SYNTHESIS, COMPLEXATION AND BIOLOGICAL ACTIVITY OF NEW ISATIN SCHIFF BASES

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ABSTRACT

Some new Schiff-bases derived from condensation of 3-hydrazono-2-oxo-2,3-dihydroindol-1-yl-acetic acid hydrazide (**3**) with benzaldehyde, p-methoxybenzaldehyde and p-chlorobenzaldehyde have been synthesized in high yields via refluxing in EtOH in the presence of catalytic amount of acetic acid. The synthesized compounds have been characterized by elemental analysis, IR, ¹H-NMR and mass spectra. Cu(II), Zn(II), Mn(II) and Fe(III) complexes of the synthesized compounds were prepared and characterized by elemental analysis, conductivity measurements, IR, UV-Vis. spectra and magnetic moment measurements. TGA and DTA confirm the chemical formulation of the complexes and their thermal decomposition were evaluated. Antimicrobial activity of the synthesized compounds have been screened using the disk diffusion method with different strains of bacteria: *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli* and *Proteus vulgaris* were used.

Keywords: Isatin Schiff-bases; Cu(II), Zn(II), Mn(II) complexes; spectral, thermal properties and biological activity.

INTRODUCTION

Isatin Schiff-bases are known to possess a wide range of pharmacological properties including antibacterial¹⁻³, anticonvulsant⁴⁻⁵, anti-HIV⁶⁻⁹, antifungal¹⁰⁻¹³ and antiviral activity¹⁴. Isatin bis-Schiff bases are characterized by their capacity to co-ordinate to metal ions forming chelate rings¹⁵, act as inhibitors of human α -thrombin¹⁶ and its copper(II) complex catalyzed the oxidation of carbohydrates¹⁷. Recently it has been reported that isatin bis-imine has antimicrobial properties¹⁸ and affects cell viability¹⁹.

We report here the synthesis and characterization of some new Schiff-bases derived from the condensation of 3-hydrazono-2-oxo-2,3-dihydroindol-1-yl-acetic acid hydrazide with benzaldehyde, p-methoxybenzaldehyde and p-chlorobenzaldehyde and also their Cu(II), Zn(II), Mn(II), and Fe(III) complexes. Biological activity of the new compounds against strains of bacteria [*Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli* and *Proteus vulgaris*] was also tested.

EXPERIMENTAL

Materials and methods

All used solvents and metal salts were of A.R. grade. They were supplied by Merck and BDH and were used as received. All melting points measured on a MEL-TempII melting point apparatus were uncorrected. Thin layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel mesh 60F 254 of 0.2 mm thick. Elemental analyses were carried out using a Heraeus CHN-rapid analyzer. Infrared spectra were recorded (KBr disc) in the 400-4000 cm⁻¹ range on Bruker Vector22 spectrophotometer. ¹H-NMR measurements were carried out on a Bruker ARX (300 MHz) using d₆-DMSO as a solvent and TMS as internal standard. Mass spectral data are measured on Varian MAT-711 mass spectrometer. GC-MS were obtained with model 5988A Hewlett-Packard 5890 spectrometer. Electronic absorption spectra were obtained using 10⁻³ M DMF solutions in 1cm quartz cell on UV-1601PC Shimadzu spectrophotometer. Magnetic susceptibility measurements were carried out using the modified Gouy method²⁰ on MSB-MK1 balance at room temperature using [HgCo(SCN)₆] as standard. The effective magnetic moment, μ_{eff} , per metal atom was calculated from the expression $\mu_{\text{eff}} = 2.83 \sqrt{\chi T}$ B.M., where χ is the molar susceptibility corrected using Pascal's constant for the diamagnetism of all atoms in the complexes. TGA, DTG and DTA were recorded on Shimadzu-60 thermal analyzer under a dynamic flow of nitrogen (30ml/min.) and heating rate 10°C/min. Electrical conductivity measurements were carried out at room temperature on freshly prepared 10⁻³M DMF solutions using WTW conductivity meter fitted with L100 conductivity cell.

Synthesis

(2,3-Dioxo-2,3-dihydro-indol-1-yl)acetic acid ethyl ester: (**2**)

To a stirred solution of isatin (**1**) (1.5 g, 10.18 mmol) in acetone (35 ml), K₂CO₃ (1.4 g, 10.18 mmol) was added and the mixture was stirred for 1 h. A solution of ethylchloroacetate (1 ml, 10.18 mmol) in acetone (15 ml) was added dropwise with stirring for 5 h at room temperature after which the mixture

was filtered. The filtrate is concentrated under reduced pressure, the resulting white crystalline precipitate was collected and crystallized from acetone-hexane mixture. Yield: 1.1 g (69.6%), m.p. 139-140°C. Anal.: Calcd. (%) for C₁₂H₁₁NO₄: C, 61.80; H, 4.75; N, 6.01. Found (%) : C, 61.79; H, 4.77; N, 5.87; IR: ν (cm⁻¹): 1696, 1675, 1653 (C=O); MS: M⁺ (%) = 233 (0.08), 205 (24), 172 (6), 162 (53), 160 (36), 148 (49.9), 120 (54), 119 (100), 91 (20).

(3-Hydrazono-2-oxo-2,3-dihydro-indol-1-yl)-acetic acid hydrazide: (**3**)

80% Hydrazine hydrate (4 ml, 80 mmol) was added to a solution of (**2**) (1 g, 4.3 mmol) in EtOH (15 ml) and the mixture was stirred for 4 h at room temperature and concentrated under reduced pressure. The resulting solid white crystals was filtered off, crystallized from ethyl acetate to give (**3**). Yield: 0.7 g (70 %); m.p. 183-186°C. Anal.: calcd. (%) for C₁₀H₁₁N₃O₂: C, 51.50, H, 4.75, N, 30.03; found (%): C, 51.48; H, 4.81; N, 29.98. IR: ν (cm⁻¹): 3525(OH), 3433, 3337(NH), 1669(C=O), 1612(C=N); MS: (M⁺NHNH₂) (%) = 202 (9.16), 201 (72), 170 (100), 140 (20), 101 (38.5); ¹H-NMR (CDCl₃) δ (ppm): 8.02 (d, 1H, H7), 7.88 (d, 1H, H6), 7.6 (m, 1H, H5), 7.5 (m, 1H, H8), 3.54 (s, 5H, 2NH₂, OH), 2.6 (s, 2H, CH₂).

