Synthesis and characterization of a novel schiff base metal complexes and their application in determination of iron in different types of natural water

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ABSTRACT

A novel and simple approach to the synthesis of macrocyclic Schiff base ligand resulted from the condensation of bisaldehyde and ethylenediamine was prepared (7, 8, 15, 16, 17, 18-hexahydrodibenzo (a, g) (14) annulene) (L) and its complexes were synthesized and characterized using different physicochemical studies as elemental analysis, FT-IR, ^{1}H NMR, conductivity, magnetic properties, thermal analysis, and their biological activities. The spectroscopic data of the complexes suggest their 1:1 complexe structures which are investigated by elemental analysis, FT-IR, ^{1}H NMR, conductivity, magnetic properties, thermal analysis, and their biological activities. The spectroscopic studies suggested the octahedral structure for the all complexes. The spectroscopic data of the complexes suggest their structure in which (N_2O_2) group act as a tetradentate ligand and two chlorides as monodentate ligands. Also electronic spectra and magnetic susceptibility measurements indicate octahedral structure of these complexes. The synthesized Schiff base and its metal complexes also were screened for their antibacterial and antifungal activity. Here we report the effect of a neutral chelating ligand on the complexation with iron to determine it in different types of natural water using recovery test. The activity data show that the metal complexes to be more potent/ antibacterial than the parent Schiff base ligand against one or more bacterial species.

Keywords: Novel Schiff Base; Transition Metal Complexes and Natural Water

1. INTRODUCTION

A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen [1], catalytic activity in the hydrogenation of olefines [2], photochromic properties [3,4] and complexing ability towards some toxic metals [5]. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards various metals [6-8]. The azomethine linkage in Schiff bases is responsible for the biological activities such as antitumor, antibacterial, antifungal and herbicidal activities [9]. Designing a suitable polydentate Schiff base ligand to combine with a metal ion along with pseudohalide anion has opened a new area of synthesizing metal complexes of particular choice [10]. Such complexes are readily assembled from diamines and various salicylaldehyde derivatives and are amenable to combinatorial syntheses [11]. Metal Schiff base complexes have been well known for their easy synthesis, stability and wide application [12-14]. A large number of Schiff base (N_2O_2) complexes have been reported so far, and their catalytic and biological properties have been studied intensively [15-21]. Numerous techniques were available in iron determination have been reported [22-24]. However, these techniques were tedious need time and rigid conditions. Also due to the very low concentrations of iron, lead and chromium in natural water samples, their determinations demand very sensitive analytical techniques including ET-AAS, ICP-MS, ICP-AES and XRF. However, relative to flame AAS, these techniques have some disadvantages such as its high cost, slowness and greater proneness to matrix interferences as well as their high sensitive advantages [25]. The present study was under taken to throw more light on the chelation behavior of Schiff base (L) towards some transition elements, which may help in more understanding of the mode of chelation of the new Schiff base towards metals and tried to used in the recovery test with a purity of more than higher than 96% for the metal ion.

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2. EXPERIMENTAL

2.1. Materials and Solutions

The chemicals used included metal (II) and (III) chlorides. Solvents of absolute ethyl alcohol, diethylether, dimethylformamide and ethylenediamine were spectroscopic pure and purchased from BDH. A 10^{-4} M solution of the metal salts ($CrCl_3 \cdot 6H_2O$ (0.341 g/L), $CoCl_2 \cdot 6H_2O$ (0.119 g/L), $NiCl_2 \cdot 6H_2O$ (0.119 g/L) (BDH), $FeCl_3 \cdot 6H_2O$ (0.117 g/L) (Prolabo), $CuCl_2 \cdot 2H_2O$ (0.085 g/L) (Sigma) and $ZnCl_2 \cdot 2H_2O$ (0.086 g/L) (Ubichem)) were prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of de-ionized water. The metal salt solutions were standardized by the recommended procedures [26].

