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SYNTHESIS AND CRYSTALLOGRAPHIC CHARACTERIZATION OF NEW HETEROTRINUCLEAR OXO-CENTERED COMPLEX

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ABSTRACT. New oxo-centered trinuclear mixed-metal complex, of $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$ was synthesized by the direct reaction between metal nitrates and dichloroacetic acid. These compounds 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 dichloroacetate ligands fulfil the bridge functions and (c) the monodentate $CHCl_2CO_2$ ligands complete the octahedral geometry of the metal ions. This complex were characterized by elemental analyses (CHN), atomic absorption spectroscopy and spectral (IR, electronic) studies. This is new types of oxo-bridged mixed-metal complex in which the carboxylate ligand is dichloroacetic acid. The UV spectra of the complex exhibited strong bands in the region 213 and 257 nm which are related to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions of the $CHCl_2CO_2$ ligands, respectively. The IR spectra of this compound showed two strong stretching vibrations bands, indicating a bridging coordination mode of the carboxylic group by presence of ν_{asym} ($M_2M'O$) vibrations of the ligand in the infrared spectra.

KEY WORDS: Oxo-centered, Trinuclear complexes, Carboxylic ligand, Crystallographic data, IR spectra

INTRODUCTION

Transition-metal carboxylate chemistry has played a key role in the conceptual development of modern inorganic chemistry [1]. The current interest in the trinuclear, oxo-centered metal carboxylate assemblies of the general composition $[M_3O(OOCR)_6L_3]^+$ (where M = trivalent 3-d metal, RCOO = carboxylic acid (R = CH_3, Ph, etc) L = monodentate ligand) is due to these complexes have served as important models to test theories of magnetic and electronic coupling between metal ions [2, 3]. They are particularly valuable as frame works for systematically studying metal-metal interactions in clusters and constitute an important class of compounds in transition metal chemistry. They have been characterized with a wide variety of first-row and heavier transition metals, with mixed-metal [4] and mixed-valency combinations [5].

Electron transfer interactions, and subtle distortions from regular structures, can be detected by their effects on molecular vibrations. These are valuable precursors for the synthesis of higher nuclearity clusters exhibiting interesting magnetic properties. Surprisingly, little attention has been paid to the consideration of substitution properties, with only a few reports of comparative studies regarding the redox properties when the terminal ligand L changes. There is interest in establishing how substitution in the carboxylate bridge affects the liability of the terminal ligand and the redox potential of the metal centers. These carboxylate complexes are of additional interest when the carboxylate is unsaturated, because there is a potential scope for further polymerization in the solid state by cross-linking of the substituents [6, 7]. Trinuclear μ_3,-oxo-bridged iron carboxylate complexes have been studied in very detail [8, 9], whereas analogous mixed-valence manganese-carboxylate complexes have been the object of only limited investigation to date. Each carboxylate anion spans two metal centers at the periphery of

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*Corresponding author. E-mail: Melika_eftekhar@yahoo.com the $[M_3(\mu_3\text{-}O)]^{6+}$ core, while the neutral monodentate ligands occupy the remaining coordination sites on each metal center, and as a result the coordination around the metal center is approximately octahedral (Figure 1).

In previous studies, we reported fabrication of some trinuclear oxo-centered complexes with saturated and unsaturated carboxylate ligands [10-14]. In this paper, the syntheses and characterization of mixed-valence and mixed-metal clusters are reported. These are, however, limited to clusters coordinated by relatively small organic ligands.

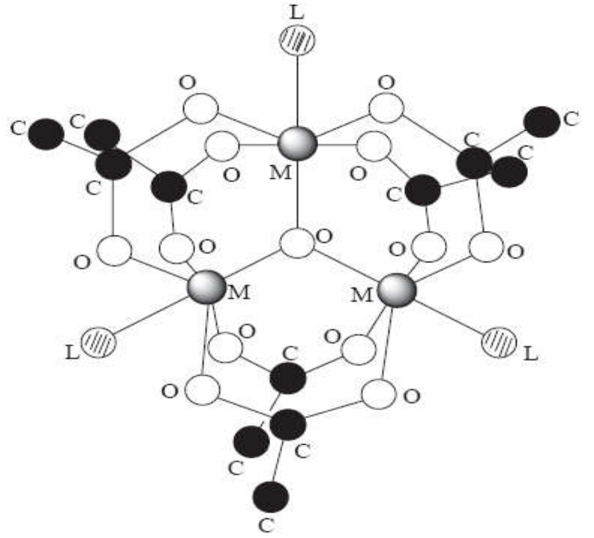

Figure 1. Schematic representation of the oxo-centered trinuclear clusters structure $[M_3O(RCOO)_6(L)_3]^z$.

