SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATIONS OF MANGANESE(II), IRON(III), COPPER(II) AND ZINC(II) HYDRAZINE COMPLEXES AS CATALYTIC ACTIVITY AGENTS

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ABSTRACT. This article deals with the preparation and coordination of NH_2—NH_2 hydrazine molecule compounds. The hydrazine sulfate complexes of Mn(II), Fe(III), Cu(II), and Zn(II) were prepared. These complexes were characterized by elemental, infrared, conduction, electron absorption spectroscopy, magnetic susceptibility, thermogravimetric analyses, X-ray powder diffraction (XRD) patterns and atomic force microscopy (AFM) studies. The magnetic measurements were confirmed that the Mn(II), Fe(III), Cu(II), and Zn(II) hydrazine complexes have an octahedral geometric structure. Thermogravimetric and its differential thermogravimetric analysis referred that all complexes passed through two-to-three thermal degradation steps with solid metal sulfate as a residual product. The infrared spectra inferred that the NH_2—NH_2 ligand forms complexes through nitrogen atoms of the—NH_2 moiety, while the elemental analysis indicates $[M(NH_2$—$NH_2)_3]SO_4$ (where M = Mn(II), Cu(II), and Zn(II)) while the iron(III) complexes have the $[Fe_2(NH_2$—$NH_2)_4(SO_4)_2]SO_4$ formula of coordination compounds, NH_2—NH_2 acts as a double bond. Both XRD and AFM analysis deduced that the synthesized hydrazine metal complexes were found to be in nano scale range 10—30 nm.

KEY WORDS: Hydrazine, FTIR, AFM, XRD, Transition metals

INTRODUCTION

Many important properties of coordination compounds embrace the nature of ligand donor, hydrazides being one of the best suited types of ligands to enhance the metal some important properties [1]. As a result of their antimicrobial, antifungal and antibacterial properties [1-3], hydrazides are of great biological importance. The formation of mineral complexes plays an important role in the growth of their biological activity [4-8]. Also, the simple organic molecule hydrazine has been widely used as a reducing agent for the synthesis of some metal nanoparticles due to its pH and temperature dependent reducing ability of hydrazine which makes controlling the rate of reduction easy. Hydrazine is basic and the chemically active free ion is the hydrazium cation. The standard reduction potential of a hydrazine ion is −0.23 eV in acidic solution, but in basic medium the standard reduction potential of hydrazine is −1.16 eV [9, 10]. Narrowly distributed nickel micropowders were prepared from the reduction of hydrazine complexes in aqueous solution at 60 °C. It was found that the phase and composition of the hydrazine compound used as a precursor depends on the structural state. Pure hydrazine complexes, $[Ni(N_2H_4)_3]Cl_2$ with the molar ratio of N_2H_4:Ni^{2+} = 3:1 [11] were prepared, while fine nickel powders with controllable particle sizes were synthesized by reducing the precursor of the nickel hydrazine complex in aqueous solution. The mechanism of formation of nickel-metal powders examines the reduction of nickel hydroxide by hydrazine released from the ligand exchange reaction between

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a nickel-hydrazine compound and NaOH. Compared with the method of preparing nickel powders from nickel salts, the method of making nickel powders by reducing the precursor of the hydrazine compound from nickel shows the advantages of using half a dose of hydrazine to completely reduce the nickel ions in the solution, and the obtained nickel particles show less agglomeration and better dispersion. Moreover, the average particle size of nickel powders can be controlled from 180 to 260 nm by adjusting the reaction molar ratio and concentration [12]. One of the bonds found in the primary explosive format is hydrazine. A research team in China prepared and studied a compound commonly referred to as NHN - nickel hydrazinium nitrate [13]. In this paper, we report the preparation of hydrazine manganese(II), iron(III), copper(II) and zinc(II) complexes as catalytic activity agents.

EXPERIMENTAL

Materials

All chemicals used in this experiment were reagent grade and used without further purification. Hydrazine monohydrate ($N_2H_4 \cdot H_2O$) solution, copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and anhydrous ($MnSO_4$, $Fe_2(SO_4)_2$, and $ZnSO_4$) metal sulfate salts were received from Aldrich Chemicals.

