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OF A NEW MIXED-VALENCE TRINUCLEAR
IRON CLUSTER**

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SYNTHESIS AND X-RAY CHARACTERISATION OF A NEW MIXED-VALENCE TRINUCLEAR IRON CLUSTER

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Abstract. This paper reports on the synthesis of a new trinuclear homometallic mixed-valence iron carboxylate cluster with furan-2-carboxylic acid. The complex with the formula $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{O}\text{COO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$ was characterized by X-ray analysis that revealed that the compound crystallizes in the triclinic centrosymmetric group *P*-1, with the following unit cell parameters: $a = 10.2758(6)$ Å, $b = 11.5991(9)$ Å, $c = 19.7349(15)$ Å, $\alpha = 105.060(7)^\circ$, $\beta = 94.216(6)^\circ$, $\gamma = 101.662(6)^\circ$.

Keywords: iron cluster, mixed valence, X-ray analysis, μ_3 -oxo, crystal structure, hydrogen bonds.

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Introduction

Transition metal carboxylate compounds have a significant importance in coordination chemistry [1]. The big variety of carboxylic acids and the extraordinary ability of carboxylic groups towards coordination favoured the existence of a great number of metal carboxylate complexes. Carboxylate groups can coordinate to the metal in different ways [2], thus leading to the formation of different type of structures: mononuclear, polynuclear, polymeric or supramolecular compounds.

The class of oxo-centered trinuclear complexes with the general formula $[\text{M}_3\text{O}(\text{OOCR})_6\text{L}_3]^{n+}$ have been widely studied during the last centuries [3,4] not only due to the structural particularities but also due to the large spectrum of properties which emerge from the metal-metal interaction in the cluster.

Although trinuclear iron complexes were studied for a long time, mixed-valence iron clusters began to be a research subject much later. The first detailed review of iron mixed-valence carboxylates was published by Robin, M. and Day, P. in 1967 [5]. However the class of mixed-valence iron carboxylate compounds was studied in detail by Turta, C. *et al.* [6-15] and they also performed the study of carboxylates by Mössbauer spectroscopy. The electron transfer processes were also studied by Oh, S. [16-19] and Wohler, S. [20].

Recently, it has been reported the possibility to use trinuclear clusters as precursors for the nanoparticle synthesis [21,22]. Some studies were devoted to the study of magnetic interaction between heterometallic atoms [23,24], another to the study of thermal behaviour of the trinuclear clusters [25].

Polynuclear homo- and hetero- clusters with furan-2-carboxylic acid as a ligand were determined to manifest a large scale of properties as interesting magnetic behaviour [26], luminescent activity [27], biological activity with anti-tuberculosis properties [28], and ability of regulation of the biochemical composition of cyanobacterium *Spirulina platensis* biomass [29].

To continue the research on the use of the furan-2-carboxylic acid as a ligand in the synthesis of trinuclear clusters, we have synthesized and structurally characterized the $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{O}\text{COO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$ compound by single crystal X-ray method. The presence of both iron(II) and iron(III) species was confirmed by using analytical methods of identification [30].

Experimental

Materials

All chemicals were purchased from commercial sources and used as received without further purification.

Starting materials were $\text{Cu}_2(\text{C}_4\text{H}_3\text{OCOO})_4 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, CH_3OH (methanol), CH_3CN (acetonitrile). The $\text{Cu}_2(\text{C}_4\text{H}_3\text{OCOO})_4 \cdot 4\text{H}_2\text{O}$ compound was synthesized by the reaction between $(\text{CuOH})_2\text{CO}_3$ and furan-2-carboxylic acid. The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ salt was synthesized by the reaction between metallic iron with hydrochloric acid.

Synthesis of $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$

The mixture of copper(II) furan-2-carboxylate salt (0.58 g, 1.8 mmol) and iron(II) chloride (0.36 g, 1.8 mmol) in methanol was stirred under argon atmosphere upon heating. After cooling, a yellow crystalline product was separated upon filtration and was further washed with methanol. Yellow prismatic crystals suitable for X-ray analysis were isolated upon recrystallization from acetonitrile solution.