EXPERIMENTAL

Materials

The C, H and N analyses were realized on a Thermo Finnigan Flash model EA1112 elemental analyzer. The atomic absorption analyses were performed on a Shimadzu model AA-670 atomic absorption spectrometer. The IR spectra of KBr discs (600–4000 cm^{-1}) were recorded on a Buck 500 spectrometer. The electronic spectra were registered in the range of 200–600 nm on a Perkin-Elmer 1600 spectrometer.

Preparation of $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$

A mixture of $Fe(NO_3)_3.9H_2O$ (1.08 g, 2.68 mmol) and $Zn(NO_3)_2.4H_2O$ (0.34 g, 1.34 mmol) was dissolved in 25 mL deionized water and was refluxed for 10 min. Then, $NaCHCl_2CO_2$ (2.22 g, 12 mmol) was added and the reflux continued for 5 h. The resulting brown solution was allowed to cool and stored for 2 days at 20 °C. The black crystals were filtered off, washed copiously with Et_2O and dried in vacuum. (Yield: 85%), m.p.: 275 °C, anal. calc. for $C_{12}H_{12}Cl_{12}Fe_2ZnNO_{22}$: C, 10.89; H, 0.45; N, 1.06; Fe, 8.47; Zn, 4.16%. Found: C, 10.64; H, 0.62; N, 1.14; Fe, 8.85; Zn, 4.39%.

RESULTS AND DISCUSSION

Description of the structure

The asymmetric unit of synthesized complex comprises a single complex anion (total charge 3-: two Fe^{3+} and a Zn^{2+} atom, an oxide dianion and nine dichloroacetate anions) and three pyridinium cations. Metal coordination spheres are slightly deformed octahedra (Table 1); oxygens from four bridging dichloroacetate (DCA) moieties form the equatorial plane, while the axial ligands are a terminal monodentate DCA and the central oxide dianion (Figure 2). The oxide dianion (O19) is coordinated by three metal atoms in a nearly perfect planar arrangement (within experimental error, Figure 2); bond angles are 120.9(2)° (Fe1-O19-Fe2), 119.5(2)° (Fe1-O19-Zn1) and 119.5(2)° (Fe2-O19-Zn1). There are six bridging bidentate and three terminal monodentate DCA moieties, and the entire complex trianion has an approximate molecular symmetry Cs (Figure 3).

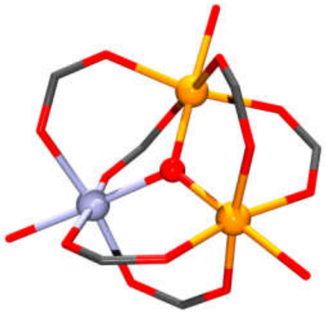

Figure 2. Coordinations of metal atoms and the central oxide dianion in [$Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3$] Dichloromethyl moieties have been omitted for clarity.

Table 1. Geometric parameters of metal coordination spheres.