Synthesis of hydrazine complexes

The compounds, $[Mn(NH_2—NH_2)_3]SO_4$ (buff colour), $[Fe_2(NH_2—NH_2)_4(SO_4)_2]SO_4$ (reddish brown colour), $[Cu(NH_2—NH_2)_3]SO_4$ (greenish black colour), and $[Zn(NH_2—NH_2)_3]SO_4$ (white colour) were prepared by mixing equal aqueous solutions of $MnSO_4$ (1.51 g, 10 mmol), $Fe_2(SO_4)_2$ (4.0 g, 10 mmol), $CuSO_4 \cdot 5H_2O$ (2.50 g, 10 mmol), and $ZnSO_4$(1.62 g, 10 mmol), in 100 mL distilled water with a 100 mL volume of hydrazine monohydrate ($N_2H_4 \cdot H_2O$) solution (1.5 g, 30 mmol) in distilled water. The mixtures could be stirred for about 1 hours on cold then heated to *Ca*. 80 °C for about 3 hours on a water bath. In case of $CuSO_4 \cdot 5H_2O$-hydrazine mixture, $[Cu(NH_2—NH_2)_3]SO_4$ was started to precipitate after 30 minutes, while in the case of the other mixtures, the products took longer time of heating to precipitate. In all the cases, the amount of the formed precipitate was increased with increasing the time of heating. The precipitated formed in each case was filtered off, washed several times with hot water, dried at 80 °C in an oven for 3 hours and then in *vacuo* over anhydrous $CaCl_2$.

Instrumentals

Type of analysis	Instruments
Elemental analyses	Perkin Elmer CHN 2400
Percentage of respected metal ions	gravimetrically
Melting point	MPS10–120 Melting point apparatus
Molar conductivities	Jenway 4010 conductivity meter
Infrared spectra	Bruker FTIR Spectrophotometer
UV-Vis absorption spectra	UV2 Unicam UV/Vis Spectrophotometer
Magnetic moments	Magnetic Susceptibility Balance Sherwood
XRD	X 'Pert PRO PANanalytical XRD
Thermal studies	TGA/DSC–50H Shimadzu analyzer
AFM	Veeco-di Innova Model-2009-AFM-USA

RESULTS AND DISCUSSION

Elemental analysis and molar conductance studies

Elemental analysis data of hydrazine complexes of Mn(II), Fe(III), Cu(II), and Zn(II) complexes are very close to the theoretical values as shown in Table 1. One of sulfate anion is presence outside the coordination sphere in all metal complexes as well as there are two sulfato groups acts as a bridged bidentate chelates in case of iron(III) complex. Elemental analysis show that the metal to ligand ratio is 1:3 concerning Mn(II), Cu(II) and Zn(II) complexes while the iron(III) complex has a 1:2 molar ratio and the compositions of metal complexes are $[M(NH_2\!\!-\!\!NH_2)_3]SO_4$ (where M = Mn(II), Cu(II), and Zn(II)) and iron(III) complex has a $[Fe_2(NH_2\!\!-\!\!NH_2)_4(SO_4)_2]SO_4$. Molar conductances of the solution of the metal complexes were determined with a Jenway 4010 conductivity meter. All measurements were carried out at room temperature with freshly prepared solution. Conductance and melting points of the complexes are given in Table 1, conductance data show that the metal complexes are electrolyte indicating the sulfate ions are located outside the coordination sphere and are directly acts as an ionic statement outside the coordination sphere. The cations and anions were estimated by using typical analytical procedure [14].

Table 1. Microanalytical and physical analyses of hydrazine complexes of Mn(II), Fe(III), Cu(II), and Zn(II).

Complexes	M.wt	Colour	H%		N%		Physical data	
			Found	Calc.	Found	Calc.	Conductance/ Ω^{-1} cm^2 mol^{-1}	Mp/°C
$[Mn(NH_2\text{-}NH_2)_3]SO_4$	247.00	Buff	4.76	4.89	39.87	34.01	73	1:3
$[Fe_2(NH_2\text{-}NH_2)_4(SO_4)_2]SO_4$	528.04	Reddish brown	3.02	3.05	21.19	21.22	96	1:2
$[Cu(NH_2\text{-}NH_2)_3]SO_4$	255.74	Greenish black	4.70	4.73	32.80	32.86	68	1:3
$[Zn(NH_2\text{-}NH_2)_3]SO_4$	257.57	White	4.67	4.70	32.58	32.63	81	1:3

