

Synthesis, X-ray crystal structure and spectroscopic characterization of heterotrinnuclear oxo-centered complex $[\text{Fe}_2\text{NiO}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3]$

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ABSTRACT

New oxo-bridge, mixed metal complex, $[\text{Fe}_2\text{NiO}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O}$ has been synthesized from the direct reaction between metal nitrate and propanoic acid and characterized by elemental analysis, infrared and electronic spectroscopy and single-crystal X-ray crystallography. This complex have a typical μ_3 -oxo trinuclear structure: (a) three metal atoms are situated in the apexes of the equilateral triangle; (b) μ_3 -oxygen atom and six propanoate ligands fulfill the bridge functions; (c) the monodentate water ligands complete the octahedral geometry of the metal ions. It crystallized in the triclinic, space group type $P\bar{1}$. Two strong bands were observed in IR spectra at ~ 1590 and ~ 1420 (cm^{-1}) stretching vibrations, the coordination mode of the carboxylate ligand can be assigned on the basis of the difference ($\Delta\nu \leq 200$ cm^{-1}) of these two frequencies.

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1. Introduction

Oxo-centered carboxylate-bridged complexes of the general composition $[\text{M}_3\text{O}(\text{RCOO})_6(\text{L})_3]^z$ (where M: metal atom; RCOOH: carboxylic acid; L: terminal ligand (water, methanol, pyridine (Py), etc.); $z = +1$ for $\text{M}_3^{(\text{III})}$ and $z = 0$ for $\text{M}_3^{(\text{II})}$ $\text{M}^{(\text{II})}$) represent one of the most intensely studied classes of polynuclear compounds. The chronology of their study begins in 1908, when Weinland [1,2] and Werner [3] first proposed the trinuclear formulation.

This initial model was then clarified in later work, with the μ_3 -O triangular geometry being predicted [4,5]. In 1965 this prediction was confirmed by X-ray crystallographic investigations of the $\text{Cr}^{(\text{III})}$ 'basic acetate' complex with $\text{R} = \text{CH}_3$, $\text{L} = \text{H}_2\text{O}$ [6]. A multitude of studies followed, of both a theoretical and an empirical nature; the vast bibliography in this area was exhaustively reviewed by Cannon and White [7].

These species have been of continual interest for several reasons: they serve as suitable models for studying electronic and magnetic metal–metal interactions in clusters, they display properties of homogenous catalysts in various oxidation reactions, they represent precursors for clusters of higher nuclearity whose unusual structural design and physical properties open new opportunities for experimental modeling of biocatalysis, and their

structural variations allow a close examination of parameters affecting the stability of metal–ligand aggregates [8–13].

Among the large number of presently known trinuclear carboxylates the most common are the 'symmetric' species (Fig. 1, the complex with identical terminal ligands $\text{L} = \text{L}' = \text{L}''$), while the 'unsymmetric' ones (with the core surrounded by different terminal ligands $\text{L} \neq \text{L}' \neq \text{L}''$) have been quite scarce. Perusal of the literature reveals that a number of transition metals form complexes with carboxylic ligands [14–16], but studies on mixed metal complexes with such ligands and with $\text{Ni}^{(\text{II})}$ ion are very limited.

We report herein the synthesis, elemental analysis, IR, UV–Vis data and single-crystal X-ray diffraction studies of a new $[\text{Fe}_2\text{NiO}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3]$ heterotrinnuclear complex in which the distribution of the metal ions in trinuclear cluster are localized.

2. Experimental

2.1. Methods and materials

C and H analysis were carried out on a Thermo Finnigan Flash model EA 1112 elemental analyzer (Italy), atomic absorption analysis was carried out on a Shimadzu model AA-670 atomic absorption spectrometer (Japan). IR spectra of KBr disc were recorded on a Buck 500 spectrometer (USA). The UV–Vis spectrum was obtained in the range of 200–700 nm by the Agilent 8453 single-beam photodiode array spectrophotometer (Italy). Melting point was determined using an electrothermal digital melting point apparatus.