IR (cm^{-1}): 3137.8 vw, 2971.8 vw, 2902.0 vw, 1708.6 vw, 1597.8 w, 1578.8 m, 1565.8 m, 1469.9 s, 1417.7 s, 1372.9 s, 1232.8 w, 1203.7 m, 1140.5 w, 1076.3 w, 1015.7 m, 935.15 w, 884.31 w, 799.5 w, 777.4 m, 758.44 m, 702.46 vw.

Physical measurements

The IR spectrum of the complex was recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer in the range 650–4000 cm^{-1} .

X-ray crystallography. Suitable crystals for single crystal X-ray diffraction study of $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$ complex were grown by slow evaporation of CH_3CN solution.

X-ray diffraction measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated $\text{MoK}\alpha$ radiation. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [31]. The structure was solved by direct methods using the Olex2 [32] software with the SHELXS structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-97 [33] using an anisotropic model for non-hydrogen atoms. All H atoms were introduced in idealised positions ($d_{\text{CH}} = 0.96 \text{ \AA}$) using the riding model. The positional parameters for H-atoms attached to O were verified by the geometric parameters of the possible hydrogen bonds. The molecular plots were obtained using the Olex2 program. The crystallographic data and refinement details are quoted in Table 1. CCDC 1851865 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or

from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

Table 1

Crystal data and details of data collection for $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$.

Parameter	Value
Empirical formula	$\text{C}_{31}\text{H}_{30}\text{Fe}_3\text{N}_{0.5}\text{O}_{24.25}$
Fw	965.10
T, K	293
Space group	P-1
a, \AA	10.2758(6)
b, \AA	11.5991(9)
c, \AA	19.7349(15)
α , $^\circ$	105.060(7)
β , $^\circ$	94.216(6)
γ , $^\circ$	101.662(6)
V, \AA^3	2204.7(3)
Z	2
ρ_{calcd} , g cm^{-3}	1.454
μ , mm^{-1}	1.056
Crystal size, mm	$0.2 \times 0.15 \times 0.15$
2 θ range	5.952 to 57.76
Reflections collected	16839
Independent reflections	9896 [$R_{\text{int}} = 0.0730$]
Data/restraints/parameters	9896/59/492
R_1^a	0.0826
wR_2^b	0.2087
GOF ^c	1.000
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.93/-0.51

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum F_o}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

^cGOF = $\left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Results and discussion

The reaction between copper furoate and iron(II) chloride under argon atmosphere in methanol solution upon heating leads to the formation of a new mixed-valence trinuclear complex with the composition $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$. It should be mentioned that in the case of furan-2-carboxylic acid, the typical reaction with an iron salt does not result in the formation of a trinuclear cluster, in this case a copper(II) furoate salt should be used instead [29].

According to X-ray crystallography, the investigated compound has a molecular crystal structure, which is built up from trinuclear mixed-valence $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3]$ neutral entities co-crystallized with acetonitrile and water molecules in 1:0.5:2.25 ratio. The trinuclear units exhibit a typical μ_3 -oxo structure

where three iron atoms situated in the edges of a triangle are linked by μ_3 -oxygen atom as well as the six furan-2-carboxylic groups acting as bridging ligands (Figure 1).

The geometric parameters of the coordination polyhedron of the metals, especially Fe-O1 bond distances could serve as a criterion

for the analysis of the distribution of the Fe^{2+} and Fe^{3+} within the trinuclear cluster. Nevertheless, the difference in the Fe1-O1 1.909(5) Å, Fe2-O1 1.891(4) Å and Fe3-O1 1.923(5) Å is not so pronounced giving rise for the statistically distribution of the metal cations in 1:2 ratio for each metal center (Table 2).

