

The properties of the new Mn(II)–Co(II)–Mn(II)-type hetero-trinuclear oxime metal complexes with N₄ and N₄O₂ ligands

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Abstract The novel one N₄ and two N₄O₂ containing hetero-trinuclear oxime metal complexes, [Co(L)₂(H₂O)₂Mn₂(dafo)₄](ClO₄)₂ (**1**), [Co(L)₂(H₂O)₂Mn₂(dafdione)₄](ClO₄)₂ (**2**), [Co(L)₂(H₂O)₂Mn₂(dcbpy)₄](ClO₄)₂ (**3**) and [Co(L)₂(H₂O)₂Mn₂(phen)₄](ClO₄)₂ (**4**), (where, L = *N,N'*-bis(ethyl-4-amino-1-piperidine carboxylate)-glyoxime, dafo = 4,5-diazafluoren-9-one, dafdione = 1H-cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione, dcbpy = 3,3'-dicarboxy-2,2'-bipyridine and phen = 1,10-phenanthroline) have been synthesized and characterized by UV–Vis, FT-IR spectra, magnetic susceptibility measurements, molar conductivity, X-ray powder techniques, mass spectra and their morphology studied by SEM measurements. The H-bonding (O–H···O) in the Mn(II)–Co(II)–Mn(II)-type hetero-trinuclear oxime metal complexes disappears, the Co(II) ion centered into the main oxime core by the coordination of the imino groups while the two Mn(II) ions coordinated to dianionic oxygen donors of the oxime groups and linked to the ligands of dafo, dafdione, dcbpy and phen.

Keywords Hetero-trinuclear metal complexes · Scanning electron microscopy (SEM) · XRD powder measurements

Introduction

The chemistry of oxime/oximate metal complexes has been widely investigated since the time of their first synthesis, e.g. preparation of nickel(II) dimethylglyoximate and recognition of the chelate five-membered character of this complex by Chugaev [1]. Extensive studies of cobaltoximes beginning in the 1960s made use of Co(DMGH)₂ as a substitute for the naturally occurring cobalt core ring system [2, 3]. Vic-dioximes have received considerable attention as model compounds due to the fact that they mimic bio-functions such as reduction of vitamin B₁₂ [4]. Coordination chemistry of the oxime ligands has been extensively studied with the 3d metal ions [5–7]. The oxime-imines represent an important class of ligands capable of to stabilize the higher oxidation states of the central metal ion through strong ligand to metal (L → M) σ -donation. The tetradentate vic-dioxime ligands behave similarly by enveloping themselves around metal ions in a planar geometry, forming a hydrogen bond between two oxime groups by removing one hydrogen ion. The strength of the hydrogen bond between the two oxime groups, which is represented by the O–O distance, depends on the size of the metal ions and chemical environment around the metal ions. The oxidation states of the central metals, number of donor atoms and core structures of the complexes are major factors in determining structure–function relations of the transition metal complexes [8]. The nature of the ligands around the metal has been found to dramatically affect the energy conversion process. Particularly, the introduction of electronic effects via electron-donor substituents on 4,5-diazafluoren-9-one (dafo), 1H-cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione (dafdione), 3,3'-dicarboxy-2,2'-bipyridine (dcbpy) and 1,10-phenanthroline (phen) ligands notably improved the absorption in the visible region for efficient sunlight collection [9–11].

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In the present study, we have prepared novel trinuclear Mn(II)–Co(II)–Mn(II)-type metal complexes. The metal complexes have been identified by combination of FT-IR spectra, UV–Vis spectra, magnetic susceptibility measurements, mass spectra, X-ray powder diffraction measurements, elemental analysis, molar conductivity measurements and their morphology studied by SEM measurements. The aim of this study is to prepare and characterize new different trinuclear metal–oxime complexes and then understand the structural properties of the coordination of different groups such as 4,5-diazafluoren-9-one (dafo), 1H-cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione (dafdione), 3,3'-dicarboxy-2,2'-bipyridine (dcbpy) and 1,10-phenanthroline (phen) to the oxime moieties through two oxygen donor atoms and also understand their crystalline or amorphous structures by X-ray powder analysis and SEM images.