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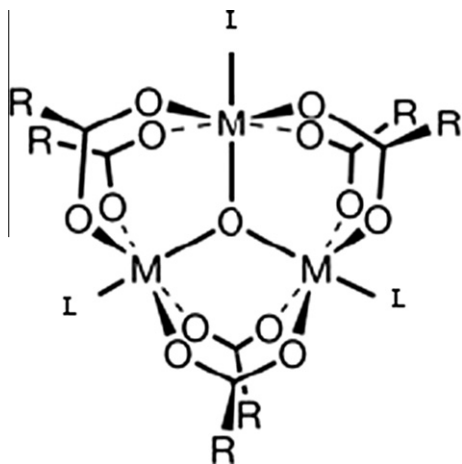


Fig. 1. The proposed structure of the cluster unit $[M_3O(RCOO)_6(L)_3]^n$.

Reagents, carboxylic acid and metal salts used in this study were purchased from Merck (Germany).

2.2. Synthesis of $[Fe_2NiO(CH_3CH_2COO)_6(H_2O)_3] \cdot 0.5H_2O$ (**1**)

0.818 g (2 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.29 g (1 mmol) $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 10 mL of water and solution containing 2 mL (6 mmol) propanoic acid and 0.32 g (3 mmol) sodium carbonate in 15 mL of water were gradually added with continuous stirring under heating on the water bath ($\sim 70^\circ C$). The solution was left at ambient temperature. After several days, the light brown crystals were collected, washed with ether and dried in vacuum (yield: 75%). mp: $165^\circ C$. Anal. Calcd. for $C_{18}H_{36}Fe_2NiO_{16} (0.5H_2O)$; C, 31.39%; H, 5.38%; Fe, 16.22%; Ni, 8.53%. Found: C, 31.22%; H, 5.49%; Fe, 16.07%; Ni, 7.94%.

2.3. Crystallographic study

Crystallographic data and refinement parameters for compound are presented in Table 1. A brown crystal of dimensions $0.26 \times 0.15 \times 0.08$ mm was attached to a thin glass fiber and mounted on a Siemens SMART 1000 CCD platform diffractometer. Data for the title compound were collected at 203(2) K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The final unit cell was determined from 9197 reflections in the range of $1.56^\circ < \theta < 29.18^\circ$.

The unit cell determination and data integration were carried out using the program APEX 2/COSMO and corrected for the effects of absorption using Bruker AXS APEX2 [17]. The structure was solved by direct methods and refined via full-matrix least-squares on F^2 using the Bruker AXS SHELXTL Vers. 6.12 software [18]. The largest peak and hole on the final difference Fourier-map were 1.119 and -1.059 e\AA^{-3} .

Riding model on idealized geometries with the 1.2-fold (1.5-fold for methyl groups) isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. Water hydrogen atom positions taken from a Fourier-map and also refined as riding group with the 1.5-fold isotropic displacement parameters of the equivalent Uij of the corresponding hydroxy atom. Refinement of the structure revealed that C_{23} , C_{43} and C_{53} indicate disorder which could not be resolved. Consequently atom distances given for these atoms have no significance.

X-ray crystallographic files in CIF format for the structure determination of title compound has been deposited with the Cambridge Crystallographic Data Center. The CCDC reference number is 614312. Copy of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge CB2

Table 1
Crystal data and structure refinement for **1**.

Parameter	Data
Empirical formula	$C_{18}H_{36}Fe_2NiO_{16} \cdot 0.5H_2O$
Formula weight	687.89 Da
Temperature	203(2) K
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 13.2516(4) \text{ \AA}$, $\alpha = 86.304(2)^\circ$ $b = 14.2676(5) \text{ \AA}$, $\beta = 89.684(2)^\circ$ $c = 16.2900(5) \text{ \AA}$, $\gamma = 66.570(2)^\circ$
Volume	$2819.42(16) \text{ \AA}^3$
Z	4
Crystal size	$0.26 \times 0.15 \times 0.08$ mm
Crystal colour	Brown
Density (calculated)	1.621 g cm^{-3}
$F(000)$	1428
Theta range for data collection	$1.56\text{--}29.18^\circ$
Index ranges	$-18 \leq h \leq 18$, $-19 \leq k \leq 19$, $-21 \leq l \leq 22$
Absorption coefficient	1.747 mm^{-1}
Max./min. transmission	0.96/0.72
Refinement method	Full-matrix least-squares on F^2
Reflections collected	80,584
Independent reflections	14,392 [$R(\text{int}) = 0.0493$]
Data/restraints/parameters	11,119/0/676
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0413$, $wR2 = 0.1081$
R indices (all data)	$R1 = 0.0585$, $wR2 = 0.1182$
Largest diff. peak and hole	1.119 and -1.059 e\AA^{-3}

