

SYNTHESIS AND CHARACTERIZATION OF NEW Mn (II, III) AND Fe(III) OXO POLYNUCLEAR COMPLEXES

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Lucrarea prezintă sinteza și caracterizarea unor noi oxo-complecși polinucleari ai Mn (II, III) and Fe (III): $[Mn_6O_2(CH_3CO_2)_{10}(CH_3CO_2H)_4]$, $[Fe_3O(CH_3CO_2)_6(bpy)_3]Cl$, $[Mn_3O(CH_3CO_2)_6(bpy)_2(CH_3COOH)]$. Formulele structurale sunt propuse pe baza analizei elementale, a măsurătorilor conductivității electrice molare, a spectrelor electronice și FTIR. Valorile momentelor magnetice indică proprietăți antiferomagnetice ale complexelor. Analizele electrochimice subliniază proprietățile redox ale complexelor.

This paper deals with the synthesis and characterization of new Mn (II, III) and Fe (III) oxo-polynuclear complexes: $[Mn_6O_2(CH_3CO_2)_{10}(CH_3CO_2H)_4]$, $[Fe_3O(CH_3CO_2)_6(bpy)_3]Cl$, $[Mn_3O(CH_3CO_2)_6(bpy)_2(CH_3COOH)]$. Structural formulae of the complexes are proposed on the basis of elemental chemical analysis, molar conductivity measurements, electronic and FTIR spectra. The values of magnetic momenta sustain the antiferromagnetic properties of the complexes. Electrochemical analysis underlines the redox properties of the compounds.

Keywords: Mn (II, III) and Fe (III) oxo-polynuclear complexes, 2,2'-bipyridine, acetic acid, magnetic susceptibility, FTIR spectra, electrochemical analysis.

1. Introduction

Trinuclear oxo-centered complex compounds of the general structure $[M_3(\mu_3-O)(\mu_2-O_2CR)_6(L)_3]^{0(+1)}$ where M= Mn (II, III), Fe (III), Cr (III) etc., R= methyl, phenyl etc. and L= pyridine, phenanthroline etc. have been intensively studied since the first structure was determined in 1965. The importance of these complexes is determined by their magnetic and biomimetic properties [1-8]. Also, they serve as excellent starting materials to make higher nuclearity clusters. Oxo complexes have antiferromagnetic properties and are models to test magnetic coupling between metal ions in multinuclear system [1]. Oxo polynuclear complexes can be used as single molecule magnets which offer a molecular

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approach to nanoscale magnetic materials [2]. They are used as in “vitro” models of some important Mn enzymes. For example photosynthetic oxygen production from water is catalyzed by photosynthetic water oxidase, a tetranuclear manganese enzyme from plant and algae [3].

Catalase enzymes contain binuclear oxo manganese motifs and are found mainly in thermophilic and heme deficient bacteria. These enzymes protect the organisms from oxidative stress by maintaining the level of hydrogen peroxide in cells. Thus catalase converts hydrogen peroxide in less harmful compounds, oxygen and water through a redox mechanism. Other examples of enzymes with oxo type sites are arginase, xylose isomerase, ribonucleotide reductase [6]. Polynuclear oxo-centered complexes of transitional metals like Mn, Cr [8], Fe [3, 8-10], Zn etc. using as ligands water [10-12], pyridine, carboxylic acids [1-14], triethanolamine, 1,3,5-cyclohexanetriol [14] etc. were studied. This paper presents the synthesis and characterization of new Mn (II, III) and Fe (III) oxo polynuclear complexes.

2. Experimental

Anhydrous MnCO_3 , FeCl_3 , KMnO_4 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, glacial acetic acid, 2,2'-bipyridine, toluene, ethanol were from Fluka and used as received.

Preparation of $[\text{Mn}_6\text{O}_2(\text{CH}_3\text{CO}_2)_{10}(\text{CH}_3\text{CO}_2\text{H})_4]$ (**1**): 5.7 g MnCO_3 (0.05 moles) and 6 g (0.1 moles) CH_3COOH were added in 60 mL toluene. The mixture was kept under reflux (48 h) resulting a black precipitate which was filtered, washed with hexane and dried in air. IR spectrum (cm^{-1}): 3243; 1708; 1562; 1418; 656; 630; 618; 596; 579; 565; 547; 532; 511; 497; 475; 447; 429; 420; 410; 401;

Preparation of $[\text{Fe}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_3]\text{Cl}$ (**2**): 0.37 g 2,2'-bipyridine (2.5 mmol) and 0.4 mL (6.7 mmol) CH_3COOH were dissolved in 30 mL ethanol and 0.405 g (2.5 mmol) FeCl_3 were added. The mixture was heated at 90°C for 2.5 h and a red brown precipitate was obtained. The precipitate was filtered, washed with ethanol and dried in air. IR spectrum (cm^{-1}): 3360; 3107; 3079; 3062; 2361; 2340; 1635; 1607; 1598; 1574; 1494; 1470; 1440; 1313; 1245; 1215; 1173; 1156; 1104; 1064; 1043; 1024; 807; 764; 728; 653; 634.

