SYNTHESIS AND CHARACTERISATION OF NEW \{Fe\textsubscript{2}Cr\} HETERO TRINUCLEAR IRON-CROMIUM CLUSTERS

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Abstract. Two new \(\mu_3\)-oxo trinuclear heterometallic \(\text{Fe}^{\text{II}}\text{Cr}^{\text{III}}\) complexes with furan-2-carboxylic and salicylic acids with the composition: \(\text{[Fe}_2\text{CrO(C}_2\text{H}_4\text{OOCO)}_6\text{(CH}_3\text{OH)}_2]NO_3\cdot 0.5\text{CH}_3\text{OH}\) and \(\text{[Fe}_2\text{CrO(C}_2\text{H}_4\text{OH)}\text{COO)}_6\cdot 2\text{CH}_3\text{OH}]\cdot2\text{DMA}\) were synthesized starting from iron(III) and chromium(III) salts mixture. The complexes structures were confirmed by elemental analysis, IR, Mössbauer spectroscopies, and X-ray analysis. The atomic absorption spectroscopy confirmed that the iron: chromium ratio is 2:1. The thermal properties of both heteronuclear complexes have been investigated in oxidizing and inert atmospheres revealing the stability of the trinuclear core up to 170 and 220°C, respectively.

Keywords: heteronuclear \(\mu_3\)-oxo complex, \(\text{Fe}_2\text{Cr}\) cluster, X-ray diffraction, thermal analysis.

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Introduction

Homo- and heterotrinuclear iron clusters have been extensively investigated during the last decades. Their wide range of properties is due not only to their interesting structure but also to metal-metal interactions in the molecules. In this process, a crucial influence is provided by the nature of metal ions.

The biological properties of furan-2-carboxylic acid [1], as well as salicylic acid [2-5] derivatives, were well studied and employed in medicine, pharmacology, and chemical synthesis, thus their use as ligands can enhance their complexes properties.

Among the coordination compounds of carboxylate ligands, the \(\mu_3\)-oxo clusters represent a separate class of compounds. These clusters can be classified into two different types of complexes: molecular compounds with the composition \{\text{M}_3\text{\text{M}_3\text{O}}\} and molecular or ionic compounds \{\text{M}_3\text{\text{M}_3\text{O}}\} which contain three tervalent similar or different metal atoms. The mixed-valence homonuclear iron furato \(\text{[Fe}_2\text{Fe}^{\text{III}}\text{O(C}_2\text{H}_4\text{OOCO)}_6\text{(L)}_2]\) [6] as well as heteronuclear furatozes \(\text{[Fe}_2\text{\text{M}_3\text{O(C}_2\text{H}_4\text{OOCO)}_6\text{(L)}_2]}\) (M= Mn, Co, Ni) [7,8] and heteronuclear salicylates \(\text{[Fe}_2\text{\text{M}_4\text{O(C}_2\text{H}_4\text{OH)}\text{COO)}_6\text{(L)}_2]}\) (M= Mg, Co [9]; Ni [10]; Mn, Ni, Cu, Zn [11]) correspond to the first type of \(\mu_3\)-oxo complexes. Whereas homonuclear furoate \(\text{[Fe}_3\text{O(C}_2\text{H}_4\text{OOCO)}_6\text{(L)}_2]\) [8] and salicylate \(\text{[Fe}_3\text{O(C}_2\text{H}_4\text{OH)}\text{COO)}_6\text{(L)}_2]\) [12] belong to the second type of \(\mu_3\)-oxo complexes.

Lately, special attention was dedicated to the mixed iron-chromium complexes due to the iron-chromium antiferromagnetic interactions [13] and their use as precursors in the synthesis of mixed iron oxides [14]. The first X-ray structures of trinuclear iron-chromium complexes \(\text{[Cr}_3\text{Fe}_2\text{CrO}3\text{(H}_2\text{O)}_3]\) and \(\text{[Fe}_2\text{CrO}3\text{(H}_2\text{O)}_3]\) were reported by Glowiak, T. et al. in 1977 [13] and Clegg, W. et al. in 1984 [15] and the number of iron-chromium \(\mu_3\)-oxo trinuclear structures has not significantly enlarged since.