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3. Results and discussion

3.1. Description of the structure

The crystal structure analysis reveals that this material consists of two iron (III) and one nickel (II) ions are situated at the apexes of the isosceles triangle (Ni(1)–Fe(1) 3.272(1), Ni(1)–Fe(2) 3.274(2), Fe(1)–Fe(2) 3.266(1) \AA) and a triply bridging oxygen atom in its center. Two $C_2H_5\text{--}COO^-$ anions, with syn–syn configuration, which bridge the same pair of metal atoms lie on the opposite sides of the Fe_2NiO plane. The perspective view of the molecular structures and unit cell of **1** are depicted in Fig. 2a and b, Crystal data, X-ray measurements and structure determination summaries are given in Table 1 and selected bonds lengths and angles are summarized in Table 2. A careful inspection of the electron-density distribution, bond lengths, and atomic vibrational parameters at the three metal sites do not indicate any definite evidence for position of the $Ni^{(II)}$ ion in a particular metal site, even though atom Ni has slightly longer $M\text{--}\mu_3\text{--}O$ bond (mean 1.891 \AA) than those $Fe^{(III)}\text{--}\mu_3\text{--}O$ (mean 1.875) which may indicate some preference for this location to be occupied by the larger $Ni^{(II)}$ ion, the difference of 0.016 \AA is significantly less than would be expected in a fully ordered structure: $Ni^{(II)}\text{--}\mu_3\text{--}O$ bonds are typically 0.1 \AA longer than $Fe^{(III)}\text{--}\mu_3\text{--}O$ bonds, and in the $Fe^{(III)}Mn^{(II)}$ complex [19] the $M\text{--}\mu_3\text{--}O$ bond distances for the position occupied by the $Mn^{(II)}$ metal exceed with an average value of 0.2 \AA , the corresponding distances for the iron (III) positions. Moreover, the three $M\text{--}O_{(H_2O)}$ bonds in **1** are approximately equal (Table 2). On the balance of the evidence, we consider that each metal ions position in this compound is too small for the observed bond lengths and angles to be used in a consequential discussion of the individual metal coordination geometries.

In this complex, the central oxygen is displaced from the plane of the three metal atoms, by 0.031(2) \AA and the three aquo oxygens, on the other hand, are all displaced toward the opposite face of the M_3 triangle, although aquo oxygen atom bonded to Ni is