Zn1		Fe1		Fe2	
Zn1-O19	1.950(4)	Fe1-O19	1.921(4)	Fe2-O19	1.906(3)
Zn1-O4	2.056(4)	Fe1-O6	2.027(4)	Fe2-O10	2.034(4)
Zn1-O1	2.065(4)	Fe1-O5	2.045(4)	Fe2-O11	2.043(4)
Zn1-O3	2.068(4)	Fe1-O7	2.045(4)	Fe2-O12	2.048(5)
Zn1-O2	2.082(4)	Fe1-O9	2.055(4)	Fe2-O8	2.069(4)
Zn1-O13	2.082(4)	Fe1-O15	2.093(4)	Fe2-O17	2.084(3)
O19-Zn1-O4	94.58(16)	O19-Fe1-O6	95.07(17)	O19-Fe2-O10	92.59(16)
O19-Zn1-O1	93.86(16)	O19-Fe1-O5	94.04(17)	O19-Fe2-O11	95.22(16)
O19-Zn1-O3	97.13(17)	O19-Fe1-O7	97.73(17)	O19-Fe2-O12	96.73(16)
O19-Zn1-O2	92.08(16)	O19-Fe1-O9	93.10(17)	O19-Fe2-O8	96.30(16)
O19-Zn1-O13	178.28(16)	O19-Fe1-O15	178.80(16)	O19-Fe2-O17	177.58(19)
O4-Zn1-O1	171.26(16)	O6-Fe1-O5	92.53(16)	O10-Fe2-O11	171.78(14)
O4-Zn1-O3	85.09(16)	O6-Fe1-O7	167.20(18)	O10-Fe2-O12	89.81(18)
O4-Zn1-O2	95.62(17)	O6-Fe1-O9	87.51(15)	O10-Fe2-O8	92.14(17)
O4-Zn1-O13	83.71(16)	O6-Fe1-O15	86.06(16)	O10-Fe2-O17	86.09(15)
O1-Zn1-O3	91.62(15)	O5-Fe1-O7	86.87(16)	O11-Fe2-O12	91.82(18)
O1-Zn1-O2	86.34(15)	O5-Fe1-O9	172.82(18)	O11-Fe2-O8	84.47(17)
O1-Zn1-O13	87.84(16)	O5-Fe1-O15	85.46(16)	O11-Fe2-O17	86.01(15)
O3-Zn1-O2	170.69(16)	O7-Fe1-O9	91.50(15)	O12-Fe2-O8	166.72(14)
O3-Zn1-O13	82.55(16)	O7-Fe1-O15	81.15(16)	O12-Fe2-O17	85.31(15)
O2-Zn1-O13	88.29(16)	O9-Fe1-O15	87.39(16)	O8-Fe2-O17	81.72(15)

The pyridinium cations are tethered to terminal monodentate DCA moieties through N-H···O hydrogen bonds; between such units exist only dispersion interactions.

The single-crystal diffraction measurement was performed on a Siemens SMART three axis goniometer with APEX II area detector system equipped with a liquid-nitrogen cooling device. Bruker AXS APEX 2 Vers. 2.0-2 2006 software was used for data reduction and multi-scan absorption correction. The structure was solved and refined using SHELXTL program implemented in the APEX 2 software; full-matrix least-squares refinement vs. F2 was used. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom. Dichloromethyl groups (atoms C72, Cl5, and Cl6) were disordered over two sites with SOF 0.63; Cl7 and Cl8 were disordered over two sites with respective SOFs 0.91 and 0.66. Crystallographic, measurement and refinement data are shown in Table 2.

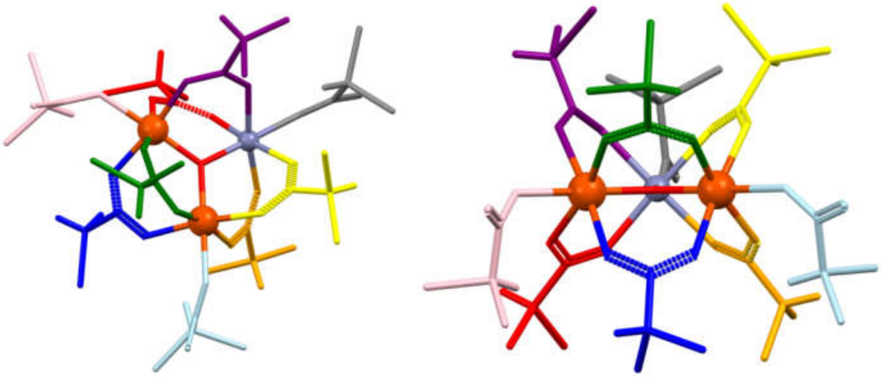

Figure 3. Molecular structure of the complex anion of $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3]$ a) the least-overlap view showing three metal cations bridged by six DCA moieties and an oxide dianion and b) view showing its pseudo-C_2 molecular symmetry. Symmetry-inequivalent dichloroacetate ligands are colour-coded; Fe atoms are shown as dark orange spheres and the Zn atom is shown as a blue-gray sphere.

