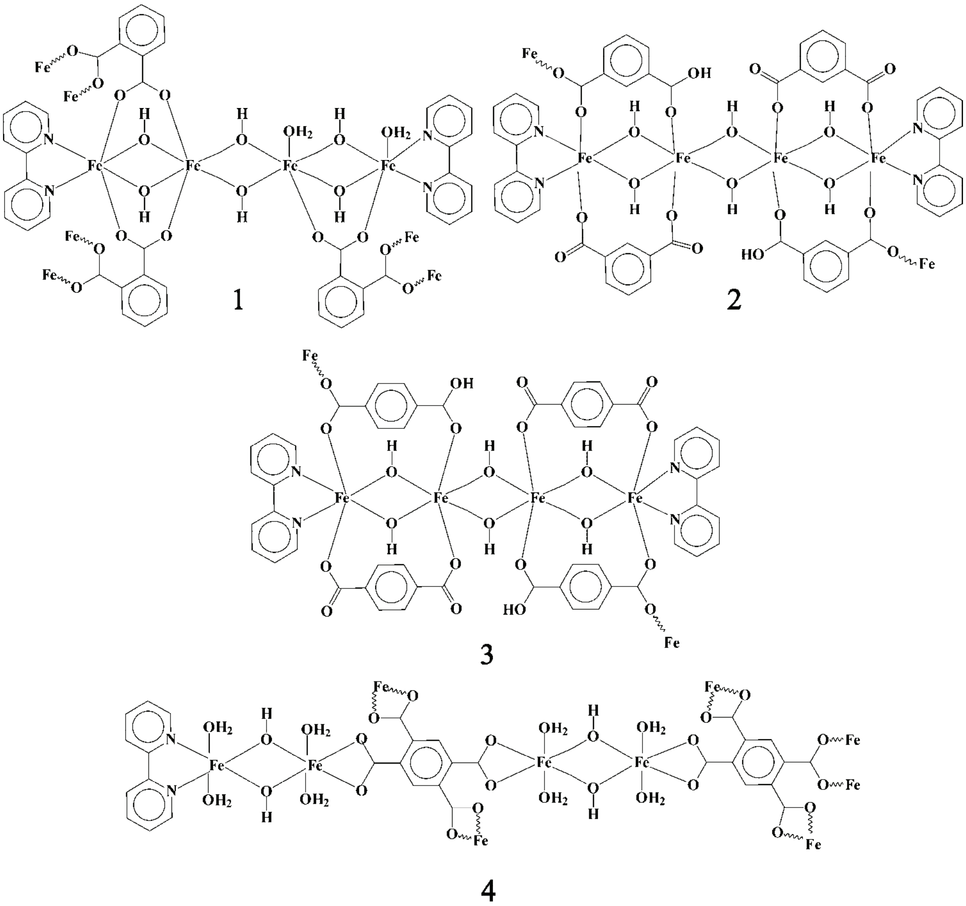

Fig. 5. Structural formulae of **1–4** (uncoordinated water molecules are not shown).

CONCLUSIONS

Four μ-hydroxido and μ-carboxylato mixed ligand iron(III) complexes, *i.e.*, $\{[Fe_4(bipy)_2(H_2O)_2(OH)_6(pht)_3]\cdot 2H_2O\}_n$ (**1**), $\{[Fe_4(bipy)_2(Hipht)_2(ipht)_2(OH)_6]\cdot 4H_2O\}_n$ (**2**), $\{[Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2]\cdot 4H_2O\}_n$ (**3**) and $\{[Fe_4(bipy)(H_2O)_8(OH)_4(pyr)_2]\cdot H_2O\}_n$ (**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 $Fe_2(OH)_2^{4+}$ 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^{-1}. 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.

Acknowledgements. This study was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. III45007).

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ГВОЖЂЕ(III)-КОМПЛЕКСА СА μ-ХИДРОКСИДО И μ-ПОЛИКАРБОКСИЛАТО МОСТОВИМА И 2,2′-БИПИРИДИНОМ

НИКОЛА ТАСИЋ[1], ЈЕЛЕНА РОГАН[2], ДЕЈАН ПОЛЕТИ[2], ЛИДИЈА РАДОВАНОВИЋ[2] и ГОРАН БРАНКОВИЋ[1]

[1]*Одсек за науку о материјалима, Институт за мултидисциплинарна истраживања, Универзитет у Београду, Кнеза Вишеслава 1, 11030 Београд* и [2]*Катедра за општу и неорганску хемију, Технолошко–металуршки факултет, Универзитет у Београду, Карнегијева 4, 11000 Београд*

Реакцијом измене лиганада 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: $\{[Fe_4(bipy)_2(H_2O)_2(OH)_6(pht)_3]\cdot 2H_2O\}_n$ (**1**), $\{[Fe_4(bipy)_2(Hipht)_2\text{-}(ipht)_2(OH)_6]\cdot 4H_2O\}_n$ (**2**), $\{[Fe_4(bipy)_2(Htpht)_2(OH)_6(tpht)_2]\cdot 4H_2O\}_n$ (**3**) и $\{[Fe_4(bipy)\text{-}(H_2O)_8(OH)_4(pyr)_2]\cdot H_2O\}_n$ (**4**). Сви комплекси су црвеномрке боје и нискоспински са деформисаном октаедарском геометријом и хромофором типа FeO_6 или FeN_2O_4. Поликарбоксилато лиганди имају мостовну улогу код свих једињења, међутим, док код **2** и **3** постоје монодентатне COO^--групе, код **1** и **4** нађене су мостовне или хелатне 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**.