Preparation of $[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_2(\text{CH}_3\text{CO}_2\text{H})]$ (**3**): 0.24 g (1.5 mmol) 2,2'-bipyridine, 0.3 mL (0.05 moles) CH_3COOH were dissolved in 10 mL water. 0.07 g (0.35 mmol) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.02 g (0.128 mmol) KMnO_4 were added. The mixture was stirred for 2h and left at room temperature for 2 days. The brown precipitate was washed with hexane and dried in air. IR spectrum (cm^{-1}): 3385; 3095; 3060; 1721; 1591; 1572; 1557; 1495; 1470; 1435; 1418; 1379; 1339; 1327; 1311; 1247; 1173; 1150; 1096; 1072; 1056; 1033; 1010; 910; 820; 773; 756; 733; 664; 651; 642; 619.

The compounds obtained were characterized by elemental analysis: Mn, Fe and Cl by gravimetical methods, N by micro-Dumas combustion and C by Pregl method. The electronic spectra were recorded on a Jasco V-560 Spectrophotometer. The infrared spectra were recorded on Bruker, EQUINOX55 spectrometers using KBr pellets in the region 4000-400 cm^{-1} . Electrical molar conductivities were measured in N,N-dimethylformamide (10^{-3} M solution) on OK-114 RADELKIS Conductometer at 25 $^{\circ}$ C.

Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) electrochemical experiments were conducted using a PGSTAT 12 AUTOLAB in a conventional three-electrode cell under argon atmosphere at 25 $^{\circ}$ C. The working electrode was a glassy carbon disk (2 mm in diameter) polished with 200 μm diamond paste. The Ag/10 mM AgNO_3 , 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in CH_3CN was used as reference electrode. All potentials were referred to the potential of ferrocene/ferricinium (Fc/Fc^+) couple, which in our experimental conditions was 0.0635 V. The CV curves were obtained regularly at 0.1 V/s and at different scan rates (0.1-10 V/s) when the influence of the scan rate was investigated. DPV curves were recorded at 10 mV/s. Magnetic susceptibility measurement was performed by Faraday method, at 24 $^{\circ}$ C using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

3. Results and discussion

In this paper are described the synthesis of new Mn (II, III) and Fe (III) oxo polynuclear complexes starting from:

- 1 - MnCO_3 , CH_3COOH , toluene (solvent)
- 2 - FeCl_3 , CH_3COOH , bipyridyl, ethanol (solvent)
- 3 - $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, CH_3COOH , bipyridyl, KMnO_4 , water (solvent)

In Table 1 are presented the characteristics of the complexes **1**, **2** and **3**: elemental analysis, conductivity and colour. Intensively colored complexes with a good matching with the predicted formula were obtained. From electrical molar conductivity data we can conclude that compound **2** is electrolyte of 1:1 type and the complexes **1** and **3** are non-electrolytes.

Table 1

Probe	Elemental analysis								Λ ($\mu\text{S}/\text{cm}$)	Colour
	M(Fe,Mn) %		C%		N%		Cl%			
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found		
1[*]	27.68	27.71	28.19	28.22	-	-	-	-	12	Black
2^{**}	16.13	16.11	48.39	48.4	8.06	8.01	3.41	3.43	75	Brown-red
3^{***}	18.19	17.8	44.98	44.5	6.17	6.25	-	-	33	Brown

* calculated according to the formulae $[\text{Mn}_6\text{O}_2(\text{CH}_3\text{CO}_2)_{10}(\text{CH}_3\text{CO}_2\text{H})_4]$

** calculated according to the formulae $[\text{Fe}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_3]\text{Cl}$

*** calculated according to the formulae $[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_2(\text{CH}_3\text{COOH})]$

Table 2 contains magnetic susceptibility data and calculated magnetic momentum. The obtained compounds have paramagnetic properties; the experimental values obtained for the complexes **1**, **2** and **3** are smaller than the calculated ones revealing their antiferromagnetic properties.