Experimental

Materials and physical measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers (Fluka). The C, H, N elemental analyses were performed on a LECO CHNS-932 model analyzer. IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer as KBr pellets. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (25 °C) using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constants [12, 13]. UV–Vis spectra were recorded on a Perkin Elmer Lambda 25 PC UV–Vis spectrometer. Molar conductivities (Λ_M) were recorded on a Inolab Terminal 740 WTW Series. MS results were recorded on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. X-ray powder analyses were recorded on a Rigaku Ultima III Series. The scanning electron microscopy (SEM) measurements were carried out on a Zeiss Series. The samples were sputter coated with carbon by Balzers Med 010 to prevent charging when analyzed by the electron beam. The complex [Co(LH)₂(H₂O)₂] [14], 4,5-Diazafluoren-9-one (dafo) [15], 1H-Cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione (dafdione) [16, 17], and 3,3'-dicarboxy-2,2'-bipyridine (dcbpy) [18] were prepared according to the literature procedures.

Synthesis of the mononuclear Co(II) complex

We have previously reported the synthesis of mononuclear Co(II) complex [14]. For a detailed comparison with mononuclear Co(II) complex and trinuclear metal

complexes, the analytical data of mononuclear Co(II) complex including IR, UV–Vis, elemental analysis etc. were given below. Yield: (56%), Color: Brown, m.p. = 193 °C. Anal. Calcd. for C₃₆H₆₆N₁₂O₁₄Co (MW: 949 g/mol): C, 45.50; H, 6.95; N, 17.70. Found: C, 45.30; H, 6.70; N, 17.50, μ_{eff} = 3.96 B.M, IR (KBr pellets, ν_{max} , cm⁻¹): 3623–3042 ν (OH/NH), 2983–2871 ν (Aliph-H), 1733 ν (O–H...O), 1675 ν (C=O), 1645 ν (C=N), 1355 ν (N–O). UV–Vis (λ_{max} , nm): 236, 263, 317, 456, 642 (in DMF).

Synthesis of the trinuclear metal complexes

The complexes [Co(L)₂(H₂O)₂Mn₂(dafo)₄](ClO₄)₂ (**1**), [Co(L)₂(H₂O)₂Mn₂(dafdione)₄](ClO₄)₂ (**2**), [Co(L)₂(H₂O)₂Mn₂(dcbpy)₄](ClO₄)₂ (**3**) and [Co(L)₂(H₂O)₂Mn₂(phen)₄](ClO₄)₂ (**4**) (where, L = *N,N'*-bis(ethyl-4-amino-1-piperidine carboxylate)-glyoxime, dafo = 4,5-diazafluoren-9-one, dafdione = 1H-Cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione, dcbpy = 3,3'-dicarboxy-2,2'-bipyridine and phen = 1,10-phenanthroline) were synthesized. As follows the mononuclear cobalt complex [Co(LH)₂(H₂O)₂] (0.05 g, 5.27 × 10⁻⁵ mmol) was added to Et₃N (0.20 mmol) in ethanol-DMF mixture (70:5 mL) and the mixture was stirred for 2 h. Mn(ClO₄)₂·6H₂O (0.04 g, 1.05 × 10⁻⁴ mmol) in absolute ethanol (20 mL) and 4,5-diazafluoren-9-one (0.04 g, 2.11 × 10⁻⁴ mmol), 1H-cyclopenta[1,2-b:5,4-*b'*]dipyridine-2,5-dione (0.04 g, 2.11 × 10⁻⁴ mmol), 3,3'-dicarboxy-2,2'-bipyridine (0.05 g, 2.11 × 10⁻⁴ mmol), or 1,10-phenanthroline monohydrate (0.04 g, 2.11 × 10⁻⁴ mmol), in absolute ethanol (25 mL) were successively added to the resulting mixture, which was boiled under reflux for 14–16 h. The dark brown product was filtered, washed with EtOH, MeOH and Et₂O respectively, then dried in vacuo at 40 °C.