(Примљено 28. октобра 2013, ревидирано 10. јануара, прихваћено 17. јануара 2014)

REFERENCES

1. A. S. Polo, M. K. Itokazu, M. Y. M. Iha, *Coord. Chem. Rev.* **248** (2004) 1343
2. S. Qiu, G. Zhu, *Coord. Chem. Rev.* **253** (2009) 2891
3. S. M. Luzan, H. Jung, H. Chun, A. V. Talyzin, *Int. J. Hydrogen Energy* **34** (2009) 9754
4. S. Ferrere, B. A. Gregg, *J. Am. Chem. Soc.* **120** (1998) 843
5. S. Ferrere, *Chem. Mater.* **12** (2000) 1083
6. S. L. James, *Chem. Soc. Rev.* **32** (2003) 276
7. J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **255** (2011) 1791
8. E. G. Bakalbassis, A. Terzis, *Inorg. Chim. Acta* **218** (1994) 167
9. D. Poleti, Lj. Karanović, G. A. Bogdanović, A. Spasojević-de Biré, *Acta Crystallogr., C* **55** (1999) 2061 and references therein
10. F. Luo, J.-M. Zheng, G. J. Long, *Cryst. Growth Des.* **9** (2009) 1271
11. W.-Z. Shen, X.-Y. Chen, P. Cheng, S.-P. Yan, B. Zhai, D.-Z. Liao, Z.-H. Jiang, *Eur. J. Inorg. Chem.* (2005) 2297
12. J. Rogan, D. Poleti, Lj. Karanović, G. Bogdanović, A. Spasojević-de Biré, D. M. Petrović, *Polyhedron* **19** (2000) 1415
13. J. Rogan, D. Poleti, Lj. Karanović, Z. Jagličić, *J. Mol. Struct.* **985** (2011) 371 and references therein
14. Lj. Karanović, D. Poleti, J. Rogan, G. A. Bogdanović, A. Spasojević-de Biré, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **58** (2002) m275
15. J. Y. Baeg, S. W. Lee, *Inorg. Chem. Commun.* **6** (2003) 313
16. E. Bakalbassis, P. Bergerat, O. Kahn, S. Jeannin, Y. Jeannin, Y. Dromzee, M. Guillot, *Inorg. Chem.* **31** (1992) 625
17. J. Rogan, D. Poleti, Lj. Karanović, *Z. Anorg. Allg. Chem.* **632** (2006) 133
18. A. M. Atria, G. Corsini, L. Gonzalez, M. T. Garland, R. Baggio, *Acta Crystallogr., C* **65** (2009) m241
19. D.-Q. Chu, J.-Q. Xu, X.-B. Cui, L.-M. Duan, T.-G. Wang, A.-Q. Tang, Y. Xing, Y.-H. Lin, H.-Q. Jia, *Mendeleev Commun.* **11** (2001) 66
20. Z. Shi, L. Li, S. Niu, J. Jin, Y. Chi, L. Zhang, J. Liu, Y. Xing, *Inorg. Chim. Acta* **368** (2011) 101
21. C. M. Flynn Jr., *Chem. Rev.* **84** (1984) 31 and references therein
22. L. Borer, L. Thalken, C. Ceccarelli, M. Glick, J. H. Zhang, W. M. Reiff, *Inorg. Chem.* **22** (1983) 1719
23. G. Lente, I. Fabian, *Inorg. Chem.* **38** (1999) 603
24. G. Lente, M. E. A. Magalhaes, I. Fabian, *Inorg. Chem.* **39** (2000) 1950
25. G. Lente, I. Fabian, *React. Kinet. Catal. Lett.* **73** (2001) 117
26. J. Carranza, J. Sletten, F. Lloret, M. Julve, *Inorg. Chim. Acta* **371** (2011) 13
27. R. Murugavel, N. Gogoi, R. Howlader, R. Clerac, *Inorg. Chim. Acta* **363** (2010) 3004
28. M. S. Masoud, A. M. Ramadan, G. M. El-Ashry, *Thermochim. Acta* **551** (2013) 164
29. J. Rogan, D. Poleti, Lj. Karanović, *J. Serb. Chem. Soc.* **69** (2004) 353
30. P. Kubelka, F. Munk, *Z. Tech. Phys.* **12** (1931) 593
31. P. Kubelka, *J. Opt. Soc. Am.* **38** (1948) 448
32. M. P. Fuller, P. R. Griffiths, *Anal. Chem.* **50** (1978) 1906
33. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley–Interscience, New York, 1988, p. 720
34. N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth–Heinemann, 1997, p. 1090

35. D. C. Luehrs, B. C. Cornilsen, C. B. Lover, T. L. Niels, *Inorg. Chim. Acta* **145** (1988) 81
36. J. F. Arenas, J. I. Marcos, *Spectrochim. Acta A* **35** (1979) 355
37. E. G. Bakalbassis, J. Mrozinski, C. A. Tsipis, *Inorg. Chem.* **25** (1986) 3684
38. a) J. F. Arenas, J. I. Marcos, *Spectrochim. Acta A* **36** (1980) 1075; b) G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **33** (1980) 227
39. C. F. Baes Jr., R. E. Mesmer, *The hydrolysis of cations*, Wiley–Interscience, New York, 1976, p. 232
40. A. B. P. Lever, *Inorganic Chemistry*, 2nd ed., Elsevier, Amsterdam, 1984, p. 452
41. R. Meier, M. Molinier, C. Anson, A. K. Powell, B. Kallies, R. van Eldik, *Dalton Trans.* (2006) 5506
42. P. S. Bassi, B. S. Randhawa, G. K. Bilaspuri, *J. Therm. Anal.* **31** (1986) 1007.