2.2. Instrumentation

Elemental microanalyses of the separated solid chelates for C, H, N and Cl were performed at the Microanalytical center, Cairo University. The molar conductance of the complexes in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, E = 3406). Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer. The spectra were recorded as KBr pellets. The UV-vis absorption spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument. The ^{H1NMR} spectra were recorded using 300 MHz Varian-Oxford Mercury. The thermal analyses were carried out in dynamic nitrogen atmosphere (20 $mL \cdot min^{-1}$) with a heating rate of $10°C \cdot min^{-1}$ using Shimadzu TG-60H thermal analyzer. XPD analyses were carried out by using Philips Analytical X-Ray BV, diffractometer type PW 1840. Radiation was provided by copper target (Cu anode 2000 W) high intensity X-ray tube operated at 40 KV and 25 mA. All spectrophotometric measurements were preformed using a Unicam UV-2 spectrophotometer using 10 mm quartz cell and a blank solution as a reference. The pH measurements were made using HANNA pH meter.

2.3. Synthesis of the Compounds

2.3.1. Synthesis of Bisaldehyde

Salicylaldehyde (20 mmol) was dissolved in hot ethanolic KOH (prepared by dissolving 1.12 g (20 mmol) of KOH in 20 ml of absolute ethanol), and the solvent was then removed in vacuo. The remaining material was dissolved in DMF (15 ml) and the appropriate 1,2-dibromoethane (10 mmol) was added. The reaction mixture was refluxed for 5 min during which KCl was separated. The solvent was then removed in vacuo and the remaining materials was washed with water and purified by crystallization.

2.3.2. Synthesis of Schiff Base

Hot solution (60°C) of ethylenediamine (0.399 g, 6.67 mmol) in 50 mL ethanol/DMF mixture as 1:1 mole ratio mixed with hot solution (60°C) of bisaldehyde (1.6 g, 6.67 mmol) in the same solvent and the reaction mixture was left under heating for 30 min. A solid mass separated was collected and washed with diethylether. Crystallization was done with ethanol and then dried over $CaCl_2$. The pale yellow ligand; L, (yield, 82%) was collected.

2.3.3. Synthesis of Metal Complexes

All the new complexes were prepared by adding hot ethanolic/DMF solution in a 1:1 molar ratio (60°C) of metal (II)/(III) (1 mmol) to hot solution (60°C) of ligand in the same solvent. The solution was stirred with heating for one hour whereupon the complexes precipitated then filtered and left for drying. A solid residue was separated and washed by diethylether. Crystallization was done with methanol and the complexes dried over anhydrous $CaCl_2$ and the metal contents were determined compleximetrically.

2.4. Biological Activity

The standard disc-agar diffusion method [27] was followed to determine the antibacterial and antifungal activeity of the synthesized compounds. The tested compounds were dissolved in DMF (which have no inhibittion activity), to get concentrations of 100 μg/mL. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (0.1 mL) from the specific concentration of dissolved tested compounds and carefully placed on incubated agar surface. After incubation for 48 h at 37°C, inhibition of the organisms which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

2.5. The Recovery Procedure

Water samples were collected according to the recommended standard methods [28]. Water samples were spiked with a definite concentration of Fe(III) soluation and 1 ml of 10^{-4} M of the Schiff base was added. After adjusting the pH with HNO_3 and/or NaOH, the solution was shaked well and transferred to the measurement cell to ensure complete complexation. The concentration of metal ion determined spectrophotometrically and obtained the recovery percentage.

3. RESULTS AND DISCUSSION

The results of elemental analyses of the ligand and its

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complexes are in good agreement with those required by the proposed formulae giving in **Table 1**. The molecular modeling of Schiff base ligand (using Chem3D ultra 8.0 program) shows that the bond lengths of all bonds in the left and right hand sides are typical due to the similarity of moieties on the two sides. Mass spectrum (**Figure 1**) of the new Schiff base showed a signal with m/z = 301 which is close to the calculated formula m/z = 294, supporting the structures of the Schiff base. The fragments observed were in good agreement with the proposed formula (**Scheme 1**).

3.1. Molar Conductance Measurements

The metal (II)/(III) complexes were dissolved in DMSO and the molar conductivities of 10^{-3} M of their solutions were measured at room temperature. The conductance values of the M(III) complexes support their electrolytic nature (1:1) types while M(II) complexes are non ionic in nature and non electrolytes. The data are listed in **Table 1**.