(3-(Benzylidene-hydrazono)-2-oxo-2,3-dihydro-indol-1-yl)-acetic acid benzylidene-hydrazide derivatives: (**4-6**)

Benzaldehyde or its derivative (20.0 mmol) was added to an acidified (few drops of CH₃COOH) stirred solution of (**3**) (2.3 g, 10.0 mmol) in EtOH (20 ml). The mixture was heated on a water bath for 2h, the precipitate was filtered, washed with EtOH and crystallized from methanol to give the following compounds:

(3-Hydrazono-2-oxo-2,3-dihydro-indol-1-yl)-acetic acid benzylidene-hydrazide: (HL¹)

Yield: 85.3%; m.p. 196-198°C. Anal.: calcd. (%) for C₁₇H₁₅N₃O₂: C, 63.54; H, 4.71; N, 21.79; found (%): C, 63.32 H, 4.77; N, 21.69. IR ν (cm⁻¹): 3478 (OH), 3351 (NH), 1657(C=O), 1596, 1565 (C=N); MS: M⁺ (%) = 321 (0.03), 305 (0.05), 291(0.17), 187 (13.75), 186 (95.36), 170 (87.18); 142 (100); ¹H-NMR δ (ppm): 12.1 (s, 1H, NH), 8.3 (s, 1H, CH), 8.0 - 7.2 (m, 11 H, 9 Ar-H, NH₂), 2.7 (s, 2H, CH₂).

(3-Hydrazono-2-oxo-2,3-dihydro-indol-1-yl)-acetic acid (4-methoxybenzylidene)-hydrazide: (HL²)

Yield 57%; m.p. 211-213°C. Anal.: calcd.(%) for C₁₈H₁₇N₃O₃: C, 61.53; H, 4.88; N, 19.93; found (%): C, 61.51; H, 4.75; N, 19.89. IR ν (cm⁻¹): 3447 (OH), 3293 (NH), 1650 (C=O), 1605, 1542 (C=N); MS: (M⁺-OCH₃) (%) = 321 (0.7), 320 (5.72), 319 (24.1), 186 (95.25), 170 (82), 142 (100), 134 (23); ¹H-NMR δ (ppm): 12.01 (s, 1H, NH), 8.26 (s, 1H, CH), 8.11-6.81 (m, 10H, 8Ar-H, NH₂), 3.81 (s, 3H, OCH₃), 2.71 (s, 2H, CH₂).

(3-Hydrazono-2-oxo-2,3-dihydro-indol-1-yl)-acetic acid (4-chlorobenzylidene)-hydrazide: (HL³)

Yield 75.5%; m.p. 197-200°C. Anal.: calcd.(%) for C₁₇H₁₄ClN₃O₂: C, 57.39; H, 3.97; N, 19.68; found (%): C, 57.37; H, 3.99; N, 19.71. IR ν (cm⁻¹): 3443 (OH), 3315 (NH), 1669 (C=O), 1594, 1559 (C=N); MS: (M+2)⁺ (%) = 357.15 (0.07), M⁺ (%) = 355.5 (0.25), 325 (2.7), 186 (85), 170 (100), 142 (84.6), 101 (27.6); ¹H-NMR δ (ppm): 12.16 (s, 1H, NH), 8.35 (s, 1H, CH), 8.14-7.1 (m, 10H (8Ar-H, NH₂), 2.72 (s, 2H, CH₂).

Synthesis of the complexes

To a solution of the Schiff-base (2 mmol) in EtOH (10 ml), a solution of

the metal salt (1 mmol) in ethanol (10 ml) was added dropwise with stirring. The pH of the mixture was increased to 7–7.5 by addition of dilute KOH solution. The whole mixture is refluxed with stirring for 2 hours. The formed precipitate was filtered, washed with hot EtOH and dried under vacuum over anhydrous CaCl_2 . Since the complexes were insoluble and non crystallizable in common organic solvents, they were purified by washing thoroughly with hot ethanol to remove unreacted metal salts.

Growth media

Nutrient agar medium of the following composition peptone 5.0 g, beef extract 3.0 g, NaCl 5.0 g, agar 18.0 g and 1000 ml water has been used for growing test organisms. The prepared media was poured into 9 cm plates and allowed to solidify. Spore suspensions from actively growing cultures were prepared using sterile distilled water. One ml of spore suspension was transferred to these plates and incubated at 37°C for appropriate growth periods (1-3 days). 100 ppm of the tested compound was dissolved in DMF, while DMF itself was used as control for comparison. The diameters of cleaning zones (in mm) have been used as a parameter for antibacterial activity. Accordingly, the resulting effects have been tentatively classified as follows: slightly active (1-10 mm); moderately active (11-20 mm); highly active (20-30 mm) and very highly active (>30 mm). Streptomycin was used as standard.

RESULTS AND DISCUSSION

Characterization of the Schiff-bases

Reaction of isatin (**1**) with ethyl chloroacetate afforded 2,3-dioxo-2,3-dihydroindol-1-yl acetic acid ethyl ester (**2**) which upon reaction with hydrazine hydrate in presence of acetic acid gave 3-hydrazono-2-oxo-2,3-dihydroindole-1-ylacetic acid hydrazide (**3**). On heating (**3**) with each of benzaldehyde, anisaldehyde and p-chlorobenzaldehyde in ethanol containing few drops of acetic acid afforded the Schiff-bases HL¹-HL³ respectively (Scheme 1)

Scheme (1)

Compound (**3**) shows three absorption bands at 3525, 3433 and 3337 cm^{-1} due to the hydrazide and hydrazone groups. This structure was also confirmed by the $^1\text{H-NMR}$ spectra which showed the presence of a broad singlet at δ 3.54 ppm assigned to the hydrazide and hydrazone groups together with two doublets and three triplets in the δ 8.03-7.41 ppm range attributed to the four aromatic protons besides a singlet at δ 2.6 ppm due to the methylene protons. Mass spectrum of compound (**3**) shows that it loses a hydrazine molecule to give the ketene radical cation with $m/z = 201$. IR spectrum of (**2**) shows three absorption bands at 1696, 1675 and 1653 cm^{-1} assigned to the frequency of the carbonyl groups. Mass spectrum of compound (**2**) showed the expected $m/z = 233$ which loses the ethyl radical to give the cation with $m/z = 205$.