[Co(L)₂(H₂O)₂Mn₂(dafo)₄](ClO₄)₂ (**1**): Yield: (64%), Color: Dark-Red, m.p. >300 °C. Anal. Calcd. for C₈₀H₈₈N₂₀O₂₆Cl₂CoMn₂ (MW: 1984 g/mol): C, 48.40; H, 4.47; N, 14.11. Found: C, 48.21; H, 4.58; N, 13.98. Λ_M = 197 Ω^{-1} cm²/mol, μ_{eff} = 5.16 B.M, IR (KBr pellets, ν_{max} , cm⁻¹): 3635–3155 ν (OH/NH), 3090–3012 ν (Ar-H), 2918–2835 ν (Aliph-H), 1722 ν (C=O), 1632 ν (C=N), 1355 ν (N–O), 1085 and 625 ν (ClO₄), 515 ν (Co–N), 482 ν (Mn–N) and 471 ν (Mn–O). UV–Vis (λ_{max} , nm): 271, 304, 317, 356, 657 (in DMF). MS (LSI, Scan ES⁺): *m/z* (%) 1985 (8) [M + 1]⁺, 1910 (35), 1864 (54), 1554 (42), 1429 (100), 1302 (50) and 1227 (70).

[Co(L)₂(H₂O)₂Mn₂(dafdione)₄](ClO₄)₂ (**2**): Yield: (60%), Color: Brown, m.p. 287 °C. Anal. Calcd. for C₈₀H₈₄N₂₀O₃₀Cl₂CoMn₂ (MW: 2043 g/mol): C, 46.98; H, 4.14; N, 13.70. Found: C, 46.54; H, 4.36; N, 13.67. Λ_M = 206 Ω^{-1} cm²/mol, μ_{eff} = 4.59 B.M, IR (KBr pellets, ν_{max} , cm⁻¹): 3629–3220 ν (OH/NH), 3096 ν (Ar-H), 2983–2854 ν (Aliph-H), 1714 ν (C=O), 1603 ν (C=N), 1375

and 971 $\nu(\text{N-O})$, 1067 and 626 $\nu(\text{ClO}_4)$, 538 $\nu(\text{Co-N})$, 486 $\nu(\text{Mn-N})$ and 471 $\nu(\text{Mn-O})$. UV-Vis (λ_{max} , nm, * = shoulder peak): 269, 287*, 344, 360, 440 (in DMF).

[Co(L)₂(H₂O)₂Mn₂(dcbpy)₄](ClO₄)₂ (3): Yield: (62%), Color: Brown, m.p. >300 °C. Anal. Calcd. for C₈₄H₉₆N₂₀O₃₈Cl₂CoMn₂ (MW: 2231 g/mol): C, 45.17; H, 4.33; N, 12.54. Found: C, 45.22; H, 4.29; N, 12.47. $\Lambda_{\text{M}} = 208 \Omega^{-1} \text{cm}^2/\text{mol}$, $\mu_{\text{eff}} = 4.72$ B.M. IR (KBr pellets, ν_{max} , cm⁻¹): 3495 $\nu(\text{OH})$, 3392 $\nu(\text{NH})$, 3061 $\nu(\text{Ar-H})$, 2977–2865 $\nu(\text{Aliph-H})$, 1716 $\nu(\text{C=O})$, 1609 $\nu(\text{C=N})$, 1395 and 988 $\nu(\text{N-O})$, 1064 and 627 $\nu(\text{ClO}_4)$, 542 $\nu(\text{Co-N})$, 482 $\nu(\text{Mn-N})$ and 468 $\nu(\text{Mn-O})$. UV-Vis (λ_{max} , nm, * = shoulder peak): 270, 337, 441* (in DMF). MS (LSI, Scan ES⁺): m/z (%) 2232 (12) [M + 1]⁺, 2099 (52), 1928 (50), 1846 (54), 1708 (100) and 1676 (5).

[Co(L)₂(H₂O)₂Mn₂(phen)₄](ClO₄)₂ (4): Yield: (72%), Color: Dark Brown, m.p. = 260 °C. Anal. Calcd. for C₈₄H₉₆N₂₀O₂₂Cl₂CoMn₂ (MW: 1975 g/mol): C, 51.02; H, 4.89; N, 14.17. Found: C, 50.97; H, 4.71; N, 14.08. $\Lambda_{\text{M}} = 218 \Omega^{-1} \text{cm}^2/\text{mol}$, $\mu_{\text{eff}} = 4.82$ B.M. IR (KBr pellets, ν_{max} , cm⁻¹): IR (KBr pellets, ν_{max} , cm⁻¹): 3418–3244 $\nu(\text{OH/NH})$, 3055 $\nu(\text{Ar-H})$, 2980–2842 $\nu(\text{Aliph-H})$, 1683 $\nu(\text{C=O})$, 1624 $\nu(\text{C=N})$, 1390 and 968 $\nu(\text{N-O})$, 1089 and 625 $\nu(\text{ClO}_4)$, 544 $\nu(\text{Co-N})$, 480 $\nu(\text{Mn-N})$ and 476 $\nu(\text{Mn-O})$. UV-Vis (λ_{max} , nm, * = shoulder peak): 272, 338, 394, 435, 448, 613* (in DMF). MS (LSI, Scan ES⁺): m/z (%) 1976 (16) [M + 1]⁺, 1761 (52), 1928 (58), 1638 (42), 1532 (100) and 1306 (56).