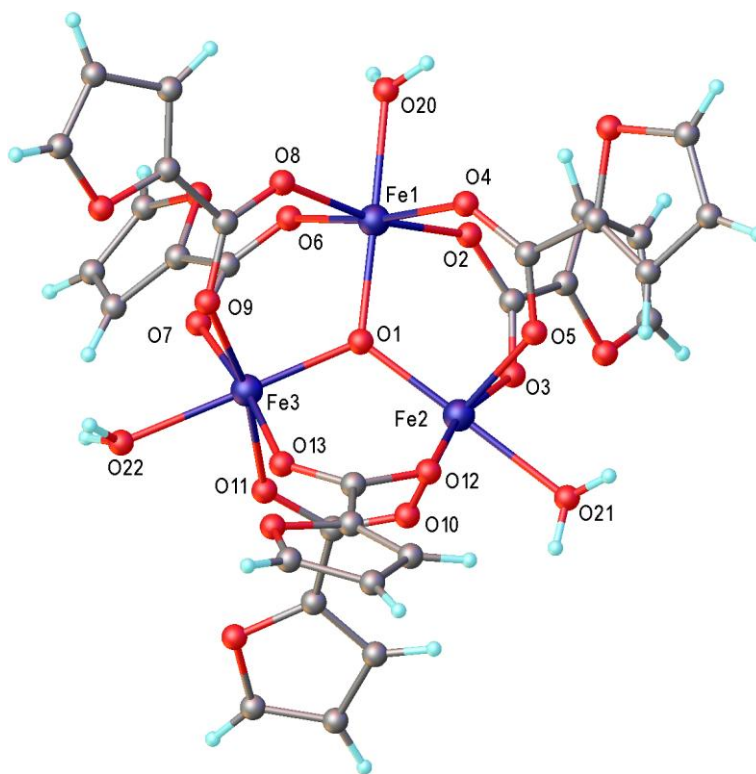


Figure 1. Molecular structure of the $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3]$ complex. Only one position of disordered moieties is shown for clarity.

Each pair of iron atoms in the trinuclear core are separated at 3.2981(16), 3.2909(18) and 3.3237(17) Å for Fe1...Fe2, Fe2...Fe3, Fe3...Fe1 atoms, respectively. The values of Fe1-O1-Fe2, Fe2-O1-Fe3, Fe3-O1-Fe1 angles vary in the range between 120.5(3) and 119.2(3)°. The sum of the angles around the μ_3 -oxygen atom is of 360(8)° which confirms the planar configuration of the $\{\text{Fe}_3\mu_3\text{-O}\}$ fragment. The iron atoms are displaced from the mean plane defined by four equatorial oxygen atoms at 1.909(5), 1.891(4), 1.923(5) Å towards the central μ_3 -O1 atom, respectively.

Each iron has six-oxygen coordination in slightly distorted octahedral geometry formed by four carboxylate oxygen atoms in the equatorial plane, the μ_3 -O atom and water molecules in the apical positions.

The analysis of crystal structure packing shows the presence of dimeric aggregates formed

due to intermolecular hydrogen bonding between one of the coordinated water molecule as donor and two carboxylate oxygen atoms of adjacent trinuclear complex as acceptor of protons, as shown in Figure 2.

A similar aggregation of trinuclear complexes was observed previously for a hetero-trinuclear complex with the composition $[\text{Fe}_2\text{MnO}(\text{CHCl}_2\text{COO})_6(\text{THF})_2\text{H}_2\text{O}]$ [34] where the water molecule involved in H-bonding is coordinated to Mn^{II} atom.

The crystal structure packing (Figure 3) is described as a three-dimensional supramolecular network consolidated through the hydrogen bonds between coordinated and solvate water molecules. A specific feature of 3D packing consists in the formation of the parallel channels along crystallographic axis *a*, accommodating statistically distributed solvate water molecules.