IR spectra of the Schiff-bases HL¹-HL³ showed a sharp medium intensity band in the 3443-3478 cm^{-1} range assigned to stretching vibration of the (OH)

group and disappearance of (NH) and amide (C=O) bands due to enolization. These considerations suggest that the ligand has keto-enol tautomerism and exist primarily in the enol form. The spectra exhibit a characteristic splitted band in the 3266-3351 cm^{-1} range which is assigned to $\nu(\text{NH}_2)$ in addition to strong intensity band in the 750-765 cm^{-1} range due to wagging vibration. A strong band appeared at 1669-1650 cm^{-1} range is due to the isatin $\nu(\text{C=O})$ group. Two bands are shown in the 1605-1594 and 1565-1542 cm^{-1} range which have been assigned as $\nu(\text{C=N})$ of ketimine and aldimine moieties. $^1\text{H-NMR}$ spectra showed signals attributed to the CH_2 , Ar-H, NH_2 , CH, and the NH. $^1\text{H-NMR}$ of compound (**5**) showed in addition to the previous signals a new singlet at δ 3.81 ppm assigned to the OCH_3 protons. Mass spectra confirm the proposed structures of compounds (**4-6**).

Metal complexes

All the complexes are stable at room temperature and non-hygroscopic in nature. The stoichiometric ratios of the complexes have been calculated from their elemental analysis. The complexes are insoluble in water and common organic solvents (methanol, ethanol, benzene, chloroform, acetone, dichloroethane and diethyl ether) but soluble in DMSO and DMF. The analytical data (Table 1) show the following formulae for the complexes: $[\text{Cu}(\text{HL}^{1-3})_2](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ where $n=5, 1\frac{1}{2}, 0$; $[\text{Fe}_2(\text{L}^{1-3})(\text{NO}_3)_x(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_z \cdot n\text{H}_2\text{O}$ where $x=5, 5, 3$; $z=0, 0, 2$; $n=4, 1, 2$ and $[\text{M}_2(\text{L}^{1-3})(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ where $\text{M}=\text{Zn}(\text{II})$ and $\text{Mn}(\text{II})$ and $n=1, 1\frac{1}{2}, 1\frac{1}{2}, 1, 3$. The molar conductance values in DMF show that the Cu(II) complexes are 1:2 electrolytes, the Fe(III) complexes are none-electrolytes except $[\text{Fe}_2(\text{L}^3)(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ which is 1:2 electrolyte, the Zn(II) and Mn(II) complexes are 1:3 electrolytes.²¹

IR Spectra

Some structurally significant IR bands of the free Schiff-bases and their transition metal complexes are set out in Table 2.

The IR spectra of the Cu(II), Fe(III), Zn(II) and Mn(II) complexes show the absence of $\nu(\text{NH}_2)$ band due to overlapping with crystallization water band while the band due to wagging vibration is shifted to lower frequency indicating coordination through the amino nitrogen atom. A slight shift with decreasing intensity of isatin $\nu(\text{C=O})$ band confirms involvement of the carbonyl oxygen in complexation. The disappearance of $\nu(\text{OH})$ band in the spectra of the complexes indicates deprotonation and participation in coordination with metal ions. On the other hand, for the Cu(II) complexes the (OH) band is disappeared due to overlapping with hydrated water band, and the deformation band $\delta(\text{OH})$ at 1250 cm^{-1} almost has the same frequency as in the free ligand indicating non-involvement of the OH group in coordination. The shifting in $\nu(\text{C=N})$ band of the aldimine moiety can be attributed to involvement in bonding while $\nu(\text{C=N})$ of the ketimine moiety appeared nearly at the same frequency as the parent ligand indicating non-participating in bonding. The presence of coordinated nitrate ions are indicated by two medium intensity bands at 1450, 1358 and 1432, 1302 cm^{-1} in the $[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and $[\text{Fe}_2\text{L}^2(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complexes due to ν_4 and ν_1 vibrations of the nitrate ion of C_{2v} Symmetry²². Since $(\nu_4-\nu_1) = 92$ and 130 cm^{-1} , the nitrate ions are coordinated as unidentate group. These two complexes also exhibit bands due to bidentate nitrate groups which show bands at 1506, 1292 and 1501, 1285 cm^{-1} with $(\nu_4-\nu_1) = 214$ and 216 cm^{-1} . This is emphasized by the molar conductance of the complexes which have values of 40 and 45 $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ of 10^{-3}M DMF solution, indicating its non-electrolytic nature and hence the nitrate ions are coordinated to the metal center. The IR spectrum of $[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ shows bands due to bidentate nitrate groups at 1500 and 1281 cm^{-1} where $(\nu_4-\nu_1) = 219 \text{ cm}^{-1}$ together with strong and a medium intensity bands at 1381 and 855 cm^{-1} due to the ν_3 and ν_2 vibrations of the ionic nitrate (D_{3h})²². The Cu(II), Zn(II) and Mn(II) complexes show strong bands in the 1367-1384 cm^{-1} range and medium intensity bands in the 837-863 cm^{-1} range, due to the ν_3 and ν_2 vibrations of the ionic nitrate (D_{3h})²³. A non ligand bands appear in the 515-612 and 413-515 cm^{-1} range in all the complexes have been assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ ²⁴. Water of crystallization is shown by a medium intensity broad band in the 3373-3525 cm^{-1} range in the spectra of the complexes.

Magnetic and spectral studies

Magnetic moments and visible spectra of the complexes were used to study the geometrical configuration of the metal complexes.

The magnetic moment values for the zinc(II) complexes are zero consistent with its d^{10} configuration. Copper(II) complexes show magnetic moment values in the 2.0-1.97 B.M. range which are close to spin only value. This range indicates the absence of any appreciable spin-spin coupling between unpaired electrons belonging to different molecules. According to Figgis²⁵, a magnetic moment value greater than 1.9 B.M. indicates tetrahedral or octahedral

stereochemistry, while magnetic moment value less than 1.9 B.M. is indicative of square planer as well as tetrahedral stereochemistry. This shows that the magnetic moment of the Cu(II) complexes is not of much use in deciding on the stereochemistry of copper(II) complex.

The magnetic moments reported for the Fe(III) and Mn(II) complexes are lower than the spin only values. The subnormal magnetic moments observed for the complexes may be accounted for by the following:

a- Antiferromagnetic exchange interaction between the metal ions, suggesting the possibility of spin-spin coupling^{26, 27}.

b- The possibility that the reduced moment represent a solid state intermolecular interaction rather than an intramolecular coupling.

These considerations confirm the binuclear structure of the complexes. Such lowering of the magnetic moment has been observed with other polynuclear complexes²⁸.