Electronic spectroscopy and magnetic susceptibility studies

All the complexes have magnetic susceptibilities except Zn(II) diamagnetic complex [15]. Manganese(II) complex has magnetic moment value of 5.56 B.M. suggesting octahedral environment. The electronic spectra of Mn(II) complex registers electronic bands at 450 nm and 550 nm, which can be assigned to $^6A_{1g}\!\rightarrow\!^4T_{2g}$ (G) and $^6A_{1g}\!\rightarrow\!^4T_{1g}$ (G) transitions of Mn(II) ion in a spin free d^5 configuration confirming to octahedral arrangement [15]. The electronic spectrum of diiron complex $[Fe_2(NH_2\!\!-\!\!NH_2)_4(SO_4)_2]SO_4$ exhibit three absorption bands at 520, 430, and 390 nm, which may be assigned to transitions $^6A_{1g}\!\rightarrow\!^4T_{1g}$, $^6A_{1g}\!\rightarrow\!^4T_{2g}$, $^6A1g\!\rightarrow\!^4A_{1g}$, ^4E_g, respectively [16] and suggests octahedral geometry. The magnetic moment of iron(III) complex obtained 5.86 B.M. is in good agreement for six-coordinated dinuclear iron(III) system and consistent with the presence of a five-unpaired electrons [17]. The spectrum of copper(II) complex showed an absorption band at 735 nm. This band appears due to $2E_g\!\rightarrow\!^2T_g$ transition in an octahedral field. The copper (II) complex has magnetic moment of 1.82 B.M., which is usually observed for octahedral Cu(II) complex [15, 17].
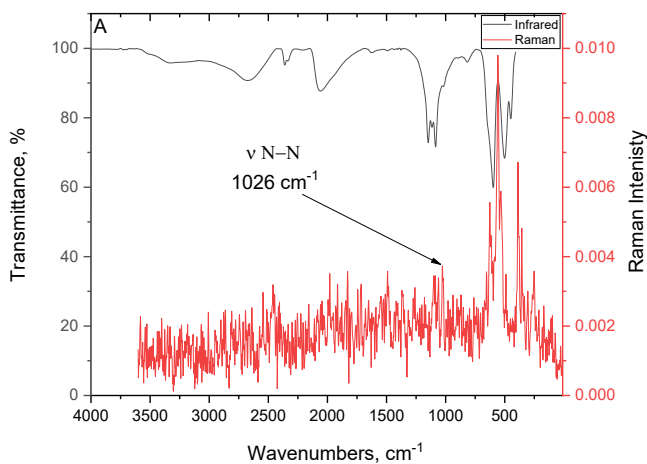
Infrared and Raman studies

Hydrazine ($H_2N\!\!-\!\!NH_2$) coordinates to a metal ion as a unidentate or a bridging bidentate ligand. According to Nicholls and Swindells [18], the complexes of the former type exhibit the $\nu(N\!\!-\!\!N)$ near 930 cm^{-1}, whereas those of the latter type show it near 970 cm^{-1}. The IR spectra of hydrazine

complexes of M(II) (M = Ni, Co, Zn, Cd) [19], Os(II) [20], and Ln(III) (Ln = Pr, Nd, Sm) [21] have been reported. In these compounds, hydrazine acts as a unidentate or bridging bidentate ligand. Characterization of most of the hydrazine complexes in the literature has relied heavily upon IR spectroscopy and as a result, the proposed structures are still not unambiguous. It has been claimed from IR studies that the position of ν(N—N) in monodentate hydrazine complexes occurs at 928-937cm^{-1} whereas for complexes which contain bidentate or bridging hydrazine ν(N—N) occurs at 948-980 cm^{-1}. These bands are all at higher frequency than free hydrazine (875 cm^{-1}) [22].

The location of the N—N stretching frequency has been widely used [23] as a criterion for determining the mode of the bonding between hydrazine and metal ions. Thus, a band in the 930 cm^{-1} region is attributed to ν(N—N) in unidentate hydrazine while a band around 970 cm^{-1} is attributed to ν(N—N) in bidentate hydrazine. In hydrazine itself there is disagreement about the assignment of ν(N—N) (as well as of other fundamentals); Durig *et al.* [23] assigning ν(N—N) in N_2H_4 to a band at 1126 cm^{-1} while other workers [18-22] assign a band in the 880 cm^{-1} region to this mode.

Table 2. Infrared frequencies assignments of the hydrazine and Mn(II), Fe(III), Cu(II), and Zn(II) complexes.

