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Antioxidant, tautomerism and antibacterial studies of Fe(III)-1,2,4-triazole based complexes

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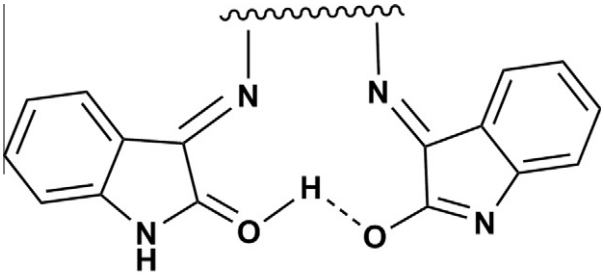
HIGHLIGHTS

- Structural characterization of Fe(III)-1,2,4-triazole based complexes.
- All the complexes were characterized by spectroscopy techniques.
- All the complexes were excellent interpretation and discussion.
- All the complexes show an effective antibacterial activity.

GRAPHICAL ABSTRACT

New Fe(III) complexes have been synthesized by 1,2,4-triazole based ligand complexes. FT-IR, ^{1}H and ^{13}H NMR studies reveal that the ligand (L_n) exists in the tautomeric enol form in both the states with intramolecular hydrogen bonding.



Keto-Enol Tautomerism

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ABSTRACT

New Fe(III) complexes have been synthesized by the reactions of ferric nitrate with Schiff base derived from 3-substituted phenyl-4-amino-5-hydrazino-1,2,4-triazole and indoline-2,3-dione. All these complexes are soluble in DMF and DMSO; low molar conductance values indicate that they are non-electrolytes. Elemental analyses suggest that the complexes have 1:1 stoichiometry of the type $[FeL_n(H_2O)(OH)]\cdot xH_2O$. Structural and spectroscopic properties have been studied on the basis of elemental analyses, infrared spectra, ^{1}H and ^{13}H NMR spectra, electronic spectra, magnetic measurements and FAB mass spectra. FT-IR, ^{1}H and ^{13}H NMR studies reveal that the ligand (L_n) exists in the tautomeric enol form in both the states with intramolecular hydrogen bonding. Magnetic moment and reflectance spectral studies reveal that an octahedral geometry has been assigned to all the prepared complexes. FRAP values indicate that all the compounds have a ferric reducing antioxidant power. The compounds 2 and 3 showed relatively high antioxidant activity while compound 1 and 4 shows poor antioxidant power. Also good antimicrobial activities of the complexes against *Staphylococcus aureus*, *Bacillus subtilis*, *Serratia marcescens*, *Pseudomonas aeruginosa* and *Escherichia coli* have been found compared to its free ligands.

Introduction

Triazoles and their derivatives are found to be associated with various biological activities, such as anticonvulsant, antifungal, anticancer, anti-inflammatory and antibacterial properties [1–9]. Several compounds containing 1,2,4-triazole ring are well known for drug synthesis [1]. 1,2,4-triazole containing amino group is also important for obtaining various Schiff base with well known

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antimicrobial properties [10–17]. Although many studies have investigated the antioxidant properties of resveratrol [18], there have been only a few reports of antioxidant and antiproliferative effects of hydroxyl-substituted Schiff bases.

Fe(III) complexes of Schiff bases are playing an important role in the development of coordination chemistry, which is evident in number of publications, including physicochemistry studies [19] and biological aspects [20–24]. Iron is one of the most important trace elements in the human body [25]. Increased iron availability in serum or tissues is associated with an increased risk of several tumors and may promote carcinogenesis [26]. Moreover, hereditary hemochromatosis is characterized by excess iron that causes tissue damage and fibrosis with irreversible damage to various organs [27]. Iron homeostasis is an important factor involved in neuroinflammation and progression of Alzheimer's disease [28].