Electronic spectra of the Schiff-bases and their complexes are recorded in DMF. The copper(II) complexes show a broad band in the 625-665 nm range which can be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition of copper(II) ion with octahedral geometry²⁹. The spectra of the Fe(III) complexes exhibit a band in the 516-485 nm range corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition consistent with octahedral Fe(III) complexes^{29,30}. The electronic spectra of the low-spin manganese complex is dominated by strong charge-transfer bands. Any d-d band occurring in the visible region is masked by strong charge-transfer bands.

Thermal Decomposition

Thermal decomposition of the complexes studied in these work represents characteristic pathways depending on the metal used as can be seen from the TGA/DTG and DTA curves shown in Figures 1 and 2. The decomposition stages, temperature ranges, decomposition products, as well as the found and calculated weight loss are given in Tables 3 and 4.

Table 1: Analytical data, conductivity values and magnetic moments of the Schiff-bases and their complexes.

Comopound	M.wt.	Color	M.p. °C.	Yield %	Elemental analysis Found Calcd. %				*Λ _M DMF	**μ _{eff} /M
					C	H	N	M		
HL ¹	320.82	yellow	198	85.3	63.49 63.58	4.51 4.67	21.91 21.81	—	—	—
[Cu(H L ₂ ¹)].(NO ₃) ₂ .5H ₂ O	918.48	green	>380	72.3	44.31 44.36	4.09 4.34	18.31 18.27	7.35 6.91	130	2.0
[Fe ₂ L ¹ (NO ₃) ₃ (H ₂ O) ₂].4H ₂ O	849.35	brown	>380	63.2	24.23 24.01	3.44 3.17	16.53 16.48	13.51 13.14	40	2.72
[Zn ₂ L ¹ (H ₂ O) ₄].(NO ₃) ₃ .H ₂ O	726.51	yellow	>380	51.66	27.93 28.07	3.55 3.44	15.76 15.41	18.43 18.00	207	Dia.
[Mn ₂ L ¹ (H ₂ O) ₄].(NO ₃) ₃ .H ₂ O	705.60	brown	>380	52.55	28.87 28.91	3.63 3.54	15.92 15.87	15.48 15.57	220	3.09
HL ²	350.82	white	213	57	61.49 61.56	4.77 4.84	19.91 19.95	—	—	—
[Cu(H L ₂ ²)].(NO ₃) ₂ .1½H ₂ O	916.12	green	196	79.65	47.21 47.13	4.12 4.03	18.11 18.33	7.42 6.93	140	1.97
[Fe ₂ L ² (NO ₃) ₃ (H ₂ O) ₂].H ₂ O	825.35	brown	220	64.22	26.36 26.17	2.69 2.78	16.73 16.96	13.53 13.95	45	1.69
[Zn ₂ L ² (H ₂ O) ₄].(NO ₃) ₃ .½H ₂ O	747.51	yellow	296	52.65	28.83 28.89	3.11 3.47	14.61 14.98	17.81 17.49	220	Dia.
[Mn ₂ L ² (H ₂ O) ₄].(NO ₃) ₃ .1½H ₂ O	744.6	brown	>380	51.32	29.11 29.00	3.63 3.75	15.31 15.04	14.91 14.75	225	2.11
HL ³	355.32	white	200	75.5	57.48 57.40	3.81 3.93	19.67 19.7	—	—	—
[Cu(H L ₂ ³)].(NO ₃) ₂	897.48	green	245	78.32	44.47 44.51	3.31 3.27	18.01 18.33	6.8 7.07	115	1.97
[Fe ₂ L ³ (NO ₃) ₃ (H ₂ O) ₂].(NO ₃) ₂ . 2H ₂ O	847.85	brown	305	68.26	24.23 24.06	2.38 2.59	16.86 16.51	13.45 13.17	145	1.66
[Zn ₂ L ³ (H ₂ O) ₄].(NO ₃) ₃ .H ₂ O	761.01	yellow	>380	53.22	26.92 26.80	2.98 3.15	14.83 14.71	17.23 17.18	207	Dia.
[Mn ₂ L ³ (H ₂ O) ₄].(NO ₃) ₃ .3H ₂ O	776.10	brown	>380	56.21	26.35 26.28	3.73 3.60	14.52 14.43	13.97 14.15	205	3.17

* Conductance of 10⁻³M (ohm⁻¹.cm².mol⁻¹)

** μ_{eff} at T=298°K B.M.

Table 2: IR spectral data of the Schiff-bases and its complexes.

Compound	ν H ₂ O ν OH ν NH ₂	ν (C=O)	ν (C=N)	ν (NO ₃)	ν (M-O)	ν (M-N)
HL ¹	— 3478s. 3351 s. 3266	1657s.	1596s. 1565s.	—	—	—
[Cu(H L ₂ ¹)](NO ₃) ₂ ·5H ₂ O	3423br.	1645m.	1596s. 1539s.	1383s. 863m.	532m.	500m.
[Fe ₂ L ¹ (NO ₃) ₃ (H ₂ O) ₂].4H ₂ O	3373br.	1647m.	1603s. 1550m.	1506m. 1450m. 1358m. 1292m.	612m.	479m.
[Zn ₂ L ¹ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	3423br.	1638m.	1595s. 1574m.	1380s. 837m.	602m.	474br.
[Mn ₂ L ¹ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	3422br.	1641m.	1596s. 1549m.	1382s. 860m.	518m.	429m.
HL ²	— 3447br. 3293 s. 3200	1650s.	1605s. 1542m.	—	—	—
[Cu(H L ₂ ²)](NO ₃) ₂ ·1½H ₂ O	3525br. 3445br	1662m.	1600s. 1530m.	1383s. 863m.	550m.	505m.
[Fe ₂ L ² (NO ₃) ₃ (H ₂ O) ₂].H ₂ O	3418br.	1668m.	1600m. 1529m.	1501m. 1432m. 1302m. 1285m.	526m.	481m.
[Zn ₂ L ² (H ₂ O) ₄](NO ₃) ₃ ·½H ₂ O	3428br.	1670m.	1601m. 1521m.	1383s. 845m.	522m.	462br.
[Mn ₂ L ² (H ₂ O) ₄](NO ₃) ₃ ·1½H ₂ O	3423br.	1633m.	1601m. 1522m.	1382s. 860m.	519br.	515br.
HL ³	— 3443s. 3315 s. 3283	1669s.	1594s. 1559s.	—	—	—
[Cu(H L ₂ ³)](NO ₃) ₂	— 3440br.	1654m.	1592m. 1540s.	1384s. 860	533m.	413m.
[Fe ₂ L ³ (NO ₃) ₃ (H ₂ O) ₂](NO ₃)·2H ₂ O	3439br.	1652m.	1592m. 1541m.	1500m. 1381s. 1281m. 855m.	515m.	467m.
[Zn ₂ L ³ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	3428br.	1650s.	1600s. 1543m.	1367s. 837m.	533m.	467m.
[Mn ₂ L ³ (H ₂ O) ₄](NO ₃) ₃ ·3H ₂ O	3419br.	1650m.	1599m. 1538m.	1383s. 855m.	526m.	450m.