3.2. IR Spectral Studies

IR spectra in the region 4000 - 400 cm^{-1} have been recorded for the ligand and its complexes and the assignments of the observed frequencies have been made to specific group vibrations by comparison with the spectra of related complexes. The IR spectrum of the ligand showed a shoulder at 1597 cm^{-1} assigned to υ(C = N) of the azomethine stretching vibration, beside a band at 1049 cm^{-1} due to C-O-C stretching frequency. These two bands are shifted to higher or lower wave numbers in the complexes indicating the participation of the azomethine nitrogen in coordination [29] and the oxygen of the ether group, **Table 2**. On the other hand, the IR spectra of the complexes exhibited new non-ligand bands in the range 432 - 467 cm^{-1} and in the range 492 - 594 cm^{-1} assigned as M-O and M-N stretching vibrations, respectively. Therefore, it can be concluded that (L) ligand binds to the metal ions through azomethine N and the ether O and the ligand behaves as neutral tetradentate ligand.

Table 1. Analytical and physical data of L ligand and its metal complexes.

Compound	Colour (%yield)	M.P. (°C)	% Found (calcd.)					$\mu_{eff.}$ (B.M)	Λ_m $\Omega^{-1} \cdot mol^{-1} \cdot cm_2$
			C	H	N	M	Cl		
L = (C$_{18}$H$_{18}$N$_2$O$_2$)	Pale Yellow (82)	154	73.75 (73.47)	6.02 (6.12)	9.82 (9.52)	-----	-----	-----	-----
[Cr(L)Cl$_2$]Cl	Pale Yellow (88)	122	47.91 (47.75)	3.41 (3.98)	6.57 (6.19)	11.65 (11.47)	23.48 (23.54)	3.64	103.9
[Fe(L)Cl$_2$]Cl	Brown (77)	148	47.16 (47.34)	3.76 (3.94)	6.49 (6.14)	12.58 (12.22)	23.39 (23.34)	5.44	104.5
[Co(L)Cl$_2$]	Green (83)	114	50.51 (50.96)	4.45 (4.25)	6.25 (6.60)	13.42 (13.89)	16.48 (16.75)	4.49	32.51
[Ni(L)Cl$_2$]	Yellowish Green (89)	120	50.96 (50.98)	4.31 (4.25)	6.88 (6.61)	13.50 (13.85)	16.49 (16.76)	3.21	31.25
[Cu(L)Cl$_2$]	Green (74)	130	50.74 (50.41)	4.90 (4.20)	6.84 (6.53)	14.63 (14.82)	16.66 (16.57)	1.99	35.14
[Zn(L)Cl$_2$]	Pale Yellow (81)	260	50.34 (50.19)	4.52 (4.18)	6.08 (6.51)	15.04 (15.19)	16.79 (16.50)	-----	17.92

m/z = 294 (301, R.I. = 22%)   m/z = 175 (176, R.I. = 54%)   m/z = 147 (148, R.I. = 71%)   m/z = 132 (131, R.I. = 81%)

m/z = 78 (77, R.I. = 73%)   m/z = 90 (93, R.I. = 44%)   m/z = 104 (103, R.I. = 42%)   m/z = 118 (120, R.I. = 83%)

m/z = 66 (67, R.I. = 42%)   m/z = 52 (51, R.I. = 100%)

Scheme 1. Mass fragmentation pattern of L ligand.
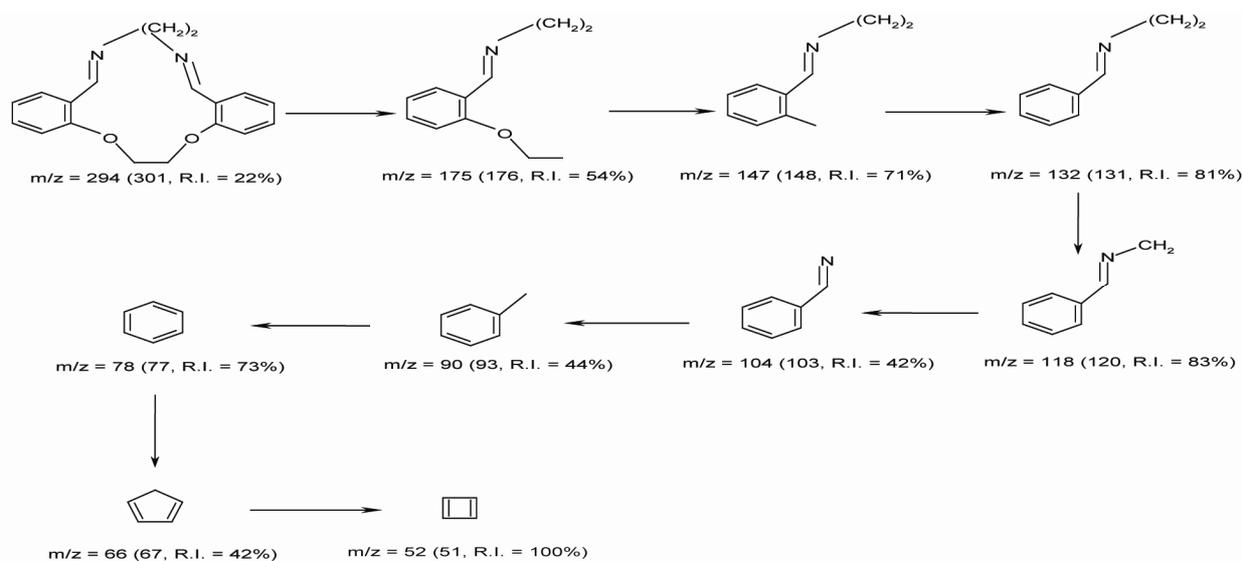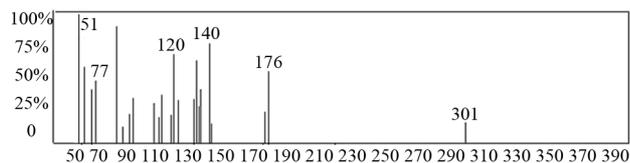
Figure 1. Mass spectra of Schiff base ligand (L).