In this study, Schiff base ligands and their Fe(III) complexes were synthesized and characterized by the analytical and spectroscopic methods. Antioxidant properties of the hydroxyl substituted Schiff base ligands were investigated. The antimicrobial activities of the ligands and their metal complexes were studied using the bacteria and yeast. The redox properties of the compounds were investigated by cyclic voltammetry. Thermal properties of the metal complexes were investigated in the 20–800 °C temperature range.

Materials and methods

Materials

The solvents were purchased from Merck and used without further purification. Ferric nitrate was purchased from Aldrich. The ligands were prepared as reported in literature [29]. Luria broth was purchased from Hi-media Laboratories Pvt. Ltd., India.

Instruments

Elemental analysis (C, H, N) was performed using a 2400-II CHN analyzer (PerkinElmer, USA). Analyses of metal ions was carried out by dissolution of the solid complexes in hot concentrated nitric acid, further diluting with distilled water and filtered to remove the precipitated organic ligands. The remaining solution was neutralized with ammonia solution and the metal ions were titrated against EDTA. The melting point of all compounds was measured using the open capillary tube method. FT-IR spectra (400–4000 cm^{-1}) were recorded with a Spectrum GX-PerkinElmer spectrophotometer using KBr pellets. ^1H NMR and ^{13}C-NMR spectra of ligands were recorded on a model Advance 400 Bruker FT-NMR instrument using tetramethylsilane as internal standard and DMSO-d_6 as solvent. The fast atom bombardment (FAB) mass spectrum of the complexes was recorded at SAIF, CDRI, Lucknow with a JEOL SX-102/DA-6000 mass spectrometer at room temperature using argon/xenon as the FAB gas. Electronic spectra (200–1200 nm) were collected using a LAMBDA 19 UV–visible/near-infrared spectrophotometer.

Thermal stability and decomposition of the complexes were determined by TG and DTG using a model 5000/2960 SDT (TA Instruments, USA). The experiments were performed in N_2 atmosphere at a heating rate of 20 °C min^{-1} in the temperature range 20–800 °C. Sample sizes ranging in mass from 3 to 8 mg were heated in an Al_2O_3 crucible. Magnetic susceptibility measurements were obtained by Gouy's method using mercury tetrathiocyanato cobaltate(II) as a calibrant ($w = 16.44 \times 10^{-6}$ c.g.s. units at 20 °C). Diamagnetic corrections were made using Pascal's constant [30].

Synthesis of ligands [31]

Synthesis of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazole

A mixture of 3-(substituted phenyl)-4-amino-5-mercapto-1,2,4-triazole and $N_2H_4{\cdot}H_2O$ in ethanol was boiled under reflux for 4–5 h on a water bath. The reaction mixture was cooled at room temperature, within an hour the compound separated from the clear solution. It was filtered, washed and recrystallized in ethanol.

Synthesis of Schiff bases

A mixture of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazole and indoline-2,3-dione in 1:2 M ratio in an alcoholic medium containing a few drops of conc. HCl was refluxed for 5–6 h. The product separated on evaporation of the alcohol was recystallized in ethanol.

General procedure for the synthesis of complexes

A general procedure was followed to synthesize these complexes. The procedure involves the addition of the appropriate ligand (0.04 mol) to an aqueous ethanolic solution of $Fe(NO_3)_3{\cdot}9H_2O$ (0.04 mol) and sodium acetate (0.08 mol). The mixture was refluxed for 10–11 h on a water bath. Reddish brown or orange precipitate obtained was filtered, washed with ethanol and hot water and dried *in vacuo* at room temperature. The complexes were obtained as powdered material.

The details of the reactions along with the analytical data of the product are given in Table 1. The general reaction scheme is given in Fig. 1.