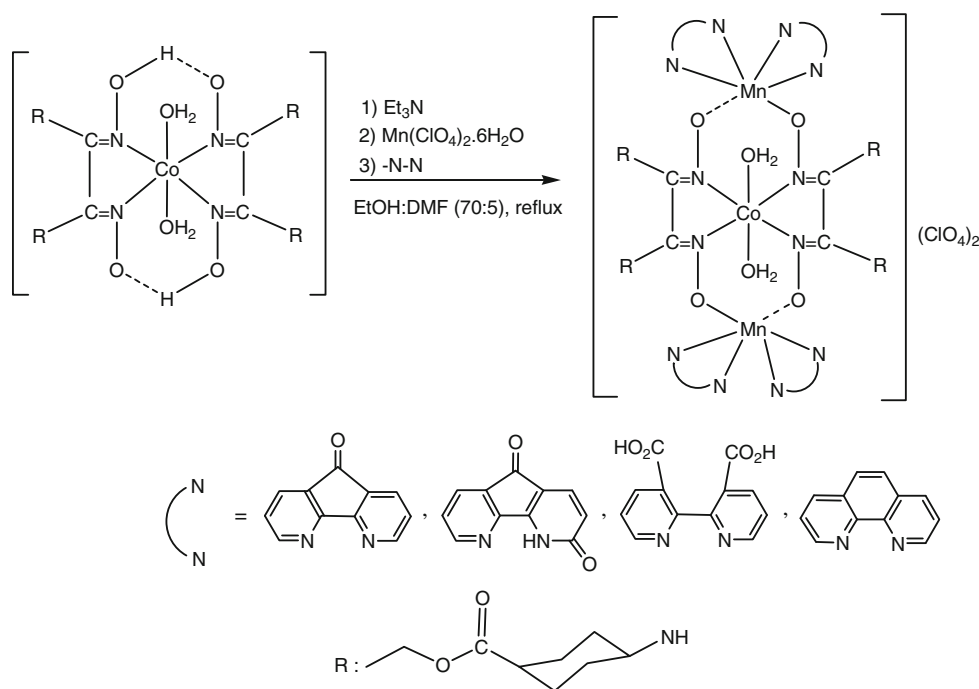
Results and discussion

The metal complexes of the general formula [Co(L)₂(H₂O)₂Mn₂(X)₄](ClO₄)₂ (where, L = ligand, X = 4,5-diazafluoren-9-one, 1H-cyclopenta[1,2-b:5,4-b']dipyridine-2,5-dione, 3,3'-dicarboxy-2,2'-bipyridine and 1,10-phenanthroline) were synthesized by the reactions of [Co(LH)₂(H₂O)₂] with the respective Mn(ClO₄)₂·6H₂O, Et₃N and dafo, dafdione, dcbpy or phen in EtOH-DMF (70:5) mixture, as shown in Scheme 1.

FT-IR spectra

The FT-IR spectra of all metal chelates were recorded in the 4000–400 cm⁻¹ range. The $\nu(\text{O-H/N-H})$ stretching vibrations were observed at between 3635 and 3155 cm⁻¹ for the all metal complexes. The intramolecular hydrogen bonding was not observed, as expected. This is because of the fact that the H-bond (O–H···O) of mononuclear Co(II) complex disappeared upon an encapsulation of the manganese ions on the formation of trinuclear metal complexes, namely Mn₂(dafo)₄, Mn₂(dafdione)₄, Mn₂(dcbpy)₄, and Mn₂(phen)₄. The spectra show strong peaks at range 1722–1683 cm⁻¹ for all trinuclear metal complexes due to carbonyl or carboxylic acid moiety. The coordination of the Co(II) metal complex to the Mn(II) metal center through the four nitrogen and two oxygen atoms are expected to reduce or increase the electron density in the N–O link and lower or higher the $\nu(\text{C=N})$ absorption