Figure 4 shows an ORTEP projection of the complex molecule $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$ that crystallize isotopically in the triclinic space group type P1. The crystal structure analysis reveals that this material consists of two iron(III) and one zinc(II) ions are situated at the apexes of the isosceles triangle (Zn(1)—Fe(1) 3.272(1), Zn(1)—Fe(2) 3.274(2), Fe(1)—Fe(2) 3.266(1) Å) and a triply bridging oxygen atom in its center. Two $CHCl_2$-COO- anions, with syn–syn configuration, which bridge the same pair of metal atoms lie on the opposite sides of the Fe_2ZnO plane. Crystal data, and selected bonds lengths and angles are summarized in Table 1. 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 Zn(II) ion in a particular metal site, even though atom Zn has slightly longer M-μ_3-O bond (mean 1.891 Å) than those Fe(III)-μ_3-O (mean 1.875) which may indicate some preference for this location to be occupied by the larger Zn(II) ion, the difference of 0.016 Å is significantly less than would be expected in a fully ordered structure: Zn(II)-μ_3-O bonds are typically 0.1 Å longer than Fe(III)-μ_3-O bonds, and in the $Fe(III)_2Zn(II)$ complex [16] the M-μ_3-O bond distances for the position occupied by the Zn(II) metal exceed with an average value of 0.2 Å, the corresponding distances for the iron(III) positions. Moreover, the three M-O($CHCl_2CO_2$) bonds in **1** are approximately equal (Table 1). 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.

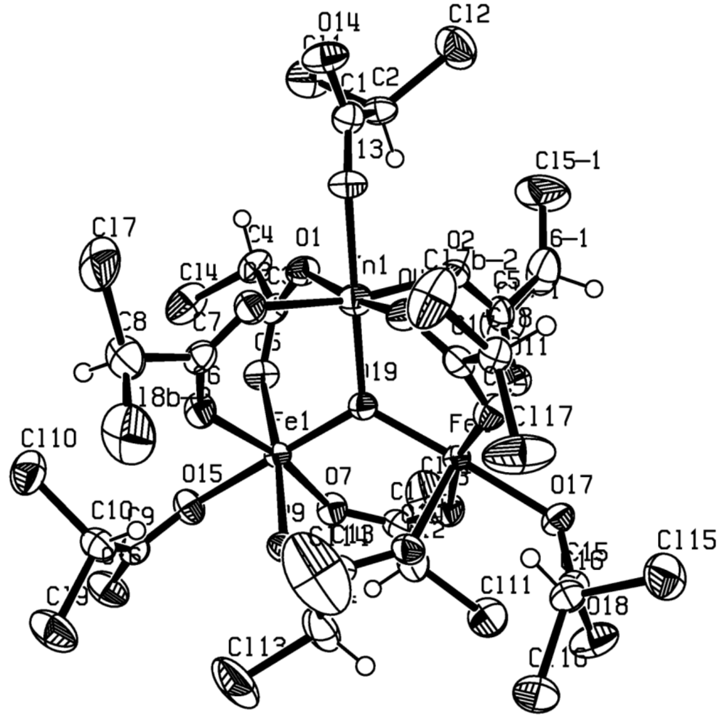

Figure 4. ORTEP-3 drawing of a molecule of [$Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3$].$NO_3$. Only major component of the disorder is shown; displacement ellipsoids are drawn for the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

IR spectroscopy

For the mixed-metal complexes, it appears from the carboxylate stretching frequencies that all six ligands are approximately equivalent and they are best represented as bidentate bridges. For a new series of trinuclear mixed metal complexes, Cannon assigned the IR spectra and identified the vibrational modes of the central M_3O core [17]. He found that the reduction in site geometry from D_3h to C_2v lifted the degeneracy of the asymmetric M_3O stretches and two bands were seen.

Buildings of metal carboxylates according to the type of metal–ligand interaction are presented in Figure 5. 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. This spectrum indicate a single pair of carboxylate stretching vibrations at 1615 and 1430 cm^{-1} for assigned to ν_{asym}(COO) and ν_{sym}(COO), respectively. Since the difference [$\Delta\nu = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] is 185 cm^{-1} for title complex and this value is less than the $\Delta\nu$ value for $NaO_2C_2HCl_2$ (type I) of (~ 200 cm-1), we expect bidentate bridging coordination of carboxylates in this compound [18]. The IR spectrum of this complex is shown in Figure 6 that indicates the presence of carboxylate ligands and $\{M_2MO\}$ groups. The observed vibrational frequencies ν_{asym}(COO) and ν_{sym}(COO) for the carboxylate ligand support the presence of bridging coordinated carboxylates in all the complexes. For identification of the metal-oxygen bonds of M_3O group, IR spectra in the range of 800-400 cm^{-1} were used [19]. The band observed for asymmetric vibration associated with the $M_2M'O$ unit splits into two components, A_1 and B_2 [20]. This spectrum shows the characteristic bands for the valence oscillations $\nu_{as}(Fe_2ZnO)$ in the region 680 cm^{-1} (A_1) and 450 cm^{-1} (B_2). All data of IR spectroscopy for this compound are given in Table 3.