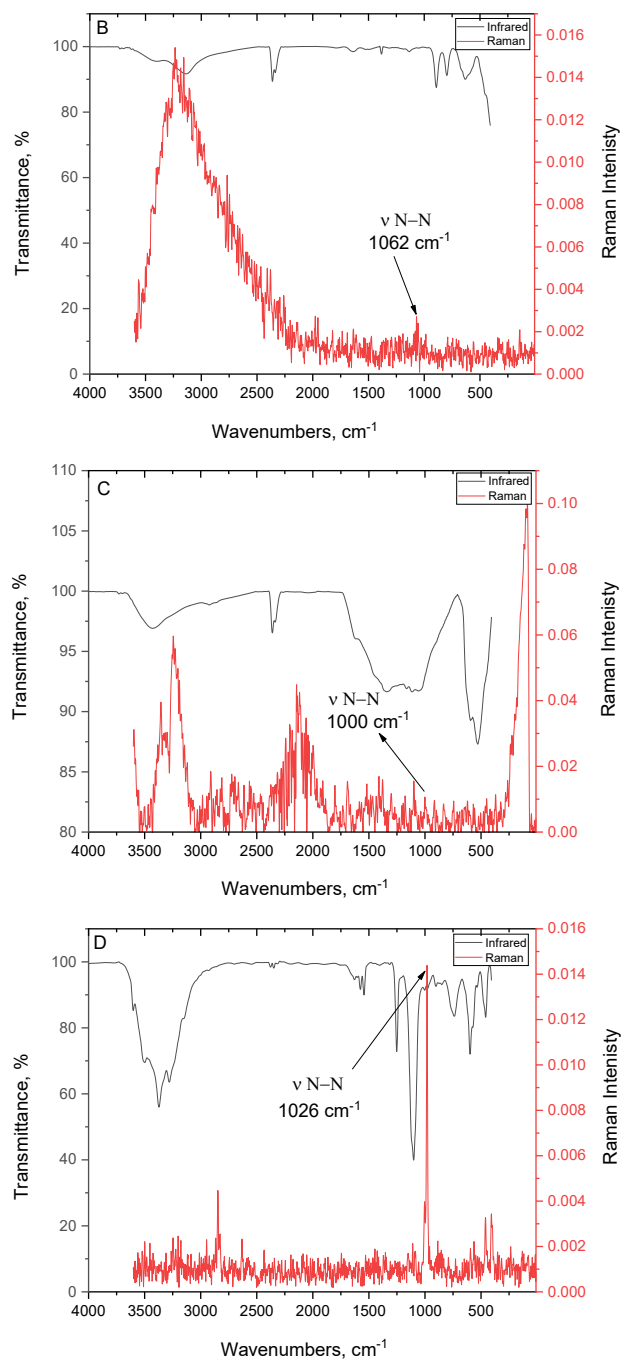| Infrared frequencies of compounds					Assignments
$H_2N—NH_2$	Mn(II) complex	Fe(III) complex	Cu(II) complex	Zn(II) complex	
3340	3327	3400	3427	3369	ν(N—H)
1613	-	1638	1622	1632	δ(HNH)
1461	-	-	-	-	δ(NNH)
1360, 1285	-	1382	1350	1250	δ_ω(NH$_2$)
1074	1110	1136	1115	1090	δ_r(NH$_2$)
880	1090	895	1042	900	ν(N—N)
-	445	440	524	456	ν(M—N)
-	-	629	-	-	ν(M—O)

Figure 1. Infrared and Raman spectra of A: Mn(II), B: Fe(III), C: Cu(II), and D: Zn(II) complexes.