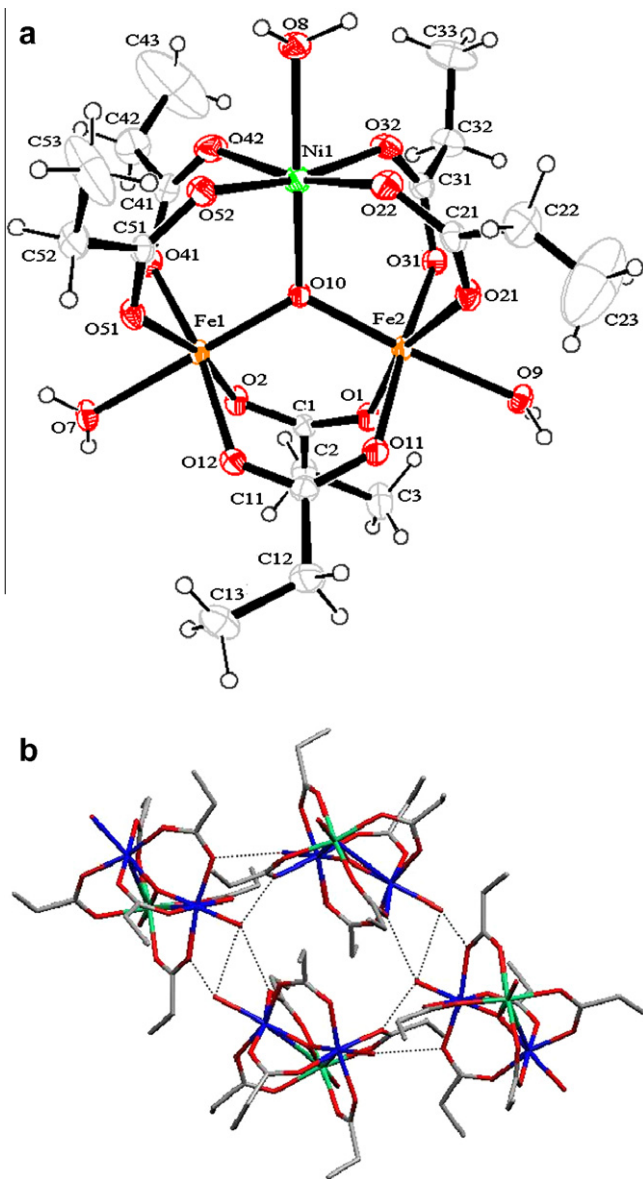


Fig. 2. Molecular structure and atomic labeling of the mixed metal trinuclear complex $[\text{Fe}_2\text{NiO}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3] \cdot 0.5\text{H}_2\text{O}$ (**1**) (a) and the packing diagram (unit cell) viewed along the *a*-axis, dashed lines represent intermolecular contacts. (Red: O atoms, blue: Fe atoms, green: Ni atoms, grey: C atoms.) (b) The thermal ellipsoids are drawn at the 50% probability level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

displaced more than two others (0.1 Å vs. 0.03 and 0.003 Å for Ni, Fe₂ and Fe₁, respectively). However the deviations are much less than that found in the pivalate-bridged iron complex $[\text{Fe}_3\text{O}(\text{OOCMe}_3)_6(\text{H}_2\text{O})_3]\text{Cl}$, where the displacement is 0.24 Å [20].

Moreover it is clear in these systems that the M–OH₂ distances are all greater than those found in the analogous mononuclear complexes $[\text{M}(\text{OH}_2)_6]^{3+}$ [21]. This confirms that M–OH₂ bonds in the oxo-centered trimer complexes are weakened, as suggested previously on the basis of vibrational spectroscopy [22] and reaction kinetics [23].

As was said, the difference between Fe^(III)–μ₃–O and Ni^(II)–μ₃–O bond distances are not considerable. The similar tendency is observed for the M–O_{carb.} distances (see Table 2). This effect may possibly be related to the fact that Ni²⁺ has the smallest radius of the divalent metal ions studied. This is in good agreement with the

Table 2
Selected bond lengths (Å) and angles (°) for title compound.

Bond lengths		Bond angles	
Fe1–O10	1.8850(18)	O10–Fe1–O41	96.12(8)
Fe1–O41	2.041(2)	O10–Fe1–O12	94.68(8)
Fe1–O2	2.0524(18)	O41–Fe1–O12	168.79(8)
Fe1–O12	2.055(2)	O2–Fe1–O51	167.24(8)
Fe1–O51	2.0642(18)	O10–Fe1–O7	178.68(8)
Fe1–O7	2.1238(19)	O10–Fe2–O21	95.44(8)
Fe2–O10	1.8944(18)	O10–Fe2–O1	99.69(8)
Fe2–O21	2.0260(19)	O21–Fe2–O1	164.43(8)
Fe2–O1	2.0369(18)	O31–Fe2–O11	172.27(8)
Fe2–O31	2.058(2)	O10–Fe2–O9	176.03(8)
Fe2–O11	2.060(2)	O10–Ni1–O42	95.35(9)
Fe2–O9	2.1056(19)	O10–Ni1–O22	97.35(8)
Ni1–O10	1.8869(18)	O42–Ni1–O22	167.25(9)
Ni1–O42	2.009(2)	O32–Ni1–O52	169.01(8)
Ni1–O32	2.030(2)	O10–Ni1–O8	178.19(8)
Ni1–O22	2.051(2)	Fe1–O10–Ni1	120.36(9)
Ni1–O52	2.059(2)	Fe1–O10–Fe2	119.58(9)
Ni1–O8	2.133(2)	Ni1–O10–Fe2	119.98(9)

values of the Fe³⁺ and Ni²⁺ atomic radii that are equal to 0.65 and 0.69 Å, correspondingly [24].