Table 2. Crystallorgraphic, measurement and structure refinement data.

Empirical formula	$C_{33}H_{24}N_3Cl_{18}Fe_2O_{19}Zn$
M_r / g mol^{-1}	1581.72
D_{calc} / g cm^{-3}	1.842
F(000)	1566
T / K	203(2)
Crystal size / mm	0.26 x 0.21 x 0.08
Crystal colour	brown
Crystal description	plate
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
a / Å	12.0183(6)
b / Å	15.4721(7)
c / Å	17.3879(8)
α / °	70.949(2)
β / °	88.423(2)
γ / °	69.662(2)
V / $Å^3$	2852.1(2)
Z	2
Cell measurement reflections used	9807
θ_{min}, θ_{max} / °	2.24 - 24.66
Completeness (to θ = 24.95°)	98.0 %
h, k, l range	$-14 < h < 14$, $-18 < k < 18$, $-20 < l < 20$
Absorption coefficient / mm^{-1}	1.831
T_{min}, T_{max}	0.7340, 0.6474
R(merg) before/after correction	0.0769 / 0.0500
Reflections measured	71525
Independent reflections	9792 [R(int) = 0.0544]
Observed reflections	8994
Data / restraints / parameters	8994 / 0 / 729
Goodness-of-fit on F^2	1.135
Weighting scheme	$w = 1/[\sigma^2 (F_o^2) + (0.0377*P)^2 + 14.8218*P]$ where $P = (F_o^2 + 2F_c^2)/3$
Final R indices [I>σ(I)]	$R1 = 0.0638$, $wR2 = 0.1383$
R indices (all data)	$R1 = 0.0705$, $wR2 = 0.1417$
Extinction coefficient	0.0016(2)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / $eÅ^{-3}$	0.627; -1.158

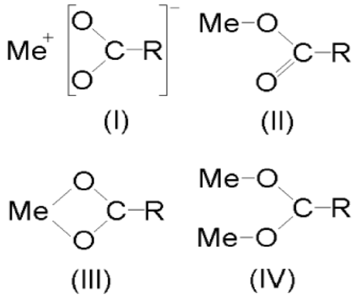

Figure 5. Structure of metal carboxylates according to the type of metal–ligand interaction. (I) Ionic or uncoordinated form, (II) unidentate coordination, (III) bidentate chelating coordination, and (IV) bidentate bridging coordination.

Table 3. Selected IR bands (cm^{-1}) for the complex.

Assignments						
ν (O-H)	ν_{asy} (CH)	ν_{asy} COO)^a	ν_{sy} (COO)^a	δ (CH_3)^a	ν (C-CH_3)^b	ρ_r (CH_3)^{a,b}
3520	2970	1615	1430	1375	1298	1080
π (CH_3)^b	ν (C-CO_2)^c	δ (OCO)^{a,d}	γ(COO)^{a,d}	ν_{asy} (Fe_2ZnO)^d	π (Fe_2ZnO)^c	
1015	812	654	611	680(A_1), 450(B_2)	329	

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

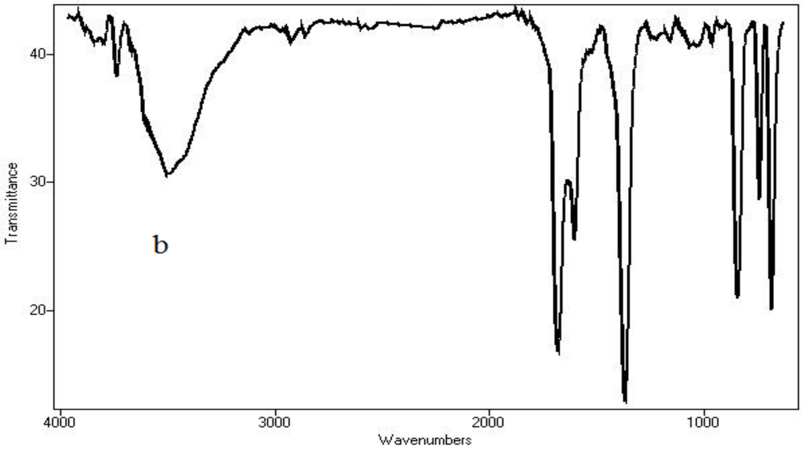

Figure 6. IR spectra of $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$ (KBr pellet).