Recently it was reported the use of trinuclear homo- and heteratomic iron clusters as precursors in the synthesis of iron oxides and mixed iron oxides nanoparticles [16,17].

Also, recently, a new approach on the use of trinuclear carboxylate clusters as building blocks in the formation of metal-organic frameworks with high porosity was reported [18].

As a continuation of our research on homo- and heteronuclear iron carboxylates, two new heterotrinnuclear iron-chromium complexes with furan-2-carboxylic and salicylic acids were
synthesised. The complexes with the composition \([\text{Fe}_2\text{CrO}(\text{C}_2\text{H}_4\text{OCOO})_6(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot0.5\text{CH}_3\text{OH}\) and \([\text{Fe}_2\text{CrO}(\text{C}_2\text{H}_4(\text{OH})\text{COO})_2(\text{CH}_3\text{OH})_2]\cdot2\text{DMA}\) were attained and investigated by means of IR analysis, Mössbauer spectroscopy, Thermal analysis and X-ray crystallography.

The aim of this work is to isolate and characterize new heteronuclear iron(III) – chromium(III) clusters with the \(\{\text{Fe}, \text{Cr}\}\) core, and to evaluate their structural and thermal particularities.

### Experimental

#### Materials

All the reagents used in this study were obtained from commercial sources and employed as received without additional purification.

As starting materials \(\text{Cu}_2(\text{C}_2\text{H}_4\text{OCOO})_4\cdot4\text{H}_2\text{O}, \ \text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}, \ \text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O}, \ \text{C}_6\text{H}_6(\text{OH})\text{COONH}_4\cdot\text{CH}_3\text{OH}\) (methanol), DMA \((\text{N},\text{N}-\text{dimethylacetamide})\), THF (tetrahydrofuran) were used. The compound \(\text{Cu}_2(\text{C}_2\text{H}_4\text{OCOO})_4\cdot4\text{H}_2\text{O}\) was prepared by the reaction between \((\text{CuOH})_2\text{CO}_3\) and furan-2-carboxylic acid. The \(\text{C}_6\text{H}_6(\text{OH})\text{COONH}_4\) compound was obtained by the reaction between salicylic acid and ammonium hydroxide.

**Synthesis of \([\text{Fe}_2\text{CrO}(\text{C}_2\text{H}_4\text{OCOO})_6(\text{CH}_3\text{OH})_2]\cdot\text{NO}_3\cdot0.5\text{CH}_3\text{OH}\) (1)**

The compound was obtained according to the previously reported method [8] by using the appropriate metal salts mixture. Briefly, the mixture of copper(II) furan-2-carboxylate salt (1.93 g, 3 mmol) with iron(III) nitrate nonahydrate (0.81 g, 2 mmol), and chromium(III) nitrate nonahydrate (1.93 g, 3 mmol) in methanol was stirred for about 1 h at room temperature, whereupon a solution of iron(III) nitrate nonahydrate (0.245 g, 0.6 mmol) in a mixture of methanol (10 mL) and DMA (5 mL) was added. The dark-violet (purple) solution was kept stirring for an additional hour at room temperature. The solution was allowed to stand at room temperature for several weeks, yielding red-brown single crystals. Yield: 0.25 g, 59% (based on Fe), \(\text{C}_9\text{H}_{10}\text{N}_2\text{O}_6\text{CrFe}_2\) (1376.79): calcld. C 51.46, H 4.39, N 2.03, Cr 3.77, Fe 8.11; found C 50.99, H 4.47, N 2.36, Cr 3.63, Fe 7.93.

**Physical measurements**

**Elemental analyses** for C, H, and N were carried out by using a Vario EL (III) Elemental Analyzer. **Atomic absorption analyses** were performed on an iCAP-6200 ICP-OES ThermoScientific spectrometer.

**IR spectra** were registered on a Perkin-Elmer 100 FT-IR spectrometer in the range of 4000 – 650 cm\(^{-1}\) at room temperature. Intensities are presented in the parenthesis as: vs= very strong, s= strong, m= medium, w= weak, vw= very weak, and sh= shoulder.