Table 2. IR data (4000 - 400 cm^{-1}) of L ligand and its metal complexes.

Compound	υ(HC=N)$_{azomethine}$	(C-O-C)$_{ether}$	υ(M-N)$_{azo}$	υ(M-O)$_{ether}$
L	1597sh	1049sh	------	-----
[Cr(L)Cl$_2$]Cl	1611sh	1061sh	502s	440s
[Fe(L)Cl$_2$]Cl	1590sh	1038sh	498m	464m
[Co(L)Cl$_2$]	1593m	1057sh	505w	432s
[Ni(L)Cl$_2$]	1600sh	1038m	521s	436s
[Cu(L)Cl$_2$]	1589sh	1053m	502w	436m
[Zn(L)Cl$_2$]	1601m	1049m	594w	467s

Sh = sharp; m = medium; br = broad; s = small; w = week.

3.3. H^{1}NMR Spectra

The H^{1}NMR spectra of Schiff base ligand (L) is recorded in d$_6$-dimethylsulfoxide (DMSO) solution using tetramethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons found in the ^{H1NMR}spectra of the Schiff base ligand is compared with its diamagnetic Zn(II) complex and shown in **Table 3**. It is found that while the ^{H1NMR}signal of (HC=N) is shifted due to complexation, the signals due to the ether CH$_2$-O does not show a significant shift in the chelation mode.

3.4. Electronic Absorption Spectra and Magnetic Moments of the Metal Complexes

The Uv-vis spectrum of the ligand showed two bands at 330 and 370 nm which are assigned to π-π* and n-π*, transition, respectively. The Uv-vis spectra of 10^{-4} M of the metal complexes, **Figure 2**, display similar absorption spectra of the ligand which are shifted to lower and higher wavelengths beside a decrease or disappearance of the peak dye to n-π* transition which confirm the coordination through azomethine nitrogen. On the other hand, π-π* transition showed shoulder at 337 nm with new band at 320 nm due to complexation. Also the d-d transition in this type of complexes may appear above 500 nm but does not appear due to the low intensity of the d-d transition. The data listed in **Table 1** summarized the measured magnetic moment values. These data support the octahedral geometry of the complexes.

Table 3. ^{H1NMR}spectral data of the organic ligand and its metal chelates.