Electronic spectroscopy

The electronic spectrum of the trinuclear complex can be interpreted to a good approximation in terms of the individual metal ions, together with ligand-metal charge transfer transitions. The electronic spectrum of the complex was recorded in the range of 200-600 nm in dichloromethane solution. The spectrum of the oxo-centered complex shows the characteristic bands provided by both metal ions. The UV spectrum of the complex (Figure 7) exhibited a strong bands in the 213 nm which is related to the (n → π^*) transition of the carboxylate ligand.

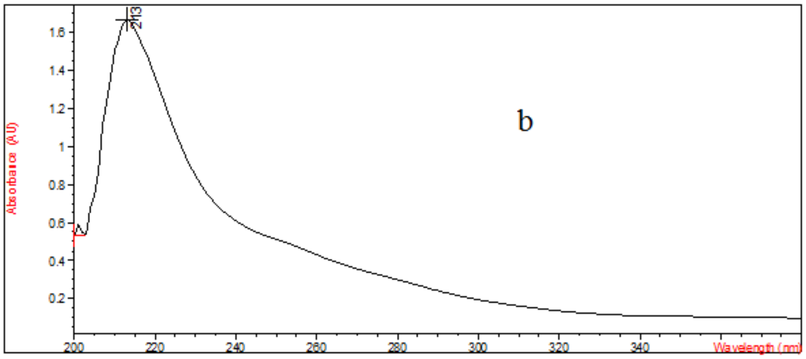

Figure 7. UV spectra of the $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$ (b)

The Vis spectrum for this complex is shown in Figure 8. As is obvious in this Figure, broad band in the region 480 nm, which can be assigned to the transition from Eg to T_2g, should be attributed to the existence of $Zn^{(II)}$ (d^{10}) ion in these complexes. Obtained data can be assigned and characterized based on other literature [21].

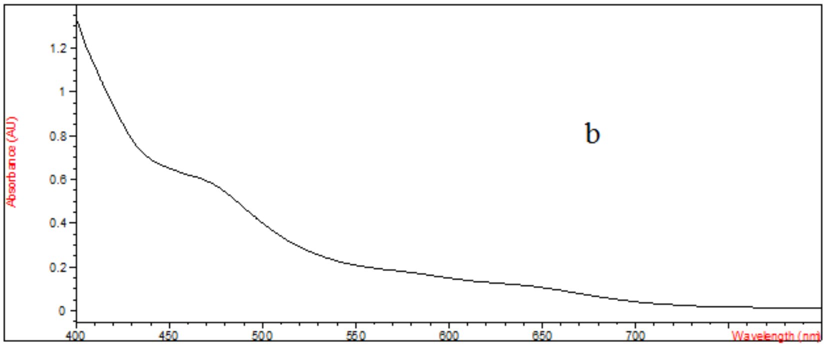

Figure 8. Vis spectra of the $[Fe_2ZnO(CHCl_2CO_2)_6(CHCl_2CO_2)_3].NO_3$.

CONCLUSION

The new oxo-centered trinuclear complex with the general formula $[M_2M'O(CHCl_2COO)_6(L)_3]$ where M = Fe, M' = Zn, L = $CHCl_2CO_2$ (**2**) were prepared and studied by elemental analysis (CHN), electronic and infrared spectroscopy and atomic absorption spectroscopy. The compound has a similar μ_3-oxo structure. The IR investigations of these compounds show intensive absorption bands, which are assigned to ν_{asym}(COO) and ν_{sym}(COO) vibrations. Furthermore, the three metal ions are bound to a central oxygen atom and adjacent metal ions are bridged by two carboxylate ligands. In addition, for mixed metal complex, the atomic absorption data show a statistical 2:1 disorder of iron and manganese atoms, respectively.

ACKNOWLEDGEMENTS

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