Scheme 1 The proposed structures for (1), (2), (3), and (4) metal complexes



frequency. The $\nu(\text{C}=\text{N})$ stretching vibrations are affected upon complexation and are situated at a frequency significantly different than that of the mononuclear $\text{Co}(\text{II})$ metal complex ($\nu_{\text{C}=\text{N}}$: 1645 cm^{-1}) [14]. The vibrations of the azomethine groups of the trinuclear metal complexes are observed at $1632\text{--}1603\text{ cm}^{-1}$, indicating that the nitrogen atoms of the azomethine groups are coordinated to the metal ion (Fig. 2) [19–21]. Perchlorate salts show strong antisymmetric stretching band at between 1089 and 1064 cm^{-1} and sharp antisymmetric stretching band at between 627 and 625 cm^{-1} , an indication of uncoordinated perchlorate anions [22, 23]. In the low frequency region, a band of medium intensity observed for the trinuclear metal complexes in the region $544\text{--}515\text{ cm}^{-1}$ is attributed to $(\text{Co}-\text{N})$ vibrations. The coordination of the dafo, dafdione, dcbpy or phen nitrogen is further supported by the appearance of a peak at $486\text{--}480$ and $476\text{--}468\text{ cm}^{-1}$, due to $\nu(\text{Mn}-\text{N})$ and $(\text{Mn}-\text{O})$ stretching vibrations that are not observed in the infrared spectra of the $[\text{Co}(\text{LH})_2(\text{H}_2\text{O})_2]$ metal complex (Fig. 1) [21, 24].

UV–Vis spectra

The UV–Vis spectra of the trinuclear metal complexes (1)–(4) in DMF showed three–six absorption bands ranging from 269 to 657 nm . The electronic spectra of the $\text{Mn}(\text{II})\text{--Co}(\text{II})\text{--Mn}(\text{II})$ -type hetero-trinuclear metal complexes showed modifications with respect to the position and intensity of the characteristic bands to the mononuclear $\text{Co}(\text{II})$ metal complex as compared. The new complexes also presented new bands (although sometimes not well-defined) attributed to the trinuclear metal complexes. In the electronic spectra of the five metal complexes, the wide range bands seems to be due to both the $\pi \rightarrow \pi^*$, and

$n \rightarrow \pi^*$ transitions of $\text{C}=\text{N}$ and charge-transfer transition arising from π electron interactions between the metal and ligand which involves either a metal-to-ligand or ligand-to-metal electron transfer [25–27]. Azomethine groups are a useful tool for the fabrication of the new $\text{Mn}(\text{II})\text{--Co}(\text{II})\text{--Mn}(\text{II})$ -type trinuclear metal complexes with specific electronic and structural properties. The absorption bands below 304 nm DMF are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring or azomethine ($-\text{C}=\text{N}$) groups. The absorption bands observed within the range of $317\text{--}394\text{ nm}$ in DMF are most probably due to the transition of $n \rightarrow \pi^*$ of imine group corresponding to the ligand or metal complexes (Fig. 2) [28–30]. The bands in the region of $435\text{--}448\text{ nm}$ were attributed to the $d \rightarrow \pi^*$ charge-transfer transitions, which are overlapping with the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the trinuclear metal complexes as a result of coordination of cobalt or manganese metal through N_4 and N_4O_2 atoms. The trinuclear metal complexes (1) and (4) exhibit new bands around 613 and 657 nm in DMF, respectively, with the absorptivity of the former being higher.

Molar conductivity and mass spectra

With a view to study the electrolytic nature of the trinuclear metal complexes, their molar conductivities were measured in DMF at 10^{-3} M . The molar conductivity (Λ_{M}) values of these trinuclear metal complexes are ranging from 218 to $197\text{ }\Omega^{-1}\text{ cm}^2/\text{mol}$ at room temperature, indicating 1:2 electrolytes or three ionic species in solution [28–30]. The higher values of trinuclear metal complexes, indicated the presence of counter ClO_4^- anions. Conductivity measurements have frequently been used in structural elucidation of metal chelates within the limits of their