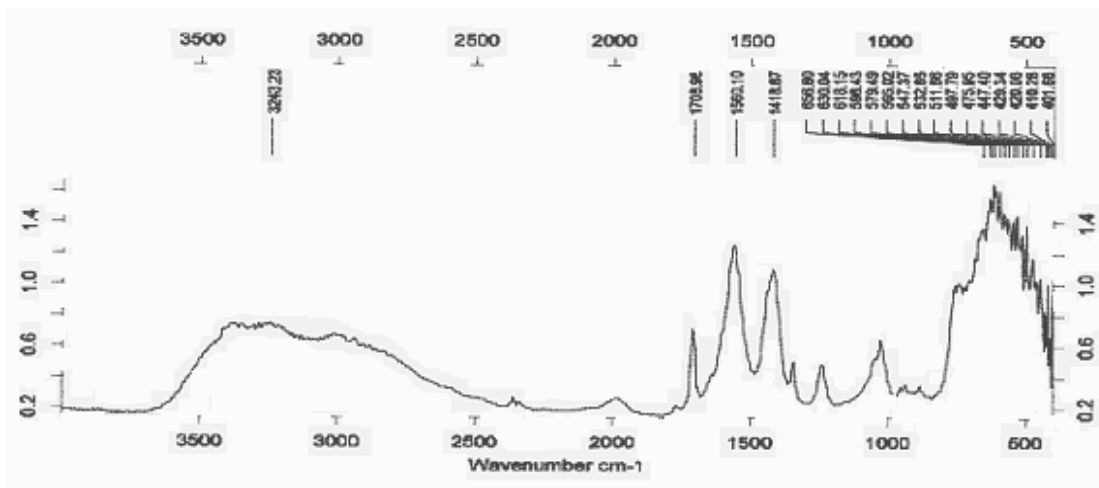
Table 2

Probe	Magnetic susceptibility $10^6 \chi_g [\text{cm}^3/\text{g}]$	Magnetic moment [*] μ_B	Theoretical magnetic moment ^{**} μ_B
1	39.5	11	29
2	40.2	10	16
3	18.5	6.5	15

^{*}Calculated with formulae $\mu = 2.82 \cdot (\chi_g \cdot T)^{0.5}$

^{**}Calculated with formulae $\mu = g \cdot [S \cdot (S+1)]^{0.5}$, where $S = n/2$, n = number of uncoupled electrons

Fig.1 shows the IR spectrum of **1**. The signals from 1708 cm^{-1} , 1562 cm^{-1} , 1418 cm^{-1} can be assigned to the bonding between Mn and carboxylic group (from acetic acid) – vibration modes $\nu_{\text{C-O-Mn}}$ (monodentate), $\nu_{\text{asym C-O-Mn}}$ (bidentate), $\nu_{\text{sym C-O-Mn}}$ (bidentate) respectively. Between $547\text{-}656 \text{ cm}^{-1}$ signals characteristic for the Mn-O vibration appear.

Fig.1. IR spectrum of **1**

From the IR spectrum of **2** (Fig.2) several relevant signals for the structure of **2** can be distinguished. The signal from 3107 cm^{-1} can be assigned to the vibration of group $\nu_{\text{C-H}}$. The signals from 1607 cm^{-1} , 1494 cm^{-1} ($\nu_{\text{C=N}}$), 1313 cm^{-1} , 1245 cm^{-1} (ω_{bpy}), 1024 cm^{-1} (Γ_{bpy}) attests the presence of bipyridyl ring. The

signals from 1598 cm^{-1} (ν_{asym} C-O-Fe (bidentate)), 1440 cm^{-1} (ν_{sym} C-O-Fe (bidentate)) are attributed to the bond formed between Fe and carboxylic group (from acetic acid).