Minimum inhibitory concentration value

An antibacterial activity assay was performed on *Staphylococcus aureus*, *Bacillus subtilis*, *Serratia marcescens*, *Pseudomonas aeruginosa* and *Escherichia coli*. The antibacterial activity for the test compounds was tested to determine the bacteriostatic concentration, i.e. minimum inhibitory concentration (MIC) in terms micromoles. The MIC value was determined by broth dilution technique [32]. A preculture of bacteria was grown in LB (Luria broth) overnight at the most favorable temperature of each species. This culture was used as a control to examine if the growth of bacteria tested was normal. In a similar second culture, 20 µl of the bacteria as well as the tested compound at the desired concentration were added and monitored for bacterial growth by measuring turbidity of the culture after 18 h. If a certain concentration of a compound inhibited bacterial growth, half of the concentration of the compound was tested. This procedure was carried out up to the concentration which inhibited the growth of bacteria. The lowest concentration that inhibited bacterial growth was considered the MIC value. All equipments and culture media were sterilized [33].

Antioxidant studies

Ferric reducing antioxidant power (FRAP) was measured by a modified method of Benzie and Strain [34]. The antioxidant potentials of the compounds were estimated as their power to reduce the TPTZ-Fe(III) complex to TPTZ-Fe(II) complex (FRAP assay), which is simple, fast, and reproducible. FRAP working solution was prepared by mixing a 25.0 mL, 10 mM TPTZ solution in 40 mM HCl, 20 mM $FeCl_3.6H_2O$ and 25 mL, 0.3 M acetate buffer at pH 3.6. A mixture of 40.0 mL, 0.5 mM sample solution and 1.2 mL FRAP reagent was incubated at 37 °C for 15 min. Absorbance of intensive blue color [Fe(II)-TPTZ] complex was measured at 593 nm. The ascorbic acid was used as a standard antioxidant compound. The results are expressed as ascorbic equivalent

Table 1
Physical properties and analytical data of Fe(III) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazole Schiff bases.

Compound	Color	Molecular weight found (Cal.)	% Analysis found (Cal.)				μ_{eff} (B.M)
			C	H	N	Fe(III)	
$L_1/C_{24}H_{16}N_8O_2$	Light yellow	448.08 (448.14)	64.22(64.28)	3.55(3.60)	24.89(24.99)	–	–
$L_2/C_{24}H_{15}ClN_8O_2$	Yellow	482.79 (482.88)	59.59(59.70)	3.09(3.13)	23.17(23.21)	–	–
$L_3/ C_{24}H_{15}ClN_8O_2$	Yellow	482.82 (482.88)	59.61(59.70)	3.01(3.13)	23.14(23.21)	–	–
$L_4/C_{24}H_{15}N_9O_4$	Light yellow	493.38 (493.43)	59.38(58.42)	3.04(3.06)	25.19(25.55)	–	–
$[FeL_1(H_2O)(OH)]\cdot 2H_2O/C_{24}H_{17}FeN_8O_4$	Reddish brown	573.23 (573.32)	50.21(50.28)	3.55(3.69)	19.30(19.54)	9.72(9.74)	5.98
$[FeL_2(H_2O)(OH)]\cdot H_2O/C_{24}H_{16}ClFeN_8O_4$	Orange	589.65 (589.75)	48.76(48.88)	3.01(3.08)	18.96(19.00)	9.45(9.47)	6.05
$[FeL_3(H_2O)(OH)]\cdot H_2O/C_{24}H_{16}ClFeN_8O_4$	Reddish brown	589.69 (589.75)	48.78(48.88)	2.97(3.08)	18.99(19.00)	9.42(9.47)	5.95
$[FeL_4(H_2O)(OH)]\cdot 2H_2O/C_{24}H_{16}FeN_9O_6$	Dull orange	618.28 (618.32)	46.58(46.62)	3.19(3.26)	20.20(20.39)	9.02(9.03)	5.99