m=medium, s=strong, br=broad

HL¹ decomposes in three steps. The first step takes place in the 95-140°C range with DTG maximum at 124°C associated with weight loss of 5.25% (calcd. 4.98%), which represents the elimination of NH₃ molecule. This step is confirmed by endothermic DTA change in the 100-140°C range with maximum at 124°C. Melting of this Schiff-base is shown by a sharp endothermic peak at 203°C. In the second step the ligand continue decomposition to lose CH₂CONHNCHC₆H₅ fragment that appears in the 233-364°C range with DTG maximum at 329°C. DTA confirms this step by appearing of a sharp exothermic change in the 221-345°C range with maximum at 271°C indicating decomposition of the ligand. Final decomposition of the ligand takes place in the 435-597°C range with DTG maximum at 490°C and weight loss of 42.85% (calcd. 43.0%). This step is confirmed by two successive exothermic changes in the 435-505°C and 506-595°C range with DTA maxima at 465 and 543°C.

The ligand has no plateau at 700 °C which indicates that it is not completely decomposed.

Copper(II) complexes decompose in four steps for [Cu(HL₂¹)](NO₃)₂·5H₂O and [Cu(HL₂²)](NO₃)₂·1½H₂O and three steps for [Cu(HL₂³)](NO₃)₂. The dehydration process takes place in the first two steps for [Cu(HL₂¹)](NO₃)₂·5H₂O complex in the 25-90 and 145-187°C range with TGA maxima at 55 and 166°C. This process is associated with mass loss of 3.9 and 5.86 % (calcd. 3.9 and 5.5%) representing the elimination of two and three molecules of crystallization water accompanied with DTA change in the 32-92 and 150-187°C range with endothermic and exothermic peaks at 62°C and 163°C. This indicates that the complex has two different types of hydrated water, loosely and strongly bound water. The dehydration process of [Cu(HL₂²)](NO₃)₂·1½H₂O complex takes place in the first step in the 30-72°C

range with DTG maximum at 56°C with mass loss of 2.97% (calcd. 2.94%) indicating dehydration of 1½ molecule of hydrated water. DTA confirms this step by endothermic change in the 32-72°C range with maximum at 53°C. Evaporation of the nitrate ions and partial decomposition of the ligand start in the third step for the $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ in the 190-270°C range with DTG maximum at 245°C associated with mass loss of 20.0% (calcd. 20.17%). This step is confirmed by appearance of exothermic change in the 202-282°C range with DTA maximum at 247°C. This process takes place in the second step for $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ in the 170-207°C range with DTG maximum at 194°C and mass loss of 15.6% (calcd. 15.5%). DTA confirms this step by sharp exothermic change in the 178-220°C with maximum at 196°C related to the melting process of the complex. $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2$ loses its nitrate ions as nitric acid in the first step in the 240-275°C range with DTG maximum at 260°C accompanied with mass loss of 14.0% (calcd. 14.03%). This step is shown by exothermic DTA change in the 252-275°C range with maximum at 259°C. The ligand continues decomposition in $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ where 33% of

the ligand decomposes in the 280-342°C range with DTG maximum at 305°C and mass loss of 23.0% (calcd. 23.13%). This complex has no plateau at 700°C indicating incomplete decomposition. In the $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ complex 44% of the ligand decomposes in the 207-347°C range with two DTG maxima at 260°C and 311°C accompanied with mass loss of 33.37% (calcd. 33.69%) and endothermic DTA change in the 262-340°C range with maximum at 302°C. The complex reaches final decomposition with formation of CuO in the 430-582°C range with DTG maximum at 487°C and mass loss of 39.56% (calcd. 39.82%). DTA confirms this step by exothermic change at 481°C. The ligand in $[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2$ decomposes in the 320-390°C and 510-570°C range with DTG maxima at 303, 346, 373 and 537°C, and mass loss of 58.52 and 6.4% (calcd. 58.59 and 5.91%), respectively. DTA confirms this decomposition by exothermic changes in the 280-511 and 512-578°C range with maxima at 308, 349, 380 and 548°C, respectively. The complex has no plateau at 700°C indicating incomplete decomposition.

Table 3: TGA. and DTG data of the HL¹, HL² and HL³ Schiff-bases and their complexes.

Compound	Temp. range °C	DTG °C	Mass loss%		Process	Product	Residue% and type
			Found	Calcd.			Found(Calcd.)
HL ¹	95-140 233-364 435-597	124 329 490	5.25 50.0 42.85	4.98 50.18 43.0	Partial decomposition Decomposition Final decomposition	NH ₃ CH ₂ CONHNCHC ₆ H ₅ 0.43 L	Not complete
$[\text{Cu}(\text{HL}_2^1)](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$	25-90 145-187 190-270 280-342	55 166 245 305	3.9 5.86 20.0 23.0	3.9 5.5 20.17 23.13	Dehydration Dehydration Partial decomposition Decomposition	2H ₂ O 3H ₂ O 2HNO ₃ +0.09 L 0.33 L	Not complete
$[\text{Fe}_2\text{L}^1(\text{NO}_3)_5(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	19-124 182-245 312-488	59 107 219 374 427	8.28 15.06 31.44	8.47 14.82 31.39	Dehydration Coordination sphere Coordination sphere	4H ₂ O 2HNO ₃ 3HNO ₃ +2H ₂ O+0.13L	Not complete
$[\text{Zn}_2\text{L}^1(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	20-130 194-335 345-447	93 254 407	2.88 9.60 8.26	2.48 9.91 8.52	Dehydration Coordinated water Ionization sphere	H ₂ O 4H ₂ O HNO ₃	Not complete
$[\text{Mn}_2\text{L}^1(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	30-132 133-192 252-392	53 154 296	2.8 4.88 4.73	2.55 5.10 5.10	Dehydration Coordinated water Coordinated water	H ₂ O 2H ₂ O 2H ₂ O	Not complete
$[\text{Cu}(\text{HL}_2)](\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	26-62 170-207 207-347 430-582	46 194 260 311 487	2.97 15.60 33.37 39.56	2.94 15.38 33.69 39.82	Dehydration Ionization sphere Partial decomposition Final Decomposition	1.5H ₂ O 2HNO ₃ + CH ₃ 0.44L 0.52L	8.52 (8.68) CuO
$[\text{Fe}_2\text{L}^2(\text{NO}_3)_5(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	22-63 205-302 330-367 418-455 456-563	47 238 267 358 443 522	2.21 27.15 15.5 5.5 28.11	2.18 27.25 15.25 5.52 28.49	Dehydration Coordination sphere Coordination sphere Partial decomposition Final decomposition	H ₂ O 3HNO ₃ +2H ₂ O 2HNO ₃ 0.13L 0.67L	Fe ₃ O ₄ 21.0 (18.7)