**Combined thermal analyses** were performed on a Q-1500 Derivatograph with a heating rate of 10°C/min up to 1000°C in the conditions of static air atmosphere and nitrogen dynamic atmosphere with the nitrogen flow of 100 cm\(^3\)/min. The measurements with the sample weight of 10 mg were carried out in a Pt crucible by using as reference \(\alpha\)-Al\(_2\)O\(_3\).

The \(^{57}\text{Fe}-\text{Mössbauer spectra}\) were obtained with a MS4 (Edina, USA) spectrometer with a \(^{57}\text{Co}\) source (3.7 GBq) in a rhodium matrix in the constant-acceleration mode. The spectra were recorded at room temperature on a powdered sample, containing 8-10 mg/cm\(^2\) of natural iron, using \(\alpha\)-Fe as reference for isomer shifts determination. The spectra were fitted by means of Mössbauer Spectral Analysis Software WMOSS [19].

**X-ray crystallography.** Suitable crystals for single crystal X-ray diffraction study of \([\text{Fe}_2\text{CrO}(\text{C}_2\text{H}_4\text{OCOO})_6(\text{CH}_3\text{OH})_2]\cdot\text{NO}_3\cdot0.5\text{CH}_3\text{OH}\) complex were grown by slow evaporation of \(\text{CH}_3\text{OH}\) solution. The intensity data were collected at 293 K on an Oxford Diffraction Xcalibur Eos diffractometer using MoK\(_\alpha\).
radiation ($\lambda = 0.71073$ Å). Data collection, cell refinement, and data reduction were performed with CrysAlisPro (Oxford Diffraction) [20]. The structure was solved with ShelXT [21] and ShelXL [22] was used for full-matrix least-squares refinement. Crystallographic data for complex 1, CCDC-1985679 can be obtained free of charge from The Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion
The reaction between copper furoate and the mixture of iron(III) and chromium(III) nitrates in methanol solution upon heating leads to the formation of a new hetero trinuclear complex 1 with the composition $[\text{Fe}_2\text{CrO(C}_4\text{H}_3\text{OCOO})_6(\text{CH}_3\text{OH})_3]\text{NO}_3\cdot0.5\text{CH}_3\text{OH}$ (Figure 1(a)). On another hand, the reaction between sodium salicylate with the sequential addition of chromium and iron nitrates in a mixture of methanol and DMA solvents gives the new heteroatomic complex 2 with the composition $[\text{Fe}_2\text{CrO(C}_6\text{H}_4(\text{OH})\text{COO})_7(\text{CH}_3\text{OH})_2]\cdot2\text{DMA}$ (Figure 1(b)). Both complexes were isolated as crystalline products however only for complex 1 suitable crystals for X-ray analysis were obtained.

The X-ray study of complex 1 was performed at room temperature on a single crystal obtained from the methanol solution in a couple of days. X-ray crystallography confirms that compound 1 crystallizes in the $P2_1/n$ space group of the monoclinic system. It indicates that this compound has similar unit cell parameters (Table 1) and is isostructural with the previously reported homo trinuclear compound $[\text{Fe}_3\text{O(C}_4\text{H}_3\text{OCOO})_6(\text{DMF})(\text{CH}_3\text{OH})_2]\text{NO}_3$ [8].

![Figure 1](image-url)

**Figure 1.** Representation of the coordination sphere of $[\text{Fe}_2\text{CrO(C}_4\text{H}_3\text{OCOO})_6(\text{CH}_3\text{OH})_3]^+$ in 1 (a) and $[\text{Fe}_2\text{CrO(C}_6\text{H}_4(\text{OH})\text{COO})_7(\text{CH}_3\text{OH})_2]$ in 2 (b).