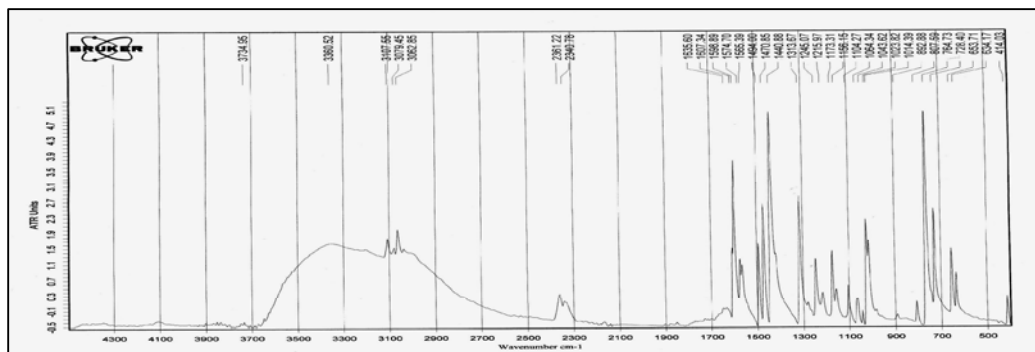


Fig. 2. IR spectrum of **2**

From the IR spectrum of **3** (fig.3) several signals can be distinguished. The signal from 3095 cm^{-1} belongs to $\nu_{\text{C-H}}$. The presence of bipyridyl ring is confirmed by the signals from 1591 cm^{-1} , 1495 cm^{-1} ($\nu_{\text{C=N}}$), 1311 cm^{-1} , 1247 cm^{-1} (ω_{bpy}), 1010 cm^{-1} (Γ_{bpy}). The signals from 1721 cm^{-1} , 1557 cm^{-1} , 1418 cm^{-1} can be assigned to the bonding between Mn and carboxylic group (from acetic acid) – vibration modes $\nu_{\text{C-O-Mn}}$ (monodentate), ν_{asym} C-O-Mn (bidentate), ν_{sym} C-O-Mn (bidentate) respectively. Between $619 - 773\text{ cm}^{-1}$ signals characteristic for the Mn-O vibration appear.

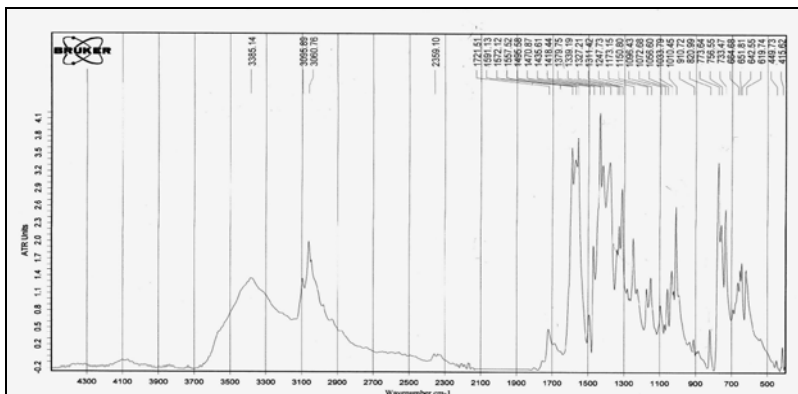


Fig.3. IR spectrum of **3**

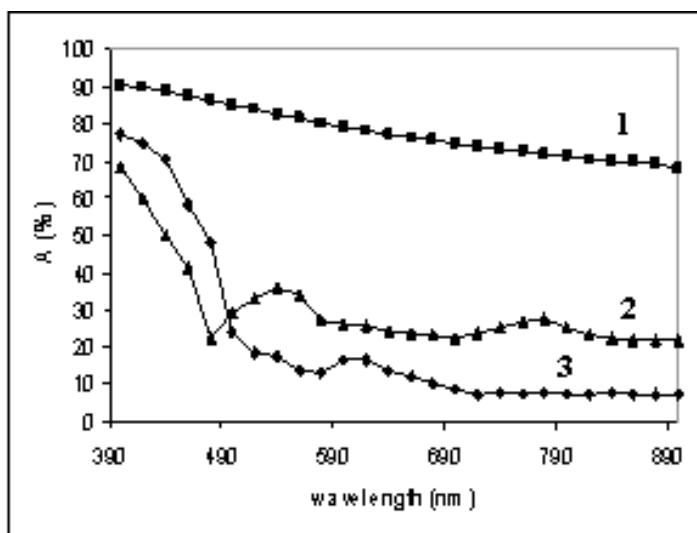
The bands from UV-VIS spectrum for **1** can be assigned to carboxylate group (210 nm) and strong charge transfer between ligand and metal (385 nm).

The assignment of the bands from UV-VIS spectrum for **2** are shown in Table 3.