Table 2

Selected bond lengths and angles for the $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3]\cdot 0.5\text{CH}_3\text{CN}\cdot 2.25\text{H}_2\text{O}$ complex.			
Bond	<i>d</i> , (Å)	Bond	<i>d</i> , (Å)
Fe1–O1	1.909(5)	Fe2–O10	2.024(5)
Fe1–O2	2.015(5)	Fe2–O12	2.026(6)
Fe1–O4	1.992(5)	Fe2–O21	2.099(4)
Fe1–O6	1.993(5)	Fe3–O1	1.923(5)
Fe1–O8	2.013(5)	Fe3–O7	1.999(6)
Fe1–O20	2.043(6)	Fe3–O9	1.991(5)
Fe2–O1	1.891(4)	Fe3–O11	1.985(5)
Fe2–O3	1.987(6)	Fe3–O13	2.010(6)
Fe2–O5	2.012(5)	Fe3–O22	2.107(5)
Angle	ω , (°)	Angle	ω , (°)
O1–Fe1–O2	95.1(2)	O5–Fe2–O10	167.2(2)
O1–Fe1–O4	94.5(2)	O5–Fe2–O12	87.5(2)
O1–Fe1–O6	94.4(2)	O5–Fe2–O21	83.78(19)
O1–Fe1–O8	95.2(2)	O10–Fe2–O12	91.9(2)
O1–Fe1–O20	178.9(2)	O10–Fe2–O21	83.4(2)
O2–Fe1–O20	85.7(2)	O12–Fe2–O21	82.2(2)
O4–Fe1–O2	88.5(2)	O1–Fe3–O7	91.6(2)
O4–Fe1–O6	170.6(3)	O1–Fe3–O9	96.1(2)
O4–Fe1–O8	90.4(2)	O1–Fe3–O11	95.2(2)
O4–Fe1–O20	86.2(2)	O1–Fe3–O13	95.0(2)
O6–Fe1–O2	88.0(2)	O1–Fe3–O22	177.3(2)
O6–Fe1–O8	91.5(2)	O7–Fe3–O13	173.4(3)
O6–Fe1–O20	84.8(2)	O7–Fe3–O22	85.9(2)
O8–Fe1–O2	169.7(3)	O9–Fe3–O7	92.6(2)
O8–Fe1–O20	84.0(2)	O9–Fe3–O13	87.0(2)
O1–Fe2–O3	96.2(2)	O9–Fe3–O22	85.2(2)
O1–Fe2–O5	96.03(19)	O11–Fe3–O7	88.8(2)
O1–Fe2–O10	96.8(2)	O11–Fe3–O9	168.6(2)
O1–Fe2–O12	96.3(2)	O11–Fe3–O13	90.3(2)
O1–Fe2–O21	178.5(2)	O11–Fe3–O22	83.6(2)
O3–Fe2–O5	89.9(2)	O13–Fe3–O22	87.5(2)
O3–Fe2–O10	87.9(2)	Fe1–O1–Fe3	120.3(2)
O3–Fe2–O12	167.4(2)	Fe2–O1–Fe1	120.5(3)
O3–Fe2–O21	85.3(2)	Fe2–O1–Fe3	119.2(3)