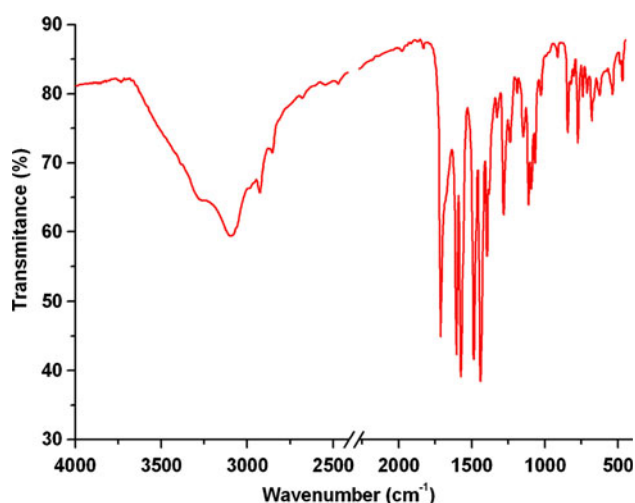


Fig. 1 FT-IR spectrum of the $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2\text{Mn}_2(\text{dafdione})_4](\text{ClO}_4)_2$ (2)

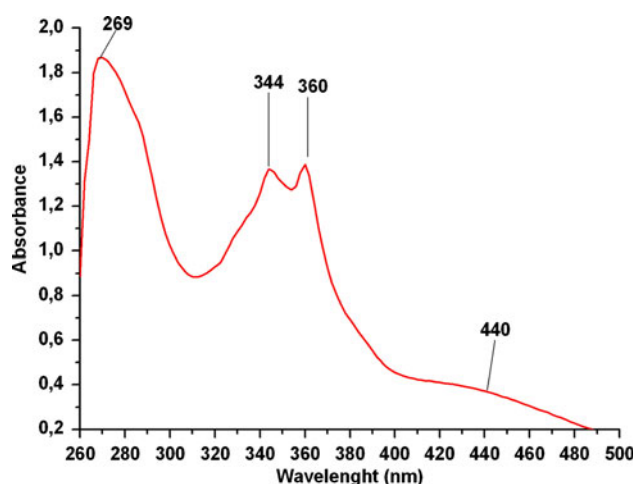


Fig. 2 UV–Vis spectrum of the $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2\text{Mn}_2(\text{dafdione})_4](\text{ClO}_4)_2$ (2)

solubility. They provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution (in case of presence of anions outside the coordination sphere), the higher will be its molar conductivity and vice versa. The molar conductivity values indicate that the anions may be present outside the coordination sphere or inside or absent [20, 31, 32].

The positive mode ESI-MS of the prepared trinuclear metal complexes can assist for better understanding the behavior of these complexes in solutions, since the generated ions in the gas phase closely reflect those in solution [33]. The ESI-MS spectra for trinuclear metal complexes are always very important for molecular weights determination, because of chemical ionization of these metal complexes and the obtained results can be used for confirmation. So, the molecular ion peak is obtained at 1985 for complex (1), at 2232 for complex (3) and at 1976 for complex (4). Around this value, some other peaks are present and can be assigned to the metal complexes with various isotopes of Cl and others groups. However, the major part of these compounds proved to present characteristic peaks m/z corresponding to their molecular weight [29].

X-ray diffractions and SEM analysis

We have attempted to prepare single crystals of trinuclear metal complexes in various solvents, but unfortunately we could not obtain single crystals suitable for X-ray