The type of interaction between the molecular units in the crystal is essential for the crystal packing [25]. The crystal structure of **1** is characterized by short intermolecular contacts and consists of the mutually interpenetrated two-dimensional layers. The structure of these layers is given in Fig. 3. There are noticeable interactions between the given trinuclear moieties. This occurs via short O···H, O···O and H···C intermolecular contacts that have the values in the range of 2.35–2.65, 2.95–3.1 and 2.7–2.8 Å, respectively.

3.2. IR spectra

Vibrational spectrum exhibits the characteristic bands associated with the building constituents from which title material was synthesized. The IR spectrum of this complex is shown in Fig. 4 that indicates the presence of carboxylate, H₂O and {Fe₂MO} groups. The characteristic vibration frequencies for H₂O groups appear at ~3400–3500 cm⁻¹. The most useful characteristic bands of metal carboxylates are a strong asymmetric CO₂ stretching vibration ($\nu_{\text{asym}}\text{COO}$) and a somewhat weaker symmetric CO₂ stretching vibration ($\nu_{\text{sym}}\text{COO}$). The IR data for compound **1** show a single pair

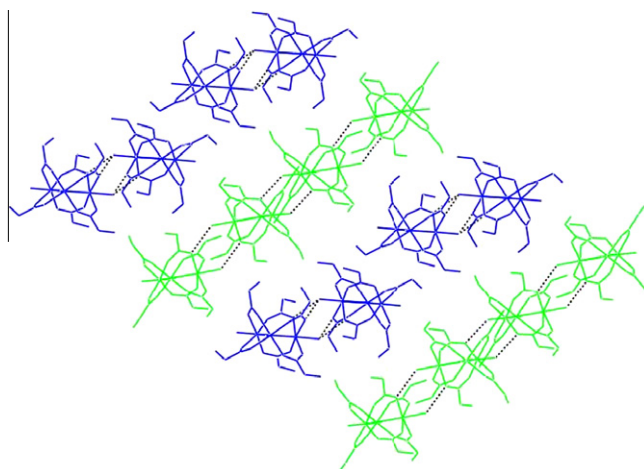


Fig. 3. Two-dimensional layers resulted from H-bonds interactions of trinuclear $[\text{Fe}_2\text{NiO}(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3]$ complexes projected along *c* axis. (Colour of moieties is caused by symmetry equivalence.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

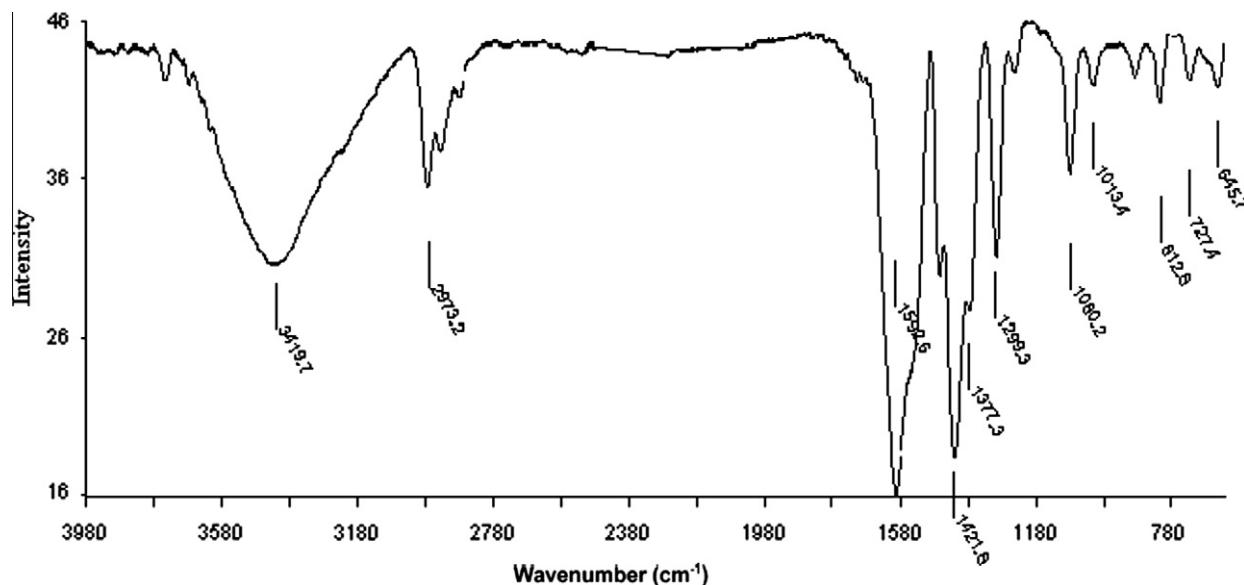
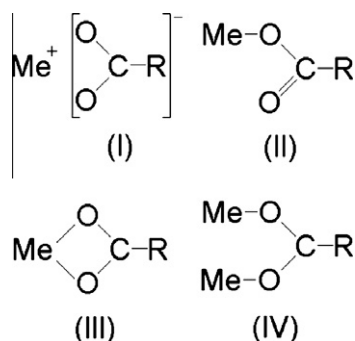