The FT-IR spectra in Figure 1 shows the vibrational peaks arising from the [Mn(NH$_2$—NH$_2$)$_3$]SO$_4$, [Fe$_2$(NH$_2$—NH$_2$)$_4$(SO$_4$)$_2$]SO$_4$, [Cu(NH$_2$—NH$_2$)$_3$]SO$_4$, and [Zn(NH$_2$—NH$_2$)$_3$]SO$_4$ complexes. The stretching vibrational mode ν(N—N) of hydrazine ligand at the frequency of 880 cm^{-1} and other vibrational peaks except the peaks in the region of 1461, 1360, and 1074 cm^{-1} are consistent with the values in the NH$_2$—NH$_2$ ligand reported in the earlier literature [18-23]. The vibrational peaks including ν(N–N) of hydrazine ligand at the frequency of 880 cm^{-1} are comparable to the values in the Mn(II), Fe(III), Cu(II), and Zn(II) complexes (Table 2 and Figure 1), that confirmed the coordination of hydrazine ligand towards metal ions through both nitrogen atoms as a bidentate (Figure 2). Accordingly, bidentate chelating and bridging sulfato groups belong to the lower symmetry C$_{2V}$. However, the vibrations of the bidentate sulphate group in this complex [Fe$_2$(NH$_2$—NH$_2$)$_4$(SO$_4$)$_2$]SO$_4$, can be assigned for the various SO$_4^{-2}$ modes [24]. Two bands with strong intensities occur in the region above 1000 cm^{-1} at 1132, 1051 and 896 cm^{-1} are assigned to the different symmetric and antisymmetric bond vibrations, ν(SO$_4$)$^{2-}$, while the bending motion of δ(SO$_4$)$^{2-}$ is assigned to the band at 630 cm^{-1}.
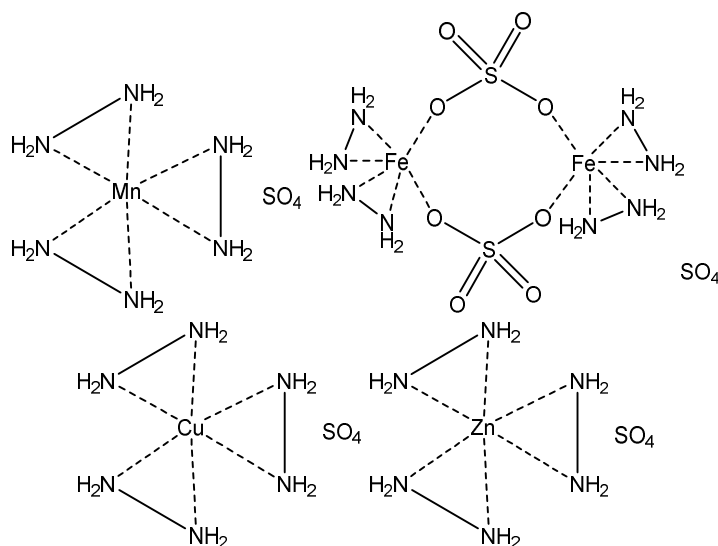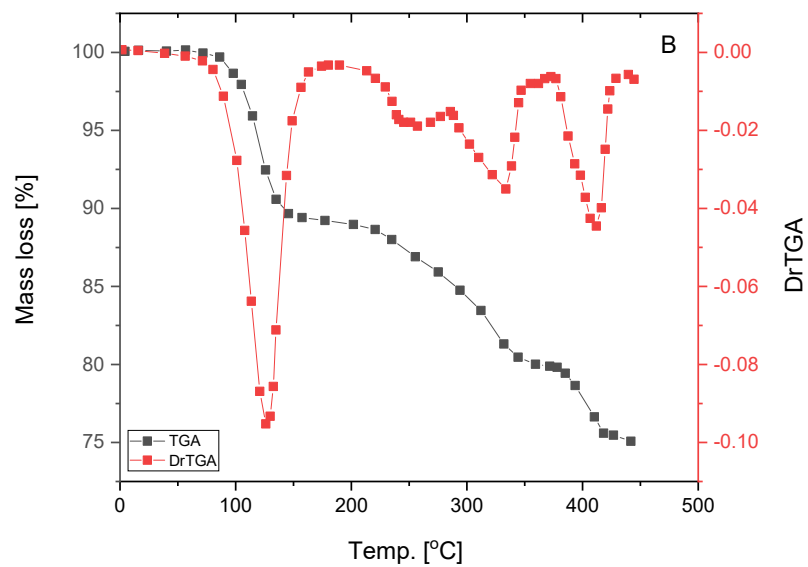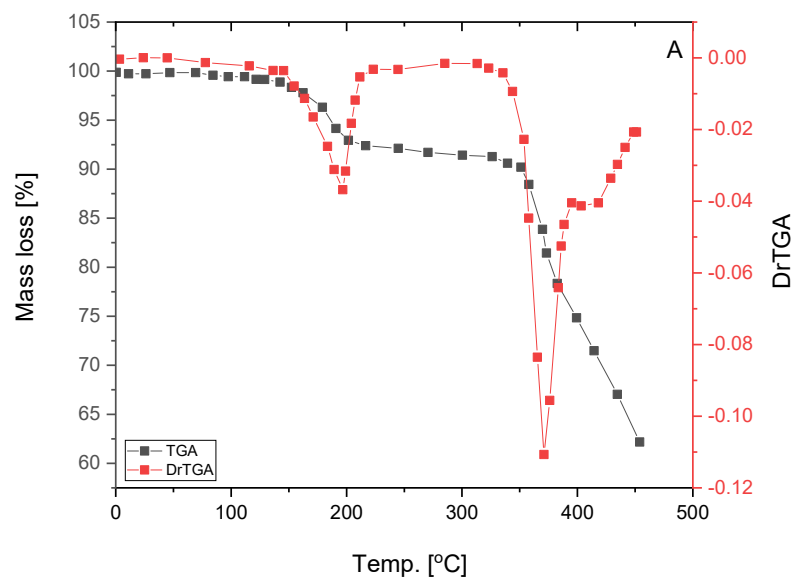

Figure 2. Speculated structures of [Mn(NH$_2$—NH$_2$)$_3$]SO$_4$, [Fe$_2$(NH$_2$—NH$_2$)$_4$(SO$_4$)$_2$]SO$_4$, [Cu(NH$_2$—NH$_2$)$_3$]SO$_4$, and [Zn(NH$_2$—NH$_2$)$_3$]SO$_4$ complexes.