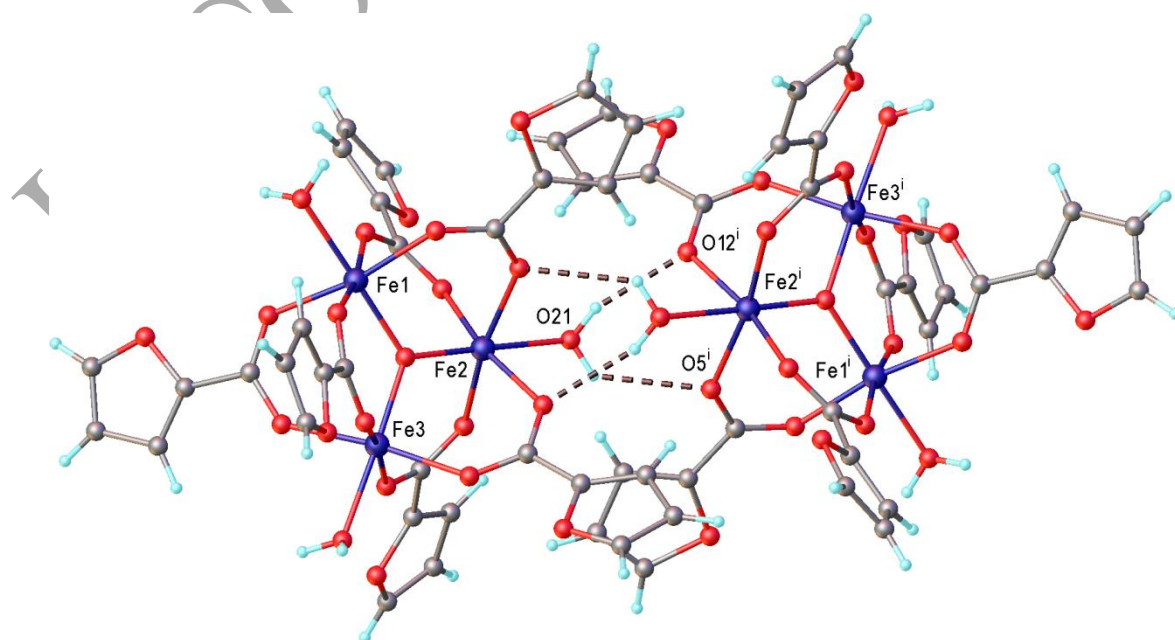


Figure 2. Two H-bonded complexes as a self-assembled centrosymmetric unit. Symmetry transformation used to generate equivalent atoms: $-x, 2-y, 1-z$.

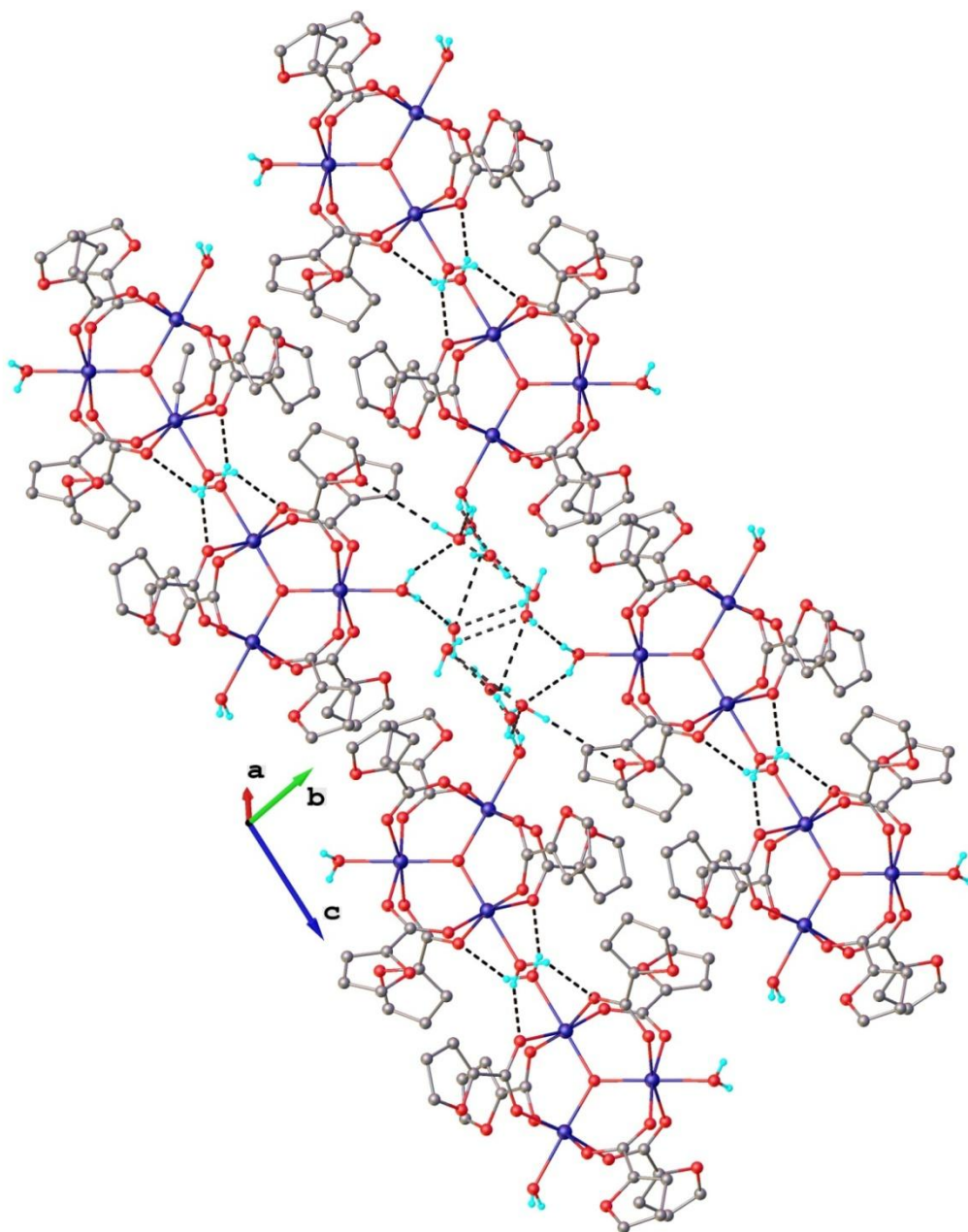


Figure 3. Partial view of the packing diagram.