Table (3): Continued

$[\text{Zn}_2\text{L}^2(\text{H}_2\text{O})_4].(\text{NO}_3)_3.1/2\text{H}_2\text{O}$	19-80 219-315 355-448	56 287 386	1.34 9.51 11.76	1.20 9.63 11.71	Dehydration Coordinated water Partial decomposition	$0.5\text{H}_2\text{O}$ $4\text{H}_2\text{O}$ $\text{HNO}_3 + 0.07\text{L}$	Not complete
$[\text{Mn}_2\text{L}^2(\text{H}_2\text{O})_4].(\text{NO}_3)_3.1/2\text{H}_2\text{O}$	26-100 105-200 201-437	67 31 187 294 332	3.96 9.42 34.97	3.62 9.66 35.26	Dehydration Coordinated water Partial decomposition	$1.5\text{H}_2\text{O}$ $4\text{H}_2\text{O}$ $3\text{HNO}_3 + 0.21\text{L}$	Not complete
$[\text{Cu}(\text{H L}_2^3)].(\text{NO}_3)_2$	240-275 320-390 510-570	260 303 346 373 537	27.35 58.52 6.4	27.57 58.59 5.91	Ionization sphere Decomposition Ligand decomposition	2HNO_3 0.74L 0.07L	Not complete
$[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2].(\text{NO}_3)_2.2\text{H}_2\text{O}$	28-110 182-298 312-400	63 230 350 379	3.90 14.67 26.21	4.24 14.85 26.52	Dehydration Ionization sphere Coordination sphere	$2\text{H}_2\text{O}$ 2HNO_3 $3\text{HNO}_3 + 2\text{H}_2\text{O}$	Not complete
$[\text{Zn}_2\text{L}^3(\text{H}_2\text{O})_4].(\text{NO}_3)_3.\text{H}_2\text{O}$	158-231 232-395 406-453 477-657	213 299 436 564	2.75 25.87 8.0 37.12	3.33 26.01 8.27 37.35	Dehydration Ionization sphere + coordinated water Ionization sphere. Final decomposition	H_2O $4\text{H}_2\text{O} + 2\text{HNO}_3$ HNO_3 0.8L	25.71/21.39 ZnO
$[\text{Mn}_2\text{L}^3(\text{H}_2\text{O})_4].(\text{NO}_3)_3.3\text{H}_2\text{O}$	13-93 237-320 377-547	53 288 409	7.35 19.68 16.95	6.95 19.43 17.39	Dehydration Partial decomposition Ionization sphere + coordinated water	$3\text{H}_2\text{O}$ $2\text{HNO}_3 + 0.07\text{L}$ $\text{HNO}_3 + 4\text{H}_2\text{O}$	Not complete

Table 4: DTA data of the HL^1 , HL^2 and HL^3 Schiff-bases and their complexes.

Compounds	Temp. rang. °C	DTA peak °C	$\Delta\text{H J/g}$	Process
HL^1	100-140 195-220 221-345 435-505 506-595	124 endo. 203 endo. 271 exo. 465 exo. 543 exo.	314 429 -300 -461 -1120	Partial decomposition Melting Decomposition Decomposition Final decomposition
$[\text{Cu}(\text{H L}_2^1)].(\text{NO}_3)_2.5\text{H}_2\text{O}$	32-92 150-187 202-282	62 endo. 163 exo. 247 exo.	132 -19 -337	Dehydration Dehydration Ionization sphere
$[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2].4\text{H}_2\text{O}$	30-124 184-206 279-494	64 endo. 109 219 endo. 379 exo. 427 exo.	70 36 58 -6430	Dehydration Coordination sphere Coordination sphere
$[\text{Zn}_2\text{L}^1(\text{H}_2\text{O})_4].(\text{NO}_3)_3.\text{H}_2\text{O}$	120-140 313-329 357-442	132 endo. 317 endo. 404 exo.	30 34 238	Dehydration Coordinated water Ionization sphere
$[\text{Mn}_2\text{L}^1(\text{H}_2\text{O})_4].(\text{NO}_3)_3.\text{H}_2\text{O}$	30-85 128-150 277-330	62 endo. 132 endo. 303 exo.	22 31 -69	Dehydration Coordinated water Coordinated water
$[\text{Cu}(\text{H L}_2^2)].(\text{NO}_3)_2.1/2\text{H}_2\text{O}$	32-72 178-220 262-340 415-598	51 endo. 196 exo. 302 endo. 481 exo.	91 -174 142 -7950	Dehydration Melting Partial decomposition Final decomposition

Table 4. Continued

$[\text{Fe}_2\text{L}^2(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	32-82 206-221 221-261 300-405 406-455 456-580	58 endo. 220 endo. 236 exo. 363 exo. 443 exo. 535 exo.	25 174 -272 -651 -240 -5150	Dehydration Melting Coordination sphere Coordination sphere Partial decomposition Final decomposition
$[\text{Zn}_2\text{L}^2(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	64-132 298-315 316-427	97 endo. 303 endo. 391 exo.	10 62 -1100	Dehydration Melting Partial decomposition
$[\text{Mn}_2\text{L}^2(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	26-61 118-150 151-239 240-335	43 endo. 137 endo. 203 endo. 299 exo.	34 59 141 -399	Dehydration Coordinated water Partial decomposition Partial decomposition
$[\text{Cu}(\text{H} \text{L}_2^3)] \cdot (\text{NO}_3)_2$	252-275 280-511 512-578	259 exo. 308 349 exo. 380 548 exo.	-308 -1071 -289	Partial decomposition Ligand decomposition Final decomposition
$[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	33-88 298-309 310-448	66 endo. 303 endo. 352 exo. 382	106 205 -2190	Dehydration Melting Coordination sphere
$[\text{Zn}_2\text{L}^3(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	166-227 350-388 427-453 474-657	210 endo. 367 endo. 443 exo. 569 exo.	190 61 -31 -5600	Dehydration Ionization sphere+ coordinated water Ionization sphere. Final decomposition
$[\text{Mn}_2\text{L}^3(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	27-100 222-322	60 endo. 290 exo.	782 -2870	Dehydration Partial decomposition