Thermogravimetric studies

The TG-DTG curves of the [Mn(NH$_2$—NH$_2$)$_3$]SO$_4$, [Fe$_2$(NH$_2$—NH$_2$)$_4$(SO$_4$)$_2$]SO$_4$, [Cu(NH$_2$—NH$_2$)$_3$]SO$_4$, and [Zn(NH$_2$—NH$_2$)$_3$]SO$_4$ complexes are shown in Figure 3a-e and the thermal data are given in Table 3. All the complexes start losing NH$_2$—NH$_2$ molecules from 115 ºC and this subsequent decomposition seems to be a continuous process with endotherms at temperature ranging from 115-450 ºC associated with hydrazine removal with no distinct intermediate formation. The end residual products were analyzed to be MnSO$_4$, Fe$_2$(SO$_4$)$_2$, CuSO$_4$ and ZnSO$_4$ for Mn(II), Fe(III), Cu(II), and Zn(II) complexes, respectively, confirmed by FTIR of residues and comparison with commercial metal sulfate salts.
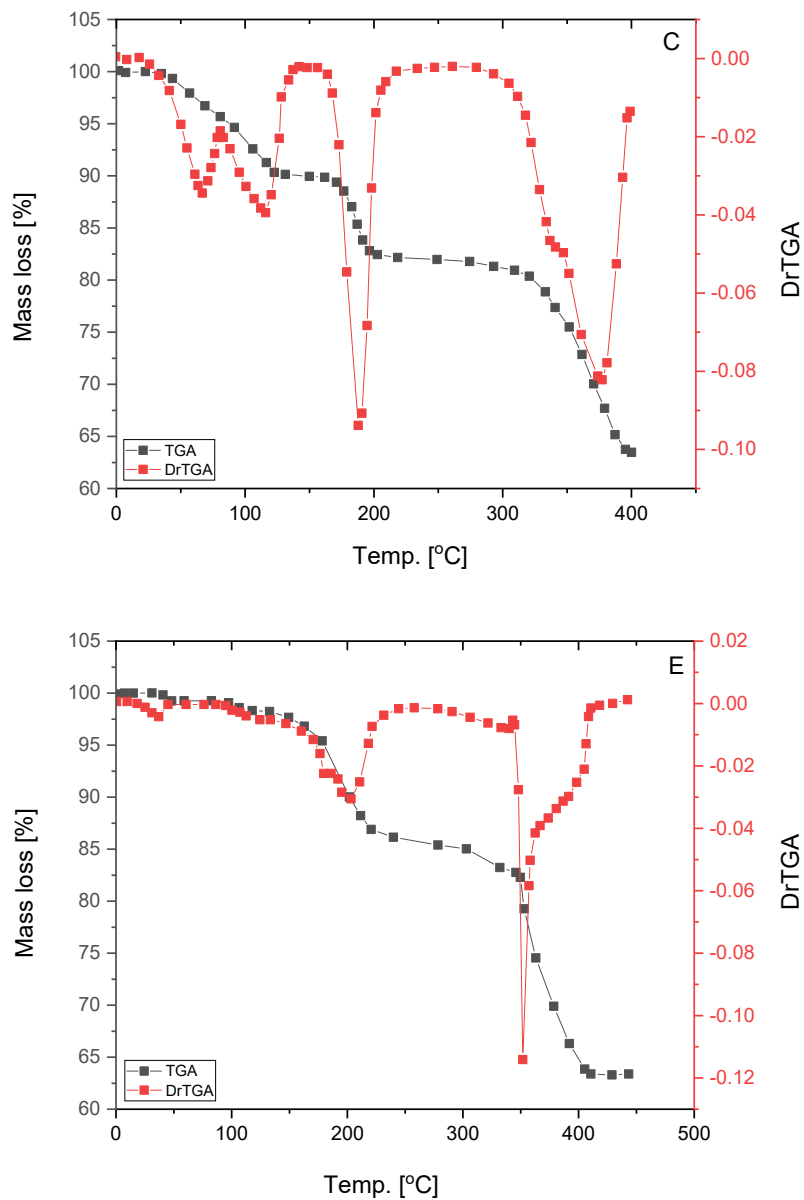
Figure 3. TG-DTG curves of the [Mn(NH₂—NH₂)₃]SO₄, [Fe₂(NH₂—NH₂)₄(SO₄)₂]SO₄, [Cu(NH₂—NH₂)₃]SO₄, and [Zn(NH₂—NH₂)₃]SO₄ complexes.

Table 3. Thermal analyses of the hydrazine and Mn(II), Fe(III), Cu(II), and Zn(II) complexes.