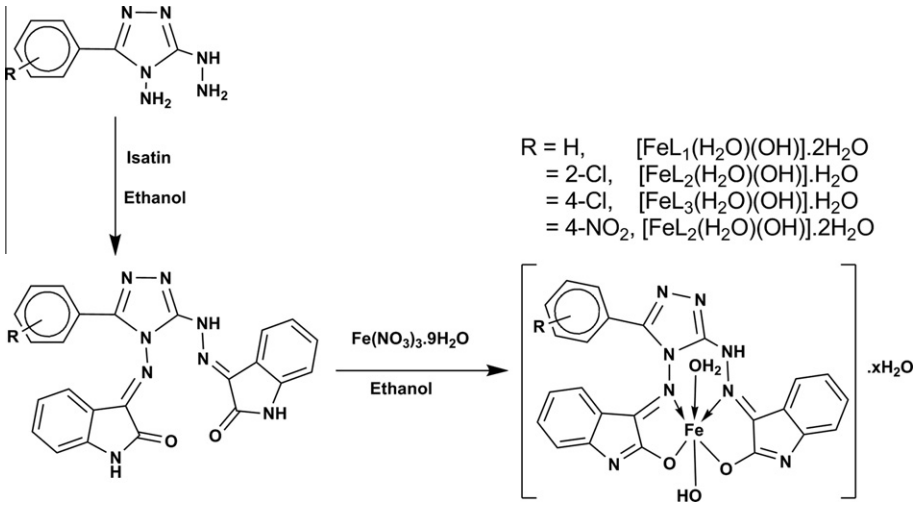

Fig. 1. Synthesis and structure of the ligand.

(mmol/100 g of dried compound). All the tests were run in triplicate and are expressed as the mean and standard deviation (SD).

Results and discussion

Chemistry

The structural investigation of all the prepared ligands (L_n) was done using elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy. The complexes were prepared by reacting ferric nitrate with variable ligands (L_1–L_4) in a 1:1 ratio. The analytical and physical data of the complexes are given in Table 1. The following chemical reaction describes the formation of the complexes:

$$Fe(NO_3)_3\cdot 9H_2O L_n \rightarrow [FeL_n(H_2O)(OH)]\cdot xH_2O + (7-m)H_2O + 3HNO_3$$
$$(\text{Where } n=1\&4, x=2; n=2\&3, x=1)$$

All the complexes are insoluble in water, ethanol, methanol, chloroform, acetonitrile, CCl_4 and hexane; while soluble in DMF and DMSO, so it is difficult to grow single crystals for X-ray Diffraction analysis.

IR spectra

The important infrared spectral bands and their tentative assignments for the synthesized ligand and its complexes were recorded as KBr disks and are discussed (Table 2).

The ligands show one medium intensity band at 1605 cm^{-1} assignable [35] to υ(C═N) which shifts to 1575 cm^{-1} in the complexes. This shift indicates the coordination of azomethine nitrogen to metal ion [36–39]. Schiff bases show broad band 2640 cm^{-1} due to intermolecular H-bonded OH group. This band disappears in their corresponding Fe(III) complexes indicating the coordination of phenolic oxygen to Fe(III) metal ion through deprotonation. This is further supported by shift in phenolic υ(C—O) band from 1285 cm^{-1} (in the free ligand) to 1380–1310 cm^{-1} in the complexes. The coordination through phenolic oxygen further confirmed by the appearance of band at 448–472 cm^{-1} assignable [40] to υ(Fe—O). The presence of coordinated water in the complexes [41] is indicated by a broad band in the region 3400 cm^{-1} and two weaker bands in the region 810–750 and 730–700 cm^{-1} due to υ(—OH) rocking and wagging mode of vibrations, respectively [42]. In the far-IR region, two new band at 448–472 and 418–420 cm^{-1} in the complexes are assigned to υ(Fe—O) and υ(Fe—N) respectively.

Tautomerism studies of ligands

The molecular structures of the ligands are such that they can exist in six tautomeric forms as shown in Fig. 2. Detailed solution and solid-state studies of this ligand were carried out to establish their geometry. The IR spectra provide valuable information regarding the Schiff base ligands appear to exist in both band (solution spectra) at 2600 cm^{-1}, due to intramolecular H-bonded OH group. The spectra of Schiff bases show a medium band at 3175 cm^{-1} due to υ(N—H) which remains almost at the same position in complex indicating the noninvolvement N—H group in bond formation. ^{1}H NMR chemical shift for the OH group was observed at δ 12.83 ppm. This signal disappeared when a D_2O exchange experiment carried out. It can be assigned either to OH of ligand group, in either case it is strongly deshielded because of hydrogen bonding with the other oxygen atom. It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragments of this signal, which suggests that only

Table 2
The importance infra red frequencies in (cm^{-1}) of Fe(III) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4- triazole Schiff bases.