Thermal decomposition of the iron(III) complexes takes place in three steps for $[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and $[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and five steps for $[\text{Fe}_2\text{L}^2(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. Dehydration process takes place in the first stage in the 30-124, 30-63 and 28-110°C range with DTG maxima at 59, 107; 52 and 63°C for $[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, $[\text{Fe}_2\text{L}^2(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and $[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. This step is correlated with mass loss of 8.28, 2.21 and 3.9 % (calcd. 8.47, 2.18 and 4.24 %) indicating the dehydration of four, one and two water molecules, respectively. DTA confirms this step by endothermic changes at 64, 109; 58 and 66°C. It is noted that $[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ dehydrate in two steps which indicates the presence of two types of crystallization water. $[\text{Fe}_2\text{L}^1(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and $[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ complexes show elimination of two coordinated nitrate ions as nitric acid in the 182-245 and 182-198°C range with DTG maximum at 219 and 230°C and mass loss of 15.06 and 14.67% (calcd. 14.82 and 14.85%). In the next step, elimination of three coordinated nitrate ions, two molecules of coordinated water and partial decomposition of the ligand take place in the 312-488 and 312-400°C range with DTG maxima at 374, 427°C and 350, 379°C associated with mass loss of 31.44 and 26.21% (calcd. 31.39 and 26.52%). This step is confirmed by a broad exothermic change in the 279-494 and 310-448°C range with maxima at 379, 427 and 352, 382°C for the two complexes. Sharp endothermic peak in the 298-309°C range with maximum at 303°C is related to the melting process for $[\text{Fe}_2\text{L}^3(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot (\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Both complexes have no plateau at 700°C which indicates incomplete decomposition. In the complex $[\text{Fe}_2\text{L}^2(\text{NO}_3)_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, three coordinated nitrate ions and coordinated water are eliminated in the second step while two nitrate ions are lost in the third step which is contrary to the other Fe(III) complexes. This happens in the 205-302 and 330-367°C range with DTG maxima at 238, 267 and 358°C correlated with mass loss of 27.15 and 15.5% (calcd. 27.25 and 15.25%). Sharp endothermic peak at 220°C indicates melting of the complex followed by decomposition at 236 and 363°C in the 221-261 and 300-405°C range. Partial decomposition of the ligand starts in the fourth step in the 418-455°C range with DTG maximum at 443°C associated with mass loss of 5.5% (calcd. 5.52%) and exothermic DTA change in the 406-455°C range with maximum at 443°C. Final decomposition with the formation of Fe_3O_4 takes place in the 456-563°C range with DTG maximum at 522°C and mass loss of 28.11% (calcd. 28.49%). DTA confirms this step by a broad

exothermic change in the 456-580°C range with maximum at 535°C.

Thermal decomposition of the Zinc(II) complexes takes place in three steps for $[\text{Zn}_2\text{L}^1(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and $[\text{Zn}_2\text{L}^2(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ complexes and four steps for $[\text{Zn}_2\text{L}^3(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ complex. The dehydration process takes place in the 30-130, 30-80 and 158-231°C range with DTG maxima at 93, 56 and 213°C associated with mass loss of 2.88, 1.34 and 2.75 (calcd. 2.48, 1.20 and 3.33 %), respectively. This step was also shown by endothermic peaks at 132, 97°C and 210°C, respectively. In $[\text{Zn}_2\text{L}^1(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, the second step is correlated with the elimination of four coordinated water molecules in the 194-335°C range with DTG maximum at 254°C and mass loss of 9.6% (calcd. 9.91%) and also accompanied with endothermic DTA peak at 317°C. Elimination of the nitrate ions as nitric acid starts in the third step in the 345-447°C range with DTG maximum at 407°C and mass loss of 8.26% (calcd. 8.52%). This step is confirmed by exothermic change in the 357-442°C range with DTA maximum at 404°C. This complex shows high thermal stability as only 26% of the complex decomposes in the temperature range of 30-700°C and so there is no plateau at 700 °C indicating incomplete decomposition. In the $[\text{Zn}_2\text{L}^2(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ complex, the coordinated water is eliminated also in the second step in the 219-315°C range with DTG maximum at 287°C accompanied with weight loss of 9.51% (calcd. 9.63%). This complex melts as shown by a sharp endothermic change in the 298-315°C range with DTA maximum at 303°C. Exothermic change in the 316-427°C range with maximum at 391°C indicates partial decomposition of the complex which appeared in the TGA/DTG curve in the 355-448°C range with maximum at 386°C and mass loss of 11.76% (calcd. 11.71%). The complex has no plateau at 700 °C which indicate that it is not completely decomposed. In the $[\text{Zn}_2\text{L}^3(\text{H}_2\text{O})_4] \cdot (\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ complex, four coordinated water molecules together with two nitrate ions are eliminated in the second step in the 232-395°C range with DTG maximum at 299°C and mass loss of 25.87% (calcd. 26.01%). DTA confirms this stage by endothermic peak at 367°C. In the third step a nitrate ion is eliminated as nitric acid in the 406-453°C range with maximum at 436°C and mass loss of 8.0% (calcd. 8.27%). This process is accompanied with exothermic DTA change in the 427-453°C range with maximum at 443°C. Final decomposition and formation of ZnO takes place in the last stage in the 477-657°C range with maximum at 564°C and mass loss of 37.12% (calcd. 37.35%). DTA calorigram shows this stage as exothermic change with maximum at 569°C.

Table 5: Antibacterial screening data of the Schiff-bases and their complexes.