Table 3

Transition	Wavenumber (cm ⁻¹)
${}^6A_{2g} - {}^4T_{1g}$	12660 (790 nm)
${}^6A_{2g} - {}^4T_{2g}$	18180 (550 nm)
C.T. (charge transfer)	24900 (402 nm)

The bands from UV spectrum for compound **3** can be assigned to six coordinated Mn(III) at 620 nm (${}^5T_{2g} - {}^5E_g$), Mn(II) at 530 nm (${}^4A_{1g} - {}^4T_{1g}$) with Oh symmetry and the presence of the large band at 400 nm is due to intense charge transfer from metal to ligand (fig.4).

Fig.4. UV-VIS spectrum for **1**, **2** and **3**

The results obtained from electrochemical studies (CV and DPV) are presented in Fig. 5 for compound **3**. The DPV curves allow to see two main anodic processes (1a and 2a in Fig. 5A) and 6 cathodic processes (1c-6c). The processes 1a and 2a are reversible while the cathodic processes are cvasi-reversible. The first anodic process has currents linearly dependent on the square root of the scan rate (Fig. 5D, E).

Based on experimental data exhibited we propose structural formula for compounds **1**, **2**, **3**. For oxo compound **1** the proposed structure consists of two MnO_4 tetrahedra sharing an edge formed by two inner manganese atoms. There are two types of coordinated carboxylates-10 bridging carboxylates; -4 monodentate carboxylates (Fig. 6).

For oxo compound **2** the proposed structure is shown in Fig. 7. The ligands are symmetrically bonded to the Fe (III).

The proposed structure of **3** is presented in Fig. 8. A monodentate carboxylate group can be noticed in the formulae (it's existence being proved by IR data).