The IR spectrum of the title compound shows multiple bands in the range of $650\text{--}4000\text{ cm}^{-1}$, which were analysed according to the oscillation group concept [35]. According to this concept, the bands interpretation in a complex compound with many atoms is made on the basis of adsorption bands characteristic to certain functional groups.

The minimal number of characteristic bands of a polyatomic compound is calculated according to the formula $3n-6$, where n is the total number of atoms in the molecule, thus for 85 atoms present in the studied complex, can be found 249 characteristic bands. Due to the fact that the range of the spectrum starts from 650 cm^{-1} , the number of bands decreases. Also,

the same value of wave number $1/\lambda$ is characteristic for many functional groups, thus the peaks overlapping phenomenon is also present.

According to the oscillation group theory, the presence of hydrogen bonds in water molecules is characterized by a broad signal (the broader the signal, the stronger the hydrogen bonds) in the range of $3200\text{--}2800\text{ cm}^{-1}$. In the given spectrum, this signal overlaps with the signals at: 3137.8 ; 2971.8 ; 2902.0 cm^{-1} , which are characteristic for $\nu(\text{C-H})$ oscillations of the furanic ring.

The presence of protonated carboxylic groups, according to the same concept, can be identified by the presence of oscillations characteristic to the wave number of 1700 cm^{-1} . It

is worth mentioning that as the result of complexation (the proton substitution and the formation of oxygen – metal bonds) the band characteristic to the wave number is shifted with 150–200 cm^{-1} , and we can identify the presence of two types of vibrations: symmetric and asymmetric valence vibrations. Thus in the studied spectrum, the bands characteristic for ν_{as} , $\nu_{\text{s}}(\text{COO})$ were identified at 1565.8 and 1417.7 cm^{-1} . The magnitude of the separation between the carboxylate stretches, $\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ has the value of 148.1 cm^{-1} which confirms the bridging behaviour of the carboxylate group of the furan-2-carboxylic ligand [36].

The values of the wave number oscillations characteristic to the 2-furan-carboxylic ligand, present in the IR spectrum follows: 1597.8; 1578.8, 1469.9, 1372.9 cm^{-1} for $\nu(\text{ring})$, 1232.8; 1140.5; 1076.3 cm^{-1} for $\beta(\text{C-H})$, 1015.7 cm^{-1} for $\nu(\text{C-O-C})$, 935.15 for ring pulsation, 884.31 for $\beta(\text{ring})$, 777.4; 758.44 cm^{-1} for $\gamma(\text{C-H})$ [37].

From the oscillations presented above should be mentioned that the band at 884.31 cm^{-1} is essential in the determination of the presence of furan-2-carboxylic acid while the band at 1015.7 cm^{-1} suggests that the oxygen atom from the furanic ring does not participate in the coordination of the ligand to the metal, thus the coordination occurs solely through the carboxylate groups.

Simultaneously, all the bands in the wave number range 1400–650 cm^{-1} can be assigned to the fingerprint region of this complex [36,38].

Conclusions

In this work, it is reported the synthesis of a new trinuclear mixed-valence iron carboxylate complex with the furan-2-carboxylic acid. The single-crystal X-ray characterization shows that the complex has a typical μ_3 -oxo structure with the composition $[\text{Fe}_2^{\text{III}}\text{Fe}^{\text{II}}\text{O}(\text{C}_4\text{H}_3\text{OCOO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{CH}_3\text{CN} \cdot 2.25\text{H}_2\text{O}$. The presence of intermolecular hydrogen bonds favours the formation of a supramolecular structure by forming channels along crystallographic axis *a*.

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