### Table 1

| Parameters | Value |
|------------|-------|
| Empirical formula | C_{33.5}H_{32}CrFe_{2}NO_{25.5} |
| Formula weight (g/mol) | 1020.30 |
| Space group | $P2_1/n$ |
| $a$ (Å) | 13.872(6) |
| $b$ (Å) | 22.374(5) |
| $c$ (Å) | 14.440(13) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| Volume (Å³) | 4455(4) |
| $Z$ | 4 |
| $\lambda$ (Å) | 0.71073 |
| $\rho_{\text{calc}}$ (g/cm³) | 1.521 |
| Crystal size (mm³), | 0.2×0.15×0.15 |
| Temperature (K) | 293(2) |
| $\mu$ (mm⁻¹) | 0.971 |
| Reflections collected | 16470 |
| Independent reflections | 7494 [R$_{int}$= 0.0786, R$_{sigma}$= 0.1576] |
| Unique data, parameters, restraints | 7494, 563, 44 |
| $R_1$ (a) | 0.0997 |
| $wR_2$ (b) | 0.2773 |
| GOF (c) | 0.946 |

Largest diff. peak/hole / e Å⁻³ 1.39/-1.15

(a) $R_1 = \Sigma ||F_o|| - |F_c|\sqrt{\Sigma |F_o|}$;

(b) $wR_2 = \sqrt{\Sigma [w(F_o^2 - F_c^2)]^2}$;

(c) $GOF = \sqrt{\Sigma [w(F_o^2 - F_c^2)]^2} / (n-p)$, where $n$ is the number of reflections and $p$ the total number of parameters refined.
X-ray crystallography data demonstrated that compound 1 has a typical $\mu_3$-oxo – trinuclear structure where three metal atoms are situated in the edges of a triangle with a tripod coordinated oxygen atom in the centre. Each metal is six coordinated with octahedral $O_6$ coordination geometry provided by four carboxylate oxygen atoms in the equatorial position and $\mu_2$-oxo bridging atom and methanol oxygen atom in the apical positions (Figure 2).

Due to the statistical distribution, the identical coordinates and displacement parameters were constrained for iron and chromium atoms which occupy the same metal sites in the crystal with a 2:1 ratio. Moreover, the identification of iron and chromium positions in the crystal are impeded by the close positions of these two elements in the periodic table.

The interatomic distances $M_1$--$M_2$, $M_2$--$M_3$, $M_3$--$M_1$ of 3.2523(15), 3.271(2) and 3.279(2) Å, and the angle values distances between $M_1$--$O_1$--$M_2$, $M_2$--$O_1$--$M_3$, $M_3$--$O_1$--$M_1$ atoms of $120.1(3)^\circ$, $119.0(3)^\circ$ and $121.0(3)^\circ$ (Table 2) indicate that the $\{\text{Fe}_{2}^{III}\text{Cr}^{III}\text{O}\}$ core has an isosceles triangle arrangement. Whereas the sum of the angles formed by the metal atoms and the $\mu_2$-oxygen atom of 360°, indicates that the $\{\text{Fe}_{2}^{III}\text{Cr}^{III}\mu_2\text{O}\}$ fragment has a planar geometry.

Each metal atom has a coordination number equal to six, where all six positions are occupied by oxygen atoms. These three octahedrons have one shared oxygen atom and are connecting via carboxylate bridges forming a trinuclear cluster. According to the X-ray data, the obtained compound possesses an ionic structure where the cluster has the role of a cation, and its charge is balanced by the $\text{NO}_3^-$ group. There is a co-crystallised methanol molecule that occupies a position with 0.5 occupancies.

| Bond | $d$, (Å) | Bond | $d$, (Å) | Bond | $d$, (Å) |
|------|---------|------|---------|------|---------|
| M1–O1 | 1.863(6) | M2–O1 | 1.891(6) | M3–O1 | 1.906(6) |
| M1–O2 | 2.024(7) | M2–O3 | 1.977(7) | M3–O7 | 1.960(7) |
| M1–O4 | 1.993(6) | M2–O5 | 1.970(7) | M3–O9 | 1.981(7) |
| M1–O6 | 1.977(7) | M2–O10 | 1.995(7) | M3–O11 | 1.967(8) |
| M1–O8 | 1.961(8) | M2–O12 | 1.962(7) | M3–O13 | 1.967(6) |
| M1–O20 | 2.059(6) | M2–O21 | 2.023(7) | M3–O22 | 2.016(7) |