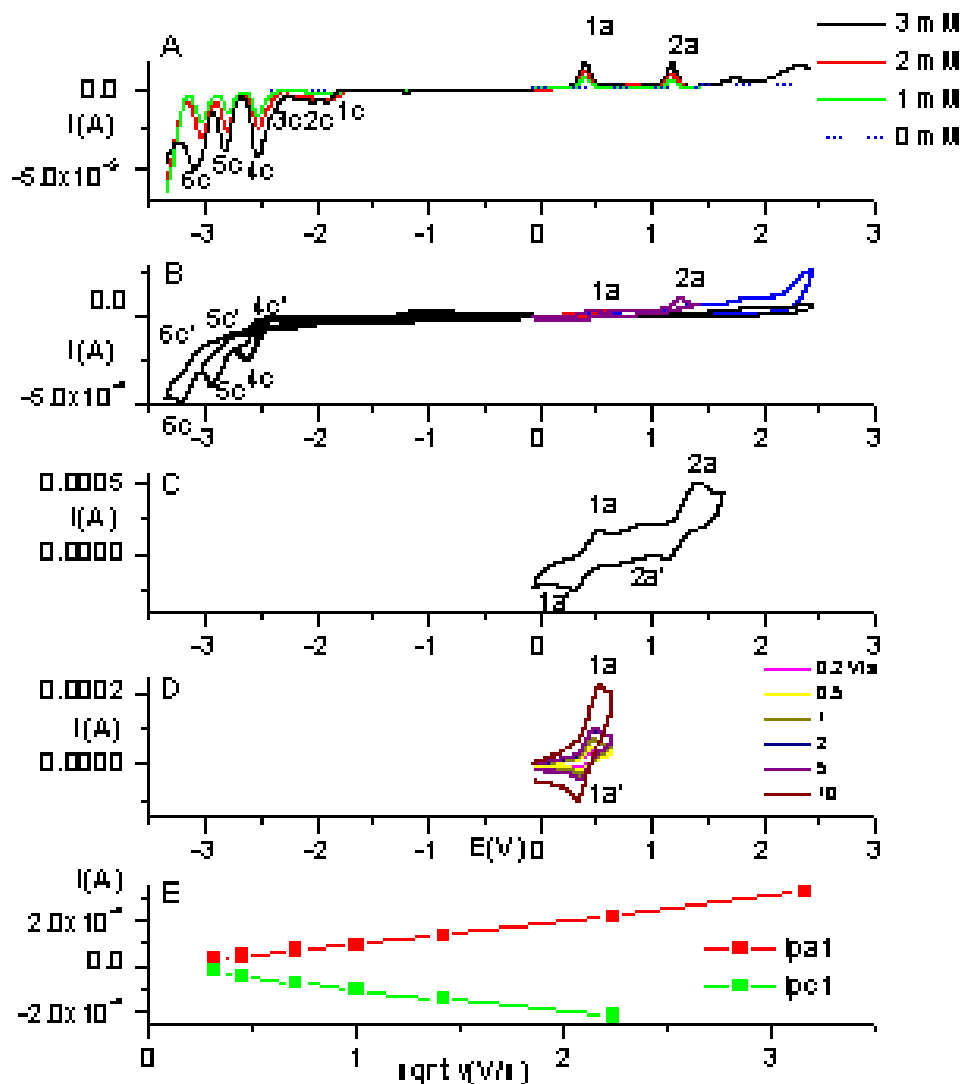


Fig.5. Electrochemical data from DPV (A) and CV (B-E) on different scan domains for different concentrations of the oxo-complex **3**; in B-E [**3**] = 1 mM; the scan rate is variable in D and 0.1 V/s in B; in C and E the scan rate is 10 V/s.

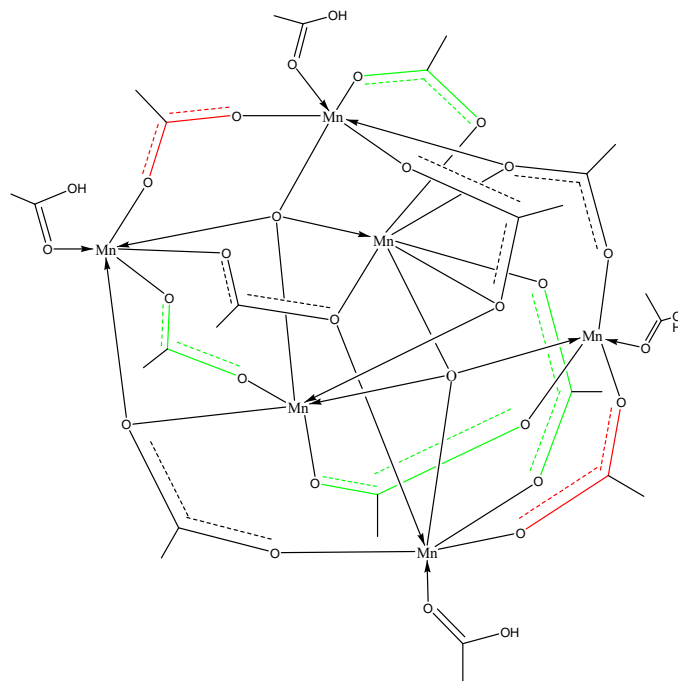


Fig.6. Proposed structural formulae for compound **1**, $[\text{Mn}_6\text{O}_2(\text{CH}_3\text{CO}_2)_{10}(\text{CH}_3\text{CO}_2\text{H})_4]$

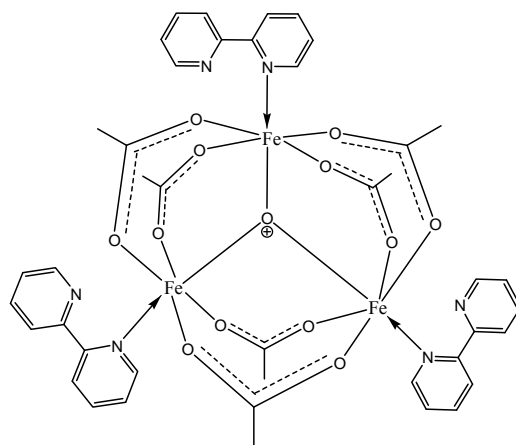


Fig.7. Proposed structural formulae for compound **2**, $[\text{Fe}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_3]^+$

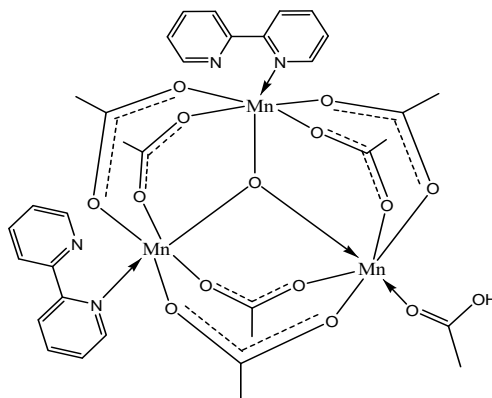


Fig.8. Proposed structural formulae for compound **3**, $[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{bpy})_2(\text{CH}_3\text{COOH})]$

4. Conclusions

Two new manganese and one new iron oxo polynuclear complex compounds have been synthesized in the paper. Complexes have antiferromagnetic properties. The proposed structural formula for these complexes are sustained by electronic and FTIR spectra, molar conductivity and voltammetric data.

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