Compound	Zone of Inhibition (mm)			
	Gram positive	Gram negative		
	<i>S. a.</i>	<i>K. p.</i>	<i>E. c.</i>	<i>P. v.</i>
DMF(Control)	-	-	-	-
HL ¹	-	8	7	-
[Cu(HL ₂ ¹)](NO ₃) ₂ ·5H ₂ O	15	7	9	-
[Fe ₂ L ¹ (NO ₃) ₃ (H ₂ O) ₂].4H ₂ O	8	16	6	-
[Zn ₂ L ¹ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	-	-	-	-
[Mn ₂ L ¹ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	7	9	6	-
HL ²	5	8	7	-
[Cu(HL ₂ ²)](NO ₃) ₂ ·1½H ₂ O	16	7	9	-
[Fe ₂ L ² (NO ₃) ₃ (H ₂ O) ₂].H ₂ O	15	6	8	-
[Zn ₂ L ² (H ₂ O) ₄](NO ₃) ₃ ·½H ₂ O	-	-	-	-
[Mn ₂ L ² (H ₂ O) ₄](NO ₃) ₃ ·1½H ₂ O	7	9	5	-
HL ³	6	8	7	-
[Cu(HL ₂ ³)](NO ₃) ₂	17	8	6	-
[Fe ₂ L ³ (NO ₃) ₃ (H ₂ O) ₂](NO ₃) ₂ ·H ₂ O	5	7	7	-
[Zn ₂ L ³ (H ₂ O) ₄](NO ₃) ₃ ·H ₂ O	16	6	7	-
[Mn ₂ L ³ (H ₂ O) ₄](NO ₃) ₃ ·3H ₂ O	5	18	8	-
Streptomycin	22	23	20	23

S. a. = *Staphylococcus aureus*.

K. p. = *Klebsiella pneumoniae*.

E. c. = *Escherichia coli*.

P. v. = *Proteus vulgaris*.

The complexes [Mn₂L¹(H₂O)₄](NO₃)₃·H₂O, [Mn₂L²(H₂O)₄](NO₃)₃·1½H₂O and [Mn₂L³(H₂O)₄](NO₃)₃·3H₂O show three decomposition steps. In the first step, the dehydration process takes place in the 30-132, 26-100 and 23-93°C range with DTG maxima at 53, 67 and 55°C with mass loss of 2.8, 3.96 and 7.35% (calcd. 2.55, 3.62 and 6.95%), respectively. DTA confirms this step by endothermic changes at 62, 63 and 60°C, respectively. In the complex [Mn₂L¹(H₂O)₄](NO₃)₃·H₂O, elimination of four coordinated water molecules takes place in the 133-192°C and 252-392°C range with TGA maxima at 154 and 296°C associated with mass loss of 4.88 and 4.73% (calcd. 5.10). DTA shows this step by endothermic and exothermic changes at 132 and 303°C. This indicates the non-equivalent bonding of the coordinated water. In the complex [Mn₂L²(H₂O)₄](NO₃)₃·1½H₂O, the coordinated water molecules are eliminated in the second step in the 105-200°C range with two DTG maxima at 131 and 187°C associated with mass loss of 9.42% (calcd. 9.66%). This is shown by endothermic changes in the 118-150 and 151-239°C range with DTA maximum at 137 and 203°C. Partial decomposition of the ligand and elimination of the nitrate ions as nitric acid begin in the third step in the 201-437°C range with two DTG maxima at 294 and 332°C. This step is accompanied with mass loss of 34.97°C (calcd. 35.26) and is confirmed by the appearing of exothermic change in the 240-335°C range with DTA maximum at 299°C. The complex has no plateau at 700 °C which indicates that it is not

completely decomposed. The complex [Mn₂L³(H₂O)₄](NO₃)₃·3H₂O shows the elimination of two nitrate ions as nitric acid and partial decomposition of the ligand in the second step in the 237-320°C range, with maximum at 288°C and mass loss of 19.68% (calcd. 19.43%). DTA confirms this step by sharp exothermic change with maximum at 290°C. In the third step elimination of the coordinated water molecules and a nitrate ion takes place. This process is accompanied with mass loss of 16.95% (calcd. 17.39%). The complex has no plateau at 700 °C indicating uncompleted decomposition.

Based on the above analytical data and physicochemical properties, the following structures are proposed in which the Cu(II) ions were coordinated through the carbonyl groups (C=O) of isatin, the amino groups and the two azomethine nitrogen C=N of the aldimine moiety. The Fe(III), Zn(II) and Mn(II) ions were bonded by the carbonyl groups (C=O) of isatin, the amino groups, C=O or the enolized carbonyl group (C-OH) of the amide, the azomethine nitrogen C=N of the aldimine moiety and the coordinated nitrate or water molecules.

R = H; x = 4
R = Cl; x = 1

R = H, OCH₃, Cl; M = Zn(II)
Mn(II)

Figure 1. TGA, DTG and DTA of the $[\text{CuL}_2](\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ complex.

R = H; x = 5
R = OCH₃; x = 1.5
R = Cl; x = 0

Figure 2. TGA, DTG and DTA of $[\text{Fe}_2\text{HL}^2(\text{NO}_3)_5(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complex.

Antibacterial activity

Antibacterial activity of the synthesized compounds has been screened using different strains of bacteria [*Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli*, *Proteus vulgaris*]. The disk diffusion method has been adapted for antibacterial activity³¹. The results are shown in Table 5.

It seems that all the synthesized compounds are devoted of activity against *Protus vulgaris* while all the compounds are slightly active against *Klebsiella pneumoniae* and *Escherichia coli*. $(\text{Cu}(\text{HL})_2(\text{NO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O})$ and $[\text{Cu}(\text{HL})_2(\text{NO}_3)_2]$ complexes are moderately active against *Staphylococcus aureus*. $[\text{Zn}_2\text{HL}^1(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and $[\text{Zn}_2\text{HL}^2(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ complexes are inactive against all the studied bacteria while $[\text{Zn}_2\text{HL}^3(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ complex is moderately active towards *Staphylococcus aureus*. $[\text{Mn}_2\text{HL}^3(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ complex has moderate activity against *Klebsiella pneumoniae* while $[\text{Mn}_2\text{HL}^1(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and $[\text{Mn}_2\text{HL}^2(\text{H}_2\text{O})_4](\text{NO}_3)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ are slightly active against *Staphylococcus aureus*. $[\text{Fe}_2\text{HL}^1(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and $[\text{Fe}_2\text{HL}^2(\text{NO}_3)_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ are moderately active against *Klebsiella pneumoniae* and *Staphylococcus aureus*.

The increased activity of the complexes compared to the free ligands can be explained on the bases of chelation theory³². Chelation reduces the polarity of the metal ion; mainly because of the partial sharing of its positive charge with donor groups and the possible π -electron delocalization over the whole chelate ring. Chelation not only reduces the polarity of metal ion, but also increases the lipophilic character of the chelate. As a result of this, interaction between metal ion and the cell walls is favored resulting in interference with normal cell processes. If the geometry and charge distribution around the molecule are incompatible with the geometry and charge distribution around the pores of the bacterial cell wall, penetration through the wall by the toxic agent cannot take place³³.

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