Fig. 4. IR spectrum of complex 1, KBr discs, $T = 298$ K, vertical scale, transmission (%).



Scheme 1. Structure of metal carboxylates according to the type of metal–ligand interaction. (I) Ionic or uncoordinated form, (II) unidentate coordination, (III) bidentate chelating coordination, (IV) bidentate bridging coordination.

of carboxylate stretching vibrations at 1593 and 1421 cm^{-1} assigned to $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$, respectively, suggesting the existence of only one type of carboxylate group in its crystal structure. Buildings of metal carboxylates according to the type of metal–ligand interaction are presented in Scheme 1. The major difference in the IR spectra between monodentate (type II) and bidentate bridging (existing in oxo-centered complexes) (type IV) groups, is that the CO_{asym} is generally smaller for the latter. Generally, a common trend for both stretching frequencies and/or band separation values can be outlined as: uncoordinated acid > unidentate coordination > bidentate (bridging > chelating) coordination.

Table 3
Main IR spectral vibrations (cm^{-1}) data of μ_3 -oxo trinuclear cluster (1).

Assignments						
$\nu(\text{O-H})$	$\nu_{\text{asy}}(\text{CH})$	$\nu_{\text{asy}}(\text{COO})^a$	$\nu_{\text{sy}}(\text{COO})^a$	$\delta(\text{CH}_3)^a$	$\nu(\text{C-CH}_3)^b$	$\rho_r(\text{CH}_3)^{a,b}$
3420	2970	1593	1421	1375	1298	1080
$\pi(\text{CH}_3)^b$	$\nu(\text{C-CO}_2)^c$	$\delta(\text{OCO})^{a,d}$	$\gamma(\text{COO})^{a,d}$	$\nu_{\text{asy}}(\text{Fe}_2\text{NiO})^d$	$\pi(\text{Fe}_2\text{NiO})^c$	
1015	812	654	611	727(A_1), 455(B_2)	329	

ν : stretching; δ : in plane bending; γ : out of plane bending; ρ_r : rocking in plane; π : rocking out of plane.

^a Ref. [27].

^b Ref. [28].

^c Ref. [29].

^d Ref. [30].

Since the difference [$\Delta\nu = \nu_{\text{asym}}(\text{CO}_2) - \nu_{\text{sym}}(\text{CO}_2)$] is 172 cm^{-1} for title complex and this value is less than the $\Delta\nu$ value for $\text{NaO}_2\text{C}_3\text{H}_5\cdot\text{H}_2\text{O}$ (type I) of ($\sim 200\text{ cm}^{-1}$), we expect bidentate bridging coordination of carboxylates in this compound [26].

Frequencies and assignments related to stretching and bending and rocking modes of (OH), (COO), (CH) and (CC) groups for μ_3 -oxo heterotrinnuclear cluster according to [27–30] are summarized in Table 3. It is worth mentioning that the band corresponding to $\nu_{\text{as}}(\text{Fe}_3\text{O}) = 595\text{ cm}^{-1}$ from homotrinnuclear basic acetates is missing in IR spectrum of compound. This band is replaced by another two bands at $\sim 720\text{ cm}^{-1}$, corresponding to $\nu_{\text{as}}(\text{Fe}_2\text{MO})$ (A_1), and at 455 cm^{-1} , corresponding to $\nu_{\text{as}}(\text{Fe}_2\text{MO})$ (B_2) according to [31]. Cannon and co-workers have examined the $\text{Fe}_2\text{M-O}$ vibration modes and such bands have been found for a number of $[\text{Fe}_2\text{M}^{\text{II}}(\mu_3\text{-O})(\text{RCOO})_6(\text{L})_3]$ complexes. Such behavior was expected because of symmetry lowering of the complexes from D_{3h} to C_{2v} [7,14,31].