Complexes	DTG peak/°C	Temp. range/°C	Weight loss		Assignments	
			Calcd.	Found	Loss species	Residual species
Mn(II)	197, 370	25-200, 200-450	38.87	39.00	$3N_2H_4$	$MnSO_4$
Fe(III)	126, 330, 410	25-150, 150-380, 380-450	24.27	25.00	$4N_2H_4$	$Fe_2(SO_4)_2$
Cu(II)	114, 189, 375	25-150, 150-250, 250-450	37.56	38.00	$3N_2H_4$	$CuSO_4$
Zn(II)	200, 350	25-300, 300-450	37.31	37.50	$3N_2H_4$	$ZnSO_4$

Kinetic thermodynamic studies

The kinetic thermodynamic parameters of $[Mn(NH_2{-}NH_2)_3]SO_4$, $[Fe_2(NH_2{-}NH_2)_4(SO_4)_2]SO_4$, $[Cu(NH_2{-}NH_2)_3]SO_4$, and $[Zn(NH_2{-}NH_2)_3]SO_4$ complexes were calculated using TGA curves. These parameters have been computed using integral method developed by Coats—Redfern [25]. The equation used for calculation of the E and A parameters is $\log [1 - (1 - \alpha)^{n-1}/(1 - n)T^2] = \log AR/\varphi E [1- 2RT/E] - E/2.303RT$ where a is the fraction reacted in time (t), T is temperature in K, A is the pre-exponential factor in min^{-1}, φ is the heating rate, E is the activation energy in kJ/mol and R is the gas constant. Plotting Y vs. 1/T gives a straight line for a parameter, n where $Y = 1 - (1 - \alpha)^{n-1}/(1-n)T^2$. The activation energy E can be calculated from the slope and the A factor from the intercept. Kinetic studies reveal that all the complexes follow same mechanism of decomposition as inferred from their computed E values. The activation energy for decomposition of the complexes is found to almost similar in the range of 6.79-1.30 J/mol^{-1}. Table 4 shows the computed kinetic parameters and the decomposition steps for all the metal complexes.

Table 4. Kinetic thermodynamic parameters using the Coats–Redfern for the Mn(II), Fe(III), Cu(II) and Zn(II) complexes.

Complexes	Stage	Parameter					r
		E^* (J mol^{-1})	A (s^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔH^* (J mol^{-1})	ΔG^* (Jmol^{-1})	
Mn(II)	1st	1.49×10^5	1.10×10^{11}	-3.78×10	1.47×10^5	1.70×10^5	0.9945
	2nd	1.30×10^5	2.11×10^7	-1.11×10^2	1.23×10^5	2.02×10^5	0.9977
Fe(III)	1st	4.35×10^5	2.28×10^4	-1.20×10^2	5.16×10^5	8.54×10^5	0.9991
	2nd	4.76×10^5	1.69×10^{43}	-5.65×10^2	4.80×10^5	1.60×10^5	0.9965
Cu(II)	1st	6.66×10^5	1.87×10^8	-8.71×10	6.50×10^5	9.01×10^4	0.9943
	2nd	6.70×10^5	1.10×10^{49}	-7.24×10^2	6.65×10^5	1.77×10^5	0.9954
Zn(II)	1st	5.48×10^5	1.62×10^6	-1.24×10^2	5.22×10^5	9.21×10^5	0.9932
	2nd	2.30×10^5	2.18×10^{14}	-2.20×10	2.15×10^5	2.00×10^5	0.9987

XRD and AFM studies

The X-ray powder diffraction patterns data of the $[Mn(NH_2{-}NH_2)_3]SO_4$, $[Fe_2(NH_2{-}NH_2)_4(SO_4)_2]SO_4$, $[Cu(NH_2{-}NH_2)_3]SO_4$, and $[Zn(NH_2{-}NH_2)_3]SO_4$ complexes are listed in Table 5 and display in Figure 4. The X-ray powder diffraction data of the complexes show similarity among the individuals in each set, implying isomorphism. Also, these complexes were found to be pure and uniform in nano scale range (10—26 nm) as found from XRD using Scherer's formula [26], $D = K\lambda/\beta \cos \theta$ where λ is the X-ray wavelength, β is the full width of height maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer's constant

Table 5. X-Ray diffraction patterns data of Mn(II), Fe(III), Cu(II) and Zn(II) complexes.