Complex	IR frequency (cm^{-1})						
	υ(O—H)	υ(N—H)	υ(C=N)	υ(C=C)	Phenolic υ(C—O)	υ(Fe—O)	υ(Fe—N)
$[FeL_1(H_2O)(OH)]\cdot 2H_2O$	3410	3165	1575	1555	1355	449	420
$[FeL_2(H_2O)(OH)]\cdot H_2O$	3414	3150	1560	1560	1320	472	418
$[FeL_3(H_2O)(OH)]\cdot H_2O$	3320	3152	1580	1595	1323	448	419
$[FeL_4(H_2O)(OH)]\cdot 2H_2O$	3425	3150	1558	1520	1350	449	420

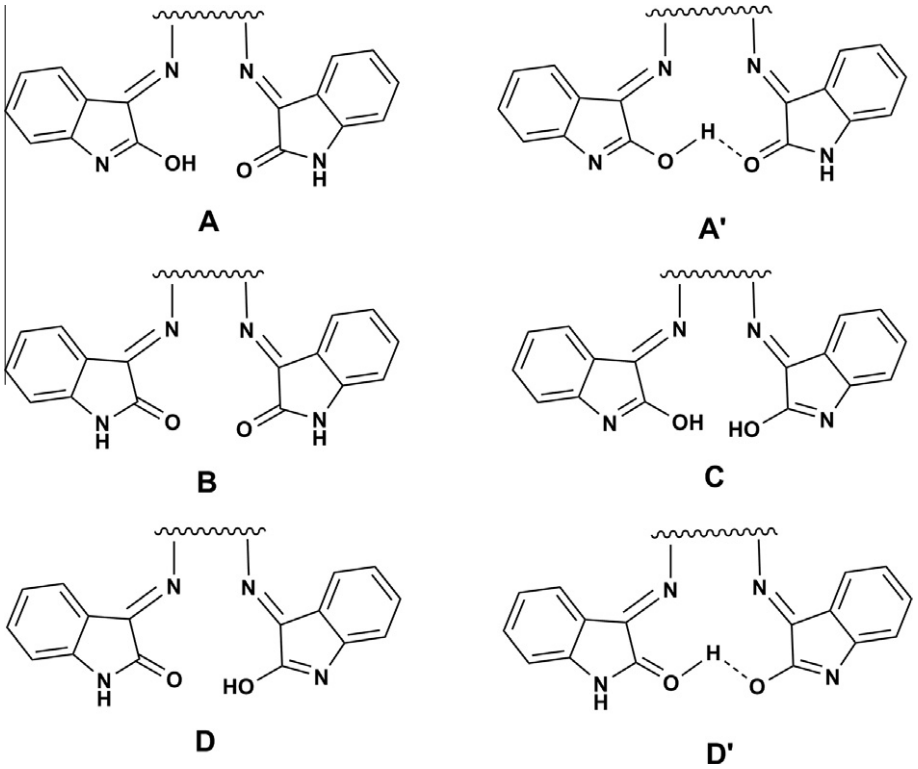

Fig. 2. Possible tautomers of the ligand.