| Angle | $\omega$, (°) | Angle | $\omega$, (°) | Angle | $\omega$, (°) |
|-------|---------------|-------|---------------|-------|---------------|
| O1–M1–O2 | 98.4(3) | O1–M2–O5 | 93.0(3) | O1–M3–O11 | 96.2(3) |
| O1–M1–O4 | 95.0(3) | O1–M2–O10 | 96.4(3) | O1–M3–O13 | 95.9(3) |
| O1–M1–O6 | 91.4(3) | O1–M2–O12 | 94.2(3) | O1–M3–O22 | 178.7(3) |
| O1–M1–O8 | 97.7(3) | O1–M2–O21 | 178.5(3) | O7–M3–O9 | 92.6(3) |
| O1–M1–O20 | 176.1(3) | O3–M2–O10 | 87.3(3) | O7–M3–O11 | 86.4(3) |
| O2–M1–O20 | 81.9(3) | O3–M2–O21 | 83.9(3) | O7–M3–O13 | 172.1(3) |
| O4–M1–O2 | 88.3(3) | O5–M2–O3 | 91.0(3) | O7–M3–O22 | 87.9(3) |
| O4–M1–O20 | 88.9(3) | O5–M2–O10 | 170.5(3) | O9–M3–O22 | 82.7(3) |
| O6–M1–O2 | 87.7(3) | O5–M2–O21 | 85.8(3) | O11–M3–O9 | 167.5(3) |
| O6–M1–O4 | 172.9(3) | O10–M2–O21 | 84.8(3) | O11–M3–O13 | 90.1(3) |
| O6–M1–O20 | 84.7(3) | O12–M2–O3 | 170.6(3) | O11–M3–O22 | 84.9(3) |
| O8–M1–O2 | 163.8(3) | O12–M2–O5 | 87.9(3) | O13–M3–O9 | 89.3(3) |
| O8–M1–O4 | 88.4(3) | O12–M2–O10 | 92.3(3) | O13–M3–O22 | 84.8(3) |
| O8–M1–O6 | 93.8(3) | O12–M2–O21 | 86.7(3) | M1–O1–M2 | 120.1(3) |
| O8–M1–O20 | 82.2(3) | O1–M3–O7 | 91.4(3) | M2–O1–M3 | 119.0(3) |
| O1–M2–O3 | 95.2(3) | O1–M3–O9 | 96.3(3) | M3–O1–M1 | 121.0(3) |
According to the atomic absorption analysis, the presence of both iron and chromium atoms in the obtained compound was confirmed in the ratio 2 to 1.

The trinuclear cations along with NO$_3^-$ out of sphere anions and co-crystallised methanol molecules are involved in the system of intermolecular interactions based on OHO and CHO hydrogen bonding. The analysis of crystal structure packing shows the presence of infinite one-dimensional supramolecular architecture as shown in Figure 3.

**IR spectroscopic characterization**

Both complexes are stable in air at room temperature, soluble in organic solvents such as methanol, ethanol, acetone, DMF, DMA, DMSO, and (C$_2$H$_5$)$_2$O. While complex 1 is insoluble in water, complex 2 turns out to be soluble in water at room temperature, this can be explained based on both, ligand nature and structural differences of the compounds, while complex 1 has an ionic structure, complex 2 possess a molecular structure where the salicylate anion coordinates to a metal atom in the apical position.

The IR spectra of the heterotrinuclear iron complex 1 and 2 display numerous absorption bands characteristic to the trinuclear carboxylate clusters in the 4000-650 cm$^{-1}$ region [23]. According to this concept, in a complex compound with many atoms, the bands interpretation is made based on the adsorption bands characteristic to certain functional groups.

In agreement with the oscillation group theory, the presence of hydrogen bonds in solvent molecules is characterized by a broad signal (the broader the signal, the stronger the hydrogen bonds) in the range of 3200-2800 cm$^{-1}$. In the spectrum of 1, this signal overlaps with the signal at 3127 cm$^{-1}$, which is characteristic for $\nu$(C-H) oscillations of the furanic ring and in the spectrum of 2 can be observed at 2934 cm$^{-1}$ characteristic for $\nu$(C-H) oscillations of the phenolic ring from the salicylic ligand as well as from DMA molecules.