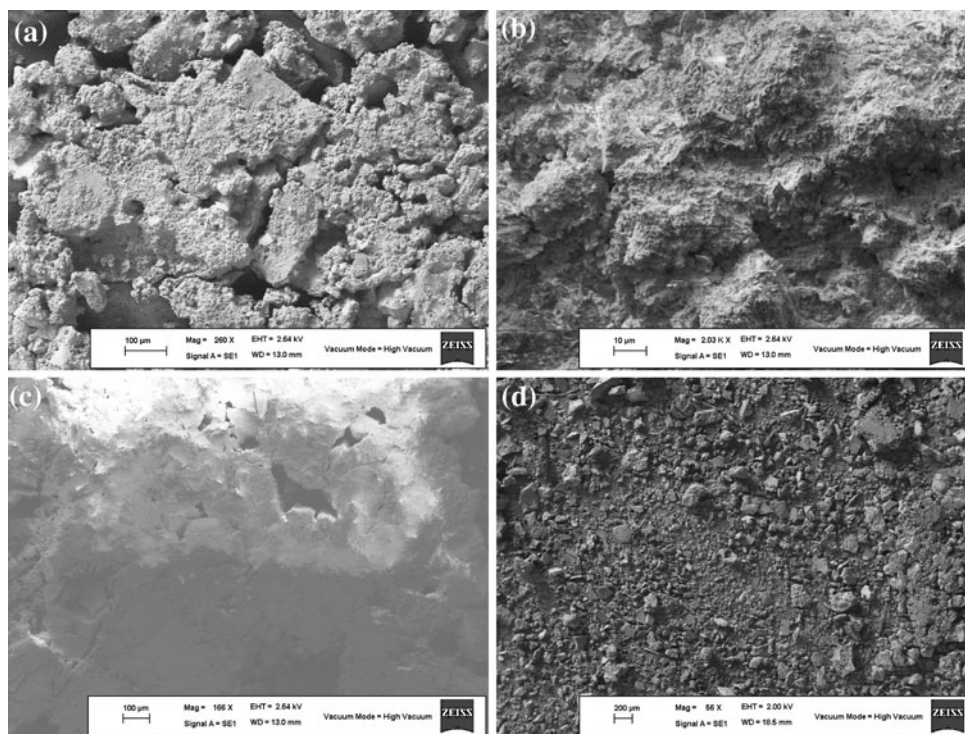
diffraction studies for all metal complexes. For more clarity, a small window, representative of the whole range, restricted to the $10^\circ < 2\theta < 80^\circ$ is presented for the all trinuclear metal complexes. However, the slightly crystalline nature of (2) and (3) and the amorphous nature of (1) and (4) can be readily evidenced from their X-ray powder patterns. The metal complexes (2) and (3) exhibit sharp reflections and all diffractograms are nearly identical, indicating the isostructural nature of these compounds. Also, the large number of reflections as well as their positions indicates low crystal symmetry [34, 35]. This results show that (2) and (3) metal complexes are indicating crystalline nature, not amorphous nature. Whereas, the X-ray powder pattern of the (1) and (4) exhibited only broad humps, indicating its amorphous nature.

The morphology of trinuclear metal complexes has been illustrated by the scanning electron microscopy (SEM). Figure 3 depicts the SEM images of (1), (2), (3) and (4) metal complexes. We noted that there is a uniform matrix of the synthesized metal complexes in the pictograph. This leads us to believe that we are dealing with homogeneous phase material. The slightly crystalline shape is observed in the (2) and (3) metal complexes and the amorphous shape is observed in the (1) and (4) metal complexes.

Magnetic moments measurements

Magnetic susceptibility measurements provide sufficient data to characterize the structure of the trinuclear metal

Fig. 3 The SEM micrographs of **a** (1), **b** (2), **c** (3) and **d** (4) metal complexes



complexes. Magnetic moments measurements of all metal complexes carried out at 25 °C. The magnetic moment of mononuclear $[\text{Co}(\text{LH})_2(\text{H}_2\text{O})_2]$ metal complex is found to be 3.96 B.M. close to the spin-only magnetic moments for three unpaired electrons. The Co(II) complexes were characterized by IR spectra and elemental analyses and it was found that two molecules of water were axially coordinated to the cobalt ion. The observation of an (O–H···O) bond leads us to consider the geometry of complexes to be octahedral. These results are given in our previous study [14]. The magnetic moments of the trinuclear metal complexes (1), (2), (3) and (4) are found between 5.16 and 4.59 B.M. for per Mn(II) molecule. These values are below the spin only value for high spin ($S = 5/2$, $\mu_{\text{eff}} = 5.92$ B.M.). So, it is obvious that the trinuclear metal complexes possess antiferromagnetic properties at room temperature by strong intramolecular antiferromagnetic spin exchange interaction for trinuclear metal complexes with oximate bridge ligand [23, 36]. Another possible explanation of the lowered μ_{eff} is that the Mn(II) ions coordinated with two dafo, dafdione, dcbpy and phen groups for per Mn(II) molecule and the intramolecular antiferromagnetic exchange interaction of dafo, dafdione, dcbpy and phen unpaired electrons with two unpaired electrons of Mn(II) leads to an $S = 3/2$ ground state.

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