Compound	Chemical shift, (δ) ppm	Assignment
	4.434	(m, 2H, -OCH$_2$)
L	2.725 - 2.888	(m, 2H, -C=N-CH$_2$)
	6.885 - 7.950	(m, 4H, ArH)
	8.479 - 8.493	(m, 1H, azomethineH)
	4.435	(m, 2H, -OCH$_2$)
[Zn(L)Cl$_2$]	2.729 - 2.887	(m, 2H, -C=N-CH$_2$)
	6.943 - 7.821	(m, 4H, ArH)
	8.546	(s, 1H, azomethineH)
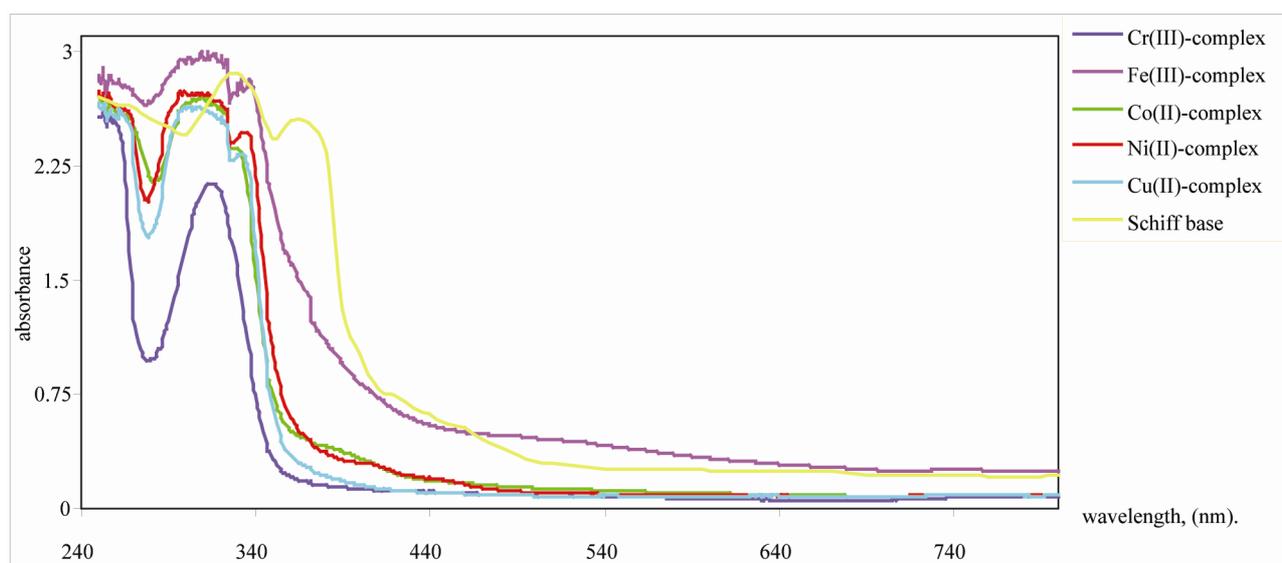
Figure 2. Uv-vis spectrum of the Schiff base and its metal complexes.

3.5. Thermal Analyses (TG and DTG) Studies

The Schiff base ligand exhibits a first estimated mass loss of 13.33% (calcd. 12.93%) at 25°C - 140°C, which may be attributed to the liberation of $2NH_3$ and $2H_2$ molecules as gases. In the following stages within the temperature range from 140°C - 750°C, the organic part $C_{17}H_8$ with CO_2 gas are lost with an estimated mass loss of 86.67% (calcd. 87.07%). The thermogram of Fe(III)-L chelate show three decomposition steps within the temperature range from 50°C - 790°C. The first step of decomposition within the temperature range from 50°C - 245°C corresponds to the loss of 2HCl gases with an estimated mass loss of 16.18% (calcd. 16.00%). While the second step occurs within the temperature range from 245°C - 520°C and corresponds to the removal of HCl,

CO and $2NH_3$ as gases with a mass loss of 21.91% (calcd. 21.58%). The final step (520°C - 790°C) corresponds to the removal of the organic part of the ligand leaving metal oxide as a residue. The overall weight loss amounts to 84.37% (calcd. 84.27%). The TG curve of the cobalt complex shows five stages of decomposition within the temperature range of 25°C - 705°C. The first three stages at 25°C - 270°C correspond to the loss of 2HCl as gases in the first step and NO and NH_3 as gases in the next steps, while the final stages involve the loss of organic molecule leaving the metal oxide as residue. The overall weight loss amounts to 82.90% (calcd. 82.33%). The Cu(II) complex decomposed in four steps. The overall weight loss amounts to 82.22% (calcd. 81.45%), **Table 4** and **Figure 3**.

Table 4. Thermoanalytical results of Schiff base and its metal complexes.