![Figure 3. Partial view of the crystal packing of complex 1 showing intermolecular hydrogen bonding.](image)
The bands characteristic for \( \nu_{as}, \nu_s(C=O) \) were identified at 1569 and 1417 cm\(^{-1}\) in the case of 1 and at 1586 and 1388 cm\(^{-1}\) in the case of 2. Also, for complex 2, at 1616 cm\(^{-1}\) can be observed the vibration characteristic for \( \nu(C=O) \) of the monodentate salicylic anion. The values of the wavenumber oscillations characteristic to the furan-2-carboxylic ligand in complex 1 are presented in the IR spectrum as follows: 1599 cm\(^{-1}\) for \( \nu(\text{ring}) \), 1232, 1141, 1077 cm\(^{-1}\) for \( \beta(\text{C-H}) \), 1014 cm\(^{-1}\) for \( \nu(\text{C=O-C}) \), 935 for ring pulsation, 884 for \( \beta(\text{ring}) \), 776, 757 cm\(^{-1}\) for \( \gamma(\text{C-H}) \) [24]. Simultaneously, in complex 1 the wavenumber values at 1470 and 1373 cm\(^{-1}\) were identified at 1569 and 1417 cm\(^{-1}\) also for complex 2, at 1616 cm\(^{-1}\) can be observed the band at 1462 and 1388 cm\(^{-1}\). The oscillations of the salicylic ligand in complex 2 can be observed at the following values of the wavenumber: 1462 cm\(^{-1}\) for (C=C) ring pulsation, 1358 and 1325 cm\(^{-1}\) for \( \nu(\text{C-H}) \) of the phenolic groups in the monodentate and bidentate ligand molecules respectively, 1146, 1095, 1017 cm\(^{-1}\) for \( \pi(\text{CH}) \), 961, 868, 812 for \( \gamma(\text{CH}) \) and 756, 706 for \( \delta(\text{CH}) \) [11]. As stated in the oscillation group theory, the vibrations characteristic to the NO\(_3\) anion in 1 were identified at 825 cm\(^{-1}\) [24]. The remaining bands in the limits 1400-650 cm\(^{-1}\) may be assigned to the fingerprint region of these complexes [25,26].

**Mössbauer spectroscopic characterization**

Both complexes 1 and 2 were investigated employing Mössbauer spectroscopy. The spectra obtained at 300 K for the two investigated compounds represent doublets which are presented in Figure 4. The parameters of the Mössbauer spectra were calculated by fitting the experimental spectra and are presented in Table 3. As can be seen from the obtained data, the isomer shift values \( \delta_{Fe}(0.439 \text{ and } 0.590 \text{ mm/s}) \) and quadrupole splitting \( \Delta E_Q(0.629 \text{ and } 1.099 \text{ mm/s}) \) for complexes 1 and 2 respectively match to iron(III) in the high spin state (\( S = 5/2 \)) [27].

The parameters of the Mössbauer spectra of the two heterotrINuclear complexes with the \{Fe\(_2\)CrO\} moiety 1 and 2 as well as the previously reported homotrinuclear complexes with the moiety \{Fe\(_3\)O\} for furan-2-carboxylic [7] and salicylic [12] ligands are presented in Table 3.

**Table 3**

Parameters of the Mössbauer spectra of the obtained \{Fe\(_2\)CrO\} compounds 1 and 2 and the homometallic \{Fe\(_3\)O\} furoate and salicylate.

| Complex |
|---------|
| \[\text{Fe}_2\text{CrO(C}_2\text{H}_3\text{O}_2\text{O})_2(\text{CH}_3\text{OH})_2\text{NO}_3 \cdot 0.5\text{CH}_3\text{OH}] \text{1} |
| \[\text{Fe}_2\text{CrO(C}_2\text{H}_4(\text{OH})\text{COO})_2(\text{CH}_3\text{OH})_2\text{2DMA \text{2}} |
| \[\text{Fe}_3\text{O(C}_2\text{H}_3\text{OCOO})_2(\text{CH}_3\text{OH})_2\text{NO}_3 \cdot 2\text{CH}_3\text{OH}] \text{[8]} |
| \[\text{Fe}_3\text{O(C}_2\text{H}_4(\text{OH})\text{COO})_2(\text{H}_2\text{O})_2\text{2DMA-MeOH-1.5THF-2.6H}_2\text{O \text{[12]} |