one tautomeric form of the ligand exists in solution under the experimental conditions. Any temperature dependent experiments have not been carried out. Comparing with the solid state study, we prefer to assign this signal to OH of the of the ligand; however, assignment of this peak to OH of the Schiff base-ring cannot be ruled out provided solid state structural evidence is not considered [43]. On the basis of ^{13}C signal for the carbonyl carbon of the Schiff base ligand-ring is observed at 166 ppm [44] clearly correspond to ketone form (Fig. 2D′). These values are very close to those already reported by other authors [45] showing that the lignds form (Fig. 2A and A′) can be excluded. The presence of ethanone form of the ligand (Fig. 2C) is not likely because this form requires an additional signal set (approximately at 195.0–204.5 ppm) [46] in ^{13}C NMR spectra, clearly correspond to a ketone form of the ligand, which was not observed. The presence of a CH form (C) is not likely because it is known that proton transfer between ligand and OH is usually slow [45,47]. Consequently, in DMSO-d_6 solution, the ligand exist mainly as hydroxyethylidene form (Fig. 2D′) with intramolecular hydrogen bond, in agreement with other reports [45,48–50].

^1H NMR and ^{13}C NMR spectra of the ligands

The proton magnetic resonance spectra of these ligands have been recorded (Table 3). The ^1H NMR studies of all the Schiff base ligands (L_n) were carried out in a polar solvent such as DMSO-d_6 at room temperature and the data are given in the experimental section. A broad singlet corresponding to one proton for all the Schiff base ligands (L_n) is observed in the range δ 12.42–12.40 ppm. This signal disappeared when a D_2O exchange experiment was carried out. It can be assigned either to OH or NH, in either case it is strongly deshielded because of hydrogen bonding with the other atom (N/O) (Fig. 1). It shows the enolic nature of ligand and broadness of singlet due to fast exchange interaction of proton via keto-enol tautomerism with nitrogen of the azomethine group [51]. It may be noted that the integration of this signal perfectly matches with one proton and there is no other fragment(s) of this signal, which suggests that only one tautomeric form of the Schiff base ligands exist in solution under the experimental conditions. We have not done any temperature dependent experiments. Comparing with the solid state study, we prefer to assign this signal to OH; however, assignment of this peak to NH cannot be ruled out provided solid state structural evidence is not considered.

Schiff base derived from indoline-2,3-dione of type (L_1–L_4) exhibit signals at 12.40 and 5.5 ppm due to NH and hydrazine proton. Multiplet is observed at 7.00–7.75 ppm due to aromatic protons in the Schiff base. The ^{13}C NMR spectra of these ligands were recorded in DMSO-d_6. Schiff bases derived from Indoline-2,3-dione (L_1) show signals at δ 166 and 156.7 aromatic (—C=N). Aromatic ring protons signals at δ 150, 131.2, 130.6, 130.2, 129.4, 127.5, 126.6, 122.

Table 3
^{1}H NMR and ^{13}C NMR Spectral band (ppm) of Fe(III) complexes of 3-(substituted phenyl)-4-amino-5-hydrazino-1,2,4- triazole Schiff base.