3.3. UV–Vis spectroelectrochemical studies

The electronic spectra of trinuclear complexes can be interpreted in a good approximation in the terms of d–d transitions of individual metal ions, together with ligand–metal charge transfer transitions. Electronic spectrum of this complex is recorded in the range $200\text{--}700\text{ nm}$ ($50,000\text{--}15,000\text{ cm}^{-1}$) in dichloromethane solution. The divalent Ni ion (d^8 ion) in octahedral crystal field gives rise to three spin-allowed electronic transitions; in this complex the spectrum exhibited two spin-allowed bands in the regions

29,050 ± 100 (344 nm) and 17,100 ± 50 cm⁻¹ (585 nm) which could be assigned to the transitions from $\nu_3[{}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3P)]$, $\nu_2[{}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3F)]$ respectively, and the third spin-allowed transition $\nu_1[{}^3A_{2g}({}^3F) \rightarrow {}^3T_{2g}({}^3F)]$ disappears in the spectra of the complex in the range of 200–700 nm.

The Racah parameters, Dq and B are calculated from the observed band positions using the energy expressions [32]:

$${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3P) : 15Dq + 13.5B = 26,100 \text{ cm}^{-1} (\nu_3\text{-band})$$

$${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3F) : 15Dq + 1.5B = 17,100 \text{ cm}^{-1} (\nu_2\text{-band})$$

The value of B (750 cm⁻¹) is obtained from the relation, $\nu_3 - \nu_2 = (26,100 - 17,100 \text{ cm}^{-1}) = 12B$.

The values of interelectronic repulsion parameter (B) and the covalency factor (β) were found 750 cm⁻¹ and 0.73, respectively ($\beta = B_{\text{complex}}/B_{\text{free ion}}$). The reduction of Racah parameter from the free Ni²⁺ value (1030 cm⁻¹) [33] suggested considerable covalent nature of metal–ligand bonds in this complex.

The UV spectrum of this complex exhibits a strong band at 44,050 cm⁻¹ (227 nm) which is a cause of ($n \rightarrow \pi^*$) transition of carboxylate groups, while $n \rightarrow \pi^*$ transitions of carboxylic acid appear in the range of 230–240 nm [34]. Hence this transition (227 nm) shows a small blue shift that attributed to coordination of the carboxylate oxygen.

The band centered at 40,000 cm⁻¹ (250 nm) can be assigned to the ligand-to-metal charge transfer. The appearance of an O → M CT band at 250 nm is a further evidence of coordination of the carboxylate oxygen to metal ion.

4. Conclusion

The crystal structure of the new triclinic complex Fe₂NiO(CH₃CH₂COO)₆(H₂O)₃·0.5H₂O has been determined using single-crystal X-ray diffractometer and fully characterized by typical spectroscopic methods. According to structural studies, the overall structure of the complex is similar to that in other oxo-bridge trinuclear carboxylate, with the μ_3 -O atom at the center of an almost equilateral triangle of metal atoms, and we shall not discuss the details except to note that the M– μ_3 -O bonds lengths are towards the low end of the range (1.88–1.94 Å) observed in compounds of this general type [35]. Furthermore, on the basis of Fe^(III)– μ_3 -O and Ni^(II)– μ_3 -O bonds lengths and slight difference between them, unambiguous determination of the position of divalent metal (Ni²⁺) in certain of the M₃– μ_3 -O core is a difficult task.

5. Supplementary information

Complete listings of bond distances and bond angles, hydrogen atoms coordinates and isotropic displacement parameters, anisotropic displacement parameters and least-squares plans are available either quoting the deposition number CCDC – 614312 (12 Union Road, Cambridge CB2 1EZ, UK) or from the authors on request.

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