| Isomer Shift, \( \delta^{**} \) | Quadrupole splitting, \( \Delta E_Q \) | Line width, \( G \) | Spin state, \( S \) |
|---------|----------------|-----------|----------|
| 0.439 | 0.629 | 0.405 | 5/2 |
| 0.590* | 1.099 | 0.697 | 5/2 |
| 0.68* | 0.59 | 0.34 | 5/2 |
| 0.459* | 1.094 | 0.363 | 5/2 |
| 0.444* | 0.569 | 0.318 | 5/2 |

* The isomer shifts are referenced to metallic iron.

**Figure 4.** Mössbauer spectrum of the complexes 1 (a) and 2 (b) at 300 K.
The comparative analysis of the Mössbauer spectra parameters reveals that in the case of compounds 1 and 2 is present the high-spin iron(III) species with the spin state of 5/2. The isomer shift values at 300 K presented in Table 3 suggest that the total density of $s$-electrons on the nucleus is not affected by the presence of Cr$^{3+}$ ions in the inner sphere or the external sphere anions and/or solvent molecules. [7,8,12].

The substitution of one iron(III) ion in the triangle arrangement by a chromium(III) ion leads to the growth of the quadrupole splitting values from 0.590 to 0.629 mm/s and from 1.094 to 1.099 mm/s in complexes 1 and 2 respectively. Although, the augmentation of these values is nonessential, it serves as evidence of the fact that the $D_3h$ symmetry in the complex was not affected since the charge of both iron and chromium ions is 3+. Nevertheless, in the case of a heterotrinuclear complex with a 2+ charged metal occurs a decrease in the symmetry of the $\{\text{Fe}_2\text{MO}\}$ moieties from $D_3h$ to $C_2v$ [7].

**Thermal analyses**

The thermal study of the complexes 1 and 2 was performed in the temperatures range from 20 to 1000°C and the measurements were performed both in air and in nitrogen atmosphere. The thermoanalytical curves are presented in Figure 5, showing that the thermal processes start at low temperatures. The thermal instability of the complexes at 50°C (in air atmosphere) and at 40-50°C (in nitrogen flow) can be explained based on the structural particularities of the compounds, thus as can be seen from crystallographic data for complex 1, solvent molecules are present both in the internal and external spheres of the complex. The decay of the complexes initiates with the solvent molecules elimination in dynamic nitrogen flow and for each complex occurs in several steps. The decomposition process occurs similarly to other previously reported $\mu_3$-oxo carboxylate clusters [11], starting with the elimination of the solvent molecules from the external sphere, followed by solvent molecules liberation from the inner coordinated sphere, further the elimination of the anion molecule undergoes (only for 1) and then the decomposition of the ligand occurs. The thermolysis process ends with the formation of the mixed Fe$_3$CrO$_{4.5}$ oxides.

![Figure 5. TG/DTG/DTA curves of the complexes 1 (a,b) and 2 (c,d) measured both in air and in nitrogen flow respectively, in the temperature range of 20-1000°C.](image-url)
The measurement conducted in inert conditions in the presence of the dynamic nitrogen flow has shown that final residue mass overcomes the calculated mass for the mixed iron oxide, suggesting the formation of a mixture with carbonic residue. The comparative thermal study of the two heteronuclear carboxylate clusters both in the oxidizing and inert atmosphere has empathized that the decomposition at 220-240°C occurs in the similar way with the elimination of co-crystallised and coordinated solvent molecules with the only difference that in nitrogen flux the elimination occurs at slightly lower temperatures due to the dynamic flow. The decomposition at higher temperatures unfolds in a totally different manner since in the air atmosphere, due to the presence of oxygen, the decomposition process is taken over by the combustion processes.