Compound	^{1}H NMR		^{13}C NMR	
	—NH(s)	Aromatic ring (M)	—C=N	Aromatic ring
$[FeL_1(H_2O)(OH)]\cdot 2H_2O$	12.40	7.51 (1H, H-5 of indol ring-1), 7.58 (1H, H-5′ of indol ring-2), 7.60–7.98 (9H, m, Ar—H), 8.30 (2H, d, *J* = 7.8, phenyl ring (H-2 and 6))	166.3, 156.7	150.2(C-7a and C-7a′(of indol ring-1 and 2)), 131.2, 130.6, 130.2, 129.4, 127.5, 126.6(Ar—C), 122(C-3a and 3a′ of indol ring 1 and 2)
$[FeL_2(H_2O)(OH)]\cdot H_2O$	12.42	7.55(1H, H-5 of indol ring-1), 7.61(1H, H-5′ of indol ring-2), 7.65–7.94 (8H, m, Ar—H), 8.21(1H, d, *J* = 8.0, phenyl ring H-3), 8.35 (1H, d, *J* = 7.4, phenyl ring 6)	166.1, 156.1	150.3(C-7a and C-7a′ (of indol ring-1 and 2)), 138.7, 132.5, 130.3, 130.0, 129.4, 128.9, 127.3(Ar—C), 126.7(C-3a and 3a′ of indol ring 1 and 2)
$[FeL_3(H_2O)(OH)]\cdot H_2O$	12.41	7.65(1H, H-5 of indol ring-1), 7.71(1H, H-5′ of indol ring-2), 7.78–8.23(8H, m, Ar—H), 8.45((2H, d, *J* = 7.8, phenyl ring (H-2 and 6))	166.2, 156.2	151.2(C-7a and C-7a′ (of indol ring-1 and 2)), 135.2, 130.2, 129.5, 128.9, 128.7(Ar—C), 122.0(C-3a and 3a′ of indol ring 1 and 2)
$[FeL_4(H_2O)(OH)]\cdot 2H_2O$	12.40	7.70(1H, H-5 of indol ring-1), 7.74(1H, H-5′ of indol ring-2), 7.77–8.05(8H, m, Ar—H), 8.10((2H, d, *J* = 8.0, phenyl ring (H-2 and 6))	166.3, 156.4	149.5(C-7a and C-7a′ (of indol ring-1 and 2)), 147.9, 130.2, 127.7, 126.6, 124.8(Ar—C), 122.3(C-3a and 3a′ of indol ring 1 and 2)

FAB-mass spectra

In the mass spectra of $[Fe(L_1)(H_2O)(OH)]\cdot 2H_2O$, the peak at *m/z* = 537 stands for the molecular ion peak of complex (without water of crystallization). The proposed fragmentation pattern of $[Fe(L_1)(H_2O)(OH)]$, obtained using m-nitro benzyl alcohol as matrix. Peaks at 136, 137, 154, 289 and 307 *m/z* value were due to the usage of matrix. Peaks at 537, 358 and 539 in spectra were assigned to (M), (M + 1) and (M + 2) of the complex molecule figure in Supplementary data.

Thermal studies of $[Fe(L_1)(H_2O)(OH)]\cdot 2H_2O$ complex

Thermal behavior of the complex ware studied by TG. The thermal decomposition occurs in four steps. According to the mass losses, all the compounds decompose progressively by the following degradation pattern for the complex. Thermal decomposition started by a dehydration process and was accompanied by endothermic effect between 80 and 130 °C due to loss of two lattice water molecules in the first step. The observed mass loss was 6.08%, which was nearly equal to the theoretical value 6.45%. The loss of 2 mol lattice water molecules was first order. In the second step, exothermic decomposition between 180 and 230 °C corresponds to loss of one water and one hydroxyl molecules. The observed mass loss was 5.45%, which was nearly equal to the theoretical value of 5.75%. The next step was exothermic, associated with elimination of coordinated ligand, respectively. As temperature 400–600 °C increases the intermediate complexes convert to CuO residue of fragments. The observed mass loss for the third stages was 46.88%, respectively. The final solid product of decomposition was CuO, accompanied by a broad exothermic effect at 600 °C [52,53].

Antibacterial screening

The results of the minimum inhibitory concentration (MIC), expressed in micromoles, are presented in Table 4. All compounds exhibited good activity compare to reference drugs. The complexes showed better antimicrobial activity than the free ligands and ciprofloxacin. The higher antimicrobial activity can be mainly attributed to the existence of the quinolone in the complexes. The antibacterial activity of all the complexes is even higher than the antibacterial activity of complexes, which were previously reported by our group [54]. It has also been suggested [55,56] that the ligands with nitrogen donor systems might inhibit enzyme production, since the enzymes that require these groups for their activity appear to be especially susceptible to deactivation by the metal ions upon chelation. Chelation reduces the polarity of the metal ion, mainly because of the partial sharing of its positive charge with the donor groups and possibly the π-electron delocalization within the whole chelate ring system thus formed during coordination. This process of chelation increases the lipophilic nature of the central metal atom, which in turn favors its permeation through the lipoid layer of the membrane, increasing the hydrophobic character and liposolubility of the molecule in crossing the cell membrane of the microorganism, and hence enhances the biological utilization ratio and activity of the testing drugs/compounds.