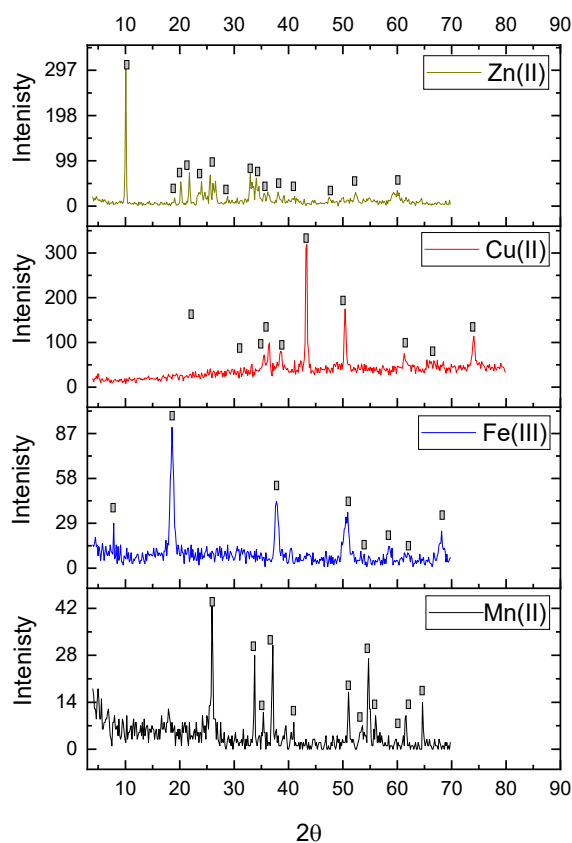| Complexes	FWHM/2θ	Particle size/nm	Diffraction patterns peaks/2θ
$[Mn(NH_2—NH_2)_3]SO_4$	25.96	24	25.96, 33.53, 35.47, 39.35, 41.09, 50.98, 53.51, 54.48, 56.03, 61.65, 64.56
$[Fe_2(NH_2—NH_2)_4(SO_4)_2]SO_4$	18.59	10	7.73, 18.59, 37.60, 40.70, 43.42, 46.91, 50.98, 58.36, 61.85, 64.17, 68.25
$[Cu(NH_2—NH_2)_3]SO_4$	43.42	23	35.47, 36.44, 38.57, 43.42, 50.40, 61.27, 66.31, 74.07
$[Zn(NH_2—NH_2)_3]SO_4$	10.06	26	10.06, 20.34, 24.02, 26.74, 28.68, 32.75, 36.05, 41.29, 44.97, 54.48, 59.71

Figure 4. XRD diffraction patterns curves of Mn(II), Fe(III), Cu(II) and Zn(II) complexes.

of the order of 0.89. For accurate particle size calculations and morphological properties of $[Zn(NH_2—NH_2)_3]SO_4$ complex surface, AFM-microscopy tapping mode was applied on the solid powder to evaluate nano-metric features of the resultant materials. Figure 5 shows the three-dimensional image for $[Zn(NH_2—NH_2)_3]SO_4$ complex through tapping mode, it was observed that movement of the tip through the z-axis not similar which means that the up and down zones of the surface is not homogeneous through the scanned area which is too small (0.5 x 0.5 μm). The

analysis of the XRD and AFM indicated that the average particle size for $[Zn(NH_2—NH_2)_3]SO_4$ complex sample is ranged $\sim$ 15 nm which confirm that $[Zn(NH_2—NH_2)_3]SO_4$ complex synthesis technique yields to nano-product.

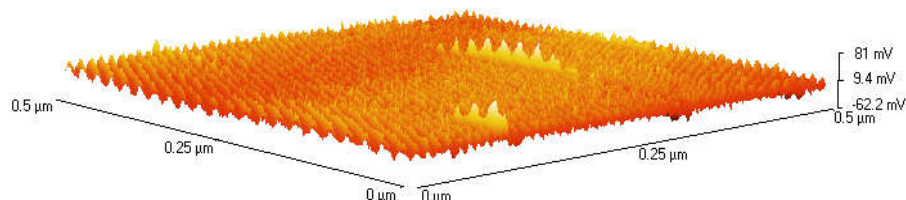

Figure 5. AFM diagram of $[Zn(NH_2—NH_2)_3]SO_4$ complex.

CONCLUSIONS

In the present study, we reported the synthesis, and characterization of Mn(II), Fe(III), Cu(II) and Zn(II) hydrazine adducts. The empirical formula of hydrazine complexes agrees with the elemental, infrared, conduction, electron absorption spectroscopy, magnetic susceptibility, thermogravimetric analyses, XRD patterns and atomic force microscopy (AFM). Results of various spectroscopic characterization of ligand and its complexes revealed that both are stable at room temperature and soluble in DMF and DMSO solvents and ligands were effectively coordinate with metal ions *via* the two nitrogens atoms of hydrazine moiety and developed into a coloured hexacoordinate stable $[M(NH_2—NH_2)_3]SO_4$ (M = Mn(II), Cu(II), and Zn(II)) and $[Fe_2(NH_2—NH_2)_4(SO_4)_2]SO_4$ complexes.

ACKNOWLEDGEMENT

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