The thermal study of the complex 1 reveals that the decomposition process in the air atmosphere occurs in several steps. The first stage of decomposition takes place at the temperature range 50-170°C corresponding to the elimination of methanol molecules both from external and coordinated spheres (10.40%, calcd. 10.99%). The second stage of decomposition 170-240°C partially overlaps with the third stage 240-440°C matching to the nitrate anion liberation and ligand decomposition in the presence of air. After 440°C the resulting compound is stable up to 1000°C and the residue corresponds to the formation of the mixed iron oxide with the composition Fe₂CrO₄.₅ (22.96%, calcd. 23.01%). The thermal study of complex 1 performed in nitrogen atmosphere shows that the first stage of decomposition in the 50-140°C temperature range and the second in 140-250°C temperature range, correspond to the elimination of methanol molecules and nitrate anion respectively (17.12%, calcd. 17.06%). Further, the decomposition of the furan-2-carboxylic ligand starts, which occurs in several steps and undergoes up to 900°C. The ligand degradation probably begins with the decarboxylation process, which undergoes further restructuring and degeneration. The final residue that corresponds to 31.03% of mass presumably consists of iron-chromium oxide and carbonic residue mixture.

The thermal study in the air atmosphere was used to confirm the composition of the complex 2. Thus, the first stage of decomposition occurs at 50-165°C temperature range, and the mass loss corresponds to the elimination of two molecules of DMA co-crystallised solvent (12.53%, calcd. 12.71%). The second stage of decomposition 165-220°C, corresponds to two methanol coordinated molecules (8.11%, calcd. 8.18%). In the temperature range from 220°C up to 600°C the decomposition and degradation of seven salicylic ligand molecules (six bridging and one coordinated molecules) occur. After 600°C up to 1000°C the complex is stable and the formed residue matches to the formation of mixed iron-chromium oxide with the content Fe₂CrO₄.₅ (17.37%, calcd. 17.19%). The thermal study in the dynamic nitrogen atmosphere of complex 2 shows that the decomposition process starts at 40-210°C with the elimination of DMA solvent molecules and methanol coordinated molecules (20.81%, calcd. 20.89%). Further, the decay of the one coordinated and six bridging salicylic ligand molecules occurs. This process undergoes through several steps up to 930°C leading to the formation of the product of 31.94% of mass which probably corresponds to the mixture of iron-chromium oxide and carbonic residue.

Conclusions

Two new μ₃-oxo trinuclear heterometallic Fe²⁺Cr³⁺ complexes with furan-2-carboxylic and salicylic acids were obtained and characterised. The metal content was studied by atomic absorption analysis which confirmed the formation of heterotrinuclear clusters and revealed the Fe and Cr ratio to be equal to 2 : 1.

The structure of complex 1 was determined by X-ray diffraction (which ascertained that it crystallizes in the $P2_1/n$ space group of the monoclinic system and is isostructural with its homo trinuclear analogue) and confirmed by elemental analysis, IR and Mössbauer spectroscopies. Whereas in the case of complex 2, the structure was confirmed through several methods, the IR studies have demonstrated the coordinated nature of salicylate molecules in the complex as well as the presence of methanol and DMA molecules in the structure and the thermal study of the compound helped to estimate the amount of DMA external solvent molecules and confirmed the presence of two coordinated methanol molecules. The Mössbauer spectroscopy allowed to confirm the presence of high-spin iron(III) species with the spin state of 5/2 in both compounds. The isomer shift values at 300 K suggest that the total density of s-electrons on the nucleus is not affected by the presence of Cr³⁺ ions in the inner coordination sphere.

The substitution of one iron(III) ion in the triangle arrangement by a chromium(III) ion leads to the growth of the quadrupole splitting values in both complexes suggesting the stability of the $D_{3h}$ symmetry.
The thermal analysis revealed that the decomposition process occurs in the temperature ranges 50–440°C and 50–600°C for complexes 1 and 2 respectively through several steps including the elimination of the solvent molecules from the external sphere, followed by solvent molecules liberation from the inner coordinated sphere, the elimination of the anion molecule (in the case of complex 1) and the decomposition of the furoate and salicylate ligand in the case of 1 and 2 respectively. The thermal stability of the trinuclear core in the complexes was established up to 170°C and 165°C respectively. The thermolysis process leads to the formation of the mixed Fe₂Cr₃O₇ oxides at temperatures above 440°C and 600°C.

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