Table 4
Minimum inhibitory concentration date of the compounds (μM).

Compounds	*S. aureus*	*B. subtilis*	*S. marcescens*	*P. aeruginosa*	*E. coil*
$Fe(NO_3)_3\cdot 9H_2O$	1.8	1.7	1.7	1.5	1.2
Ciprofloxacin	1.6	1.1	1.6	1.4	1.4
Norfloxacin	2.5	2.5	4.1	3.8	2.8
Enrofloxacin	1.9	3.9	1.7	1.4	1.4
Pefloxacin	2.1	2.4	5.1	5.7	2.7
Levofloxacin	1.7	2.2	1.7	1.7	1.0
Sparfloxacin	1.3	2.0	1.5	1.5	1.3
Ligand 1 (A^1)	500	525	575	525	550
Ligand 2 (A^2)	575	550	525	575	550
Ligand 3 (A^3)	775	725	700	750	725
Ligand 4 (A^4)	650	650	675	700	625
$[FeL_1(H_2O)(OH)]\cdot 2H_2O$ (1)	2.7	2.7	2.7	2.3	2.8
$[FeL_2(H_2O)(OH)]\cdot H_2O$ (2)	2.8	2.7	2.9	2.4	2.9
$[FeL_3(H_2O)(OH)]\cdot H_2O$ (3)	3.3	3.2	3.3	2.9	3.5
$[FeL_4(H_2O)(OH)]\cdot 2H_2O$ (4)	3.1	3.1	3.2	2.4	2.9

Electronic spectra and magnetic moments

The information regarding geometry of the complexes was obtained from their electronic spectral data and magnetic moment values. The diffused reflectance spectra of the complexes $[FeL_n(H_2O)(OH)]\cdot xH_2O$ exhibited two bands at about ~20,000 cm^{-1}, assigned to the $^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ transitions, and at ~32,500 cm^{-1}, assigned to MLCT in the d^5-system of the Fe(III) atom. The Fe(III) complexes exhibited magnetic moment of 5.90–6.01 B.M. From the electronic spectra and magnetic measurement data of Fe(III) complexes, an octahedral geometry around the central metal ion is suggested [57–59].

Table 5
Antioxidant results of compounds.

Compounds	Antioxidant Activity FRAP value (mmol/100 g)
$[FeL_1(H_2O)(OH)]\cdot 2H_2O$ (1)	87.42
$[FeL_2(H_2O)(OH)]\cdot H_2O$ (2)	82.76
$[FeL_3(H_2O)(OH)]\cdot H_2O$ (3)	76.65
$[FeL_4(H_2O)(OH)]\cdot 2H_2O$ (4)	74.83

Cyclic voltametric studies

The electrochemistry of Fe(III) complex is devoid of any redox potential over the entire range of the experiment. Attempts to carry out cyclic voltammetric studies at various scan rates, i.e. 5, 10, 50 and 100 mV s^{-1} gave no redox activity. The observed inactivity points to high stability of complexes, due to presence of (1) phenyl groups (and perhaps CH_3) in parent heterocyclic β-diketone which is good electro donors, (2) the Schiff-base is N-rich and N is a better σ donor and (3) the chelate ring of the complexes which may stabilize the chelate.

Antioxidant

A capacity to transfer a single electron i.e. the antioxidant power of all compounds was determined by a FRAP assay. The FRAP value was expressed as an equivalent of standard antioxidant ascorbic acid (mmol/100 g of dried compound). FRAP values indicate that all the compounds have a ferric reducing antioxidant power. The compounds 1 and 2 showed relatively high antioxidant activity while compound 3 and 4 shows poor antioxidant power (Table 5).

Conclusions

The results of antioxidant and antimicrobial studies revealed that the metal complexes are more effective than that of the respective free ligands under identical experimental conditions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.03.068.

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