Compound	TG Range (°C)	DTG_{max} (°C)	n*	Mass Loss (Estim) %	Total Mass Loss Calcd	Assignment	Metallic Residue
L		62					------
	25 - 140	318,399	1	12.93 (13.33)		-Loss of $2NH_3$ and $2H_2$	
	140 - 750	501,612	4	87.07 (86.67)	100 (100)	-Loss of CO_2 and $C_{17}H_8$	
$[Fe(L)Cl_2]Cl$							FeO
	50 - 245	187	1	16.00 (16.18)		-Loss of 2HCl	15.74
	245 - 520	384	1	21.59 (21.91)		-Loss of HCl, CO and $2NH_3$	(15.63)
	520 - 790	681	1	46.68 (46.28)	84.27 (84.37)	-Loss of $C_{17}H_9$	
$[Co(L)Cl_2]$							CoO
	25 - 270	30,205	2	17.22 (17.03)		-Loss of 2HCl	17.67
	270 - 415	362	1	11.09 (11.58)		-Loss of NO and NH_3	(17.10)
	415 - 705	625,937	2	54.02 (54.29)	82.33 (82.90)	-Loss of $C_{18}H_{13}$	
$[Cu(L)Cl_2]$						-Loss of 2HCl	CuO
	35 - 220	125,229	2	17.04 (17.84)		-Loss of $2NH_3$, $\frac{1}{2}O_2$ and	18.55
	220 - 775	345,593	2	64.41 (64.38)	81.45 (82.22)	$C_{18}H_{10}$	(17.78)

n* = number of decomposition steps.
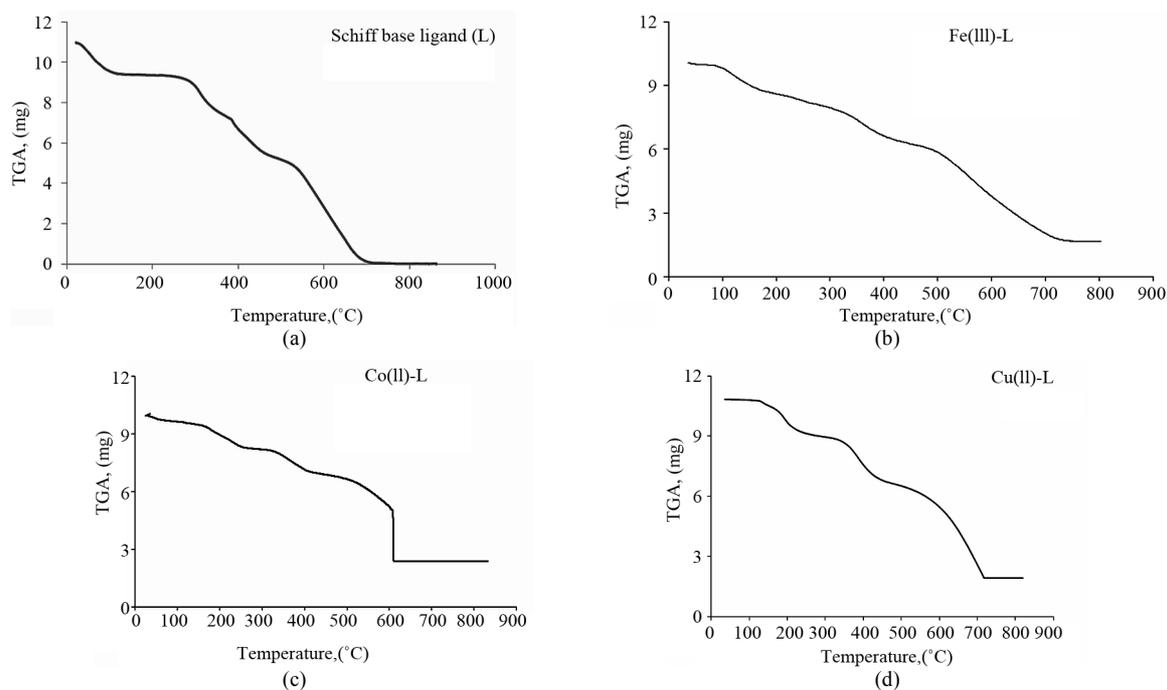
Figure 3. Thermal analyses of (a) Schiff base ligand (L), (b) Fe(III)-L, (c) Co(II)-L and (d) Cu(II)-L. complexes.

3.6. Calculation of Activation Thermodynamic Parameters

The thermodynamic activation parameters of decomposition processes of the complexes are evaluated graphically by employing the Coats-Redfern relation [30].

$$
\log\left[\log\left\{W_f/(W_f - W)\right\}/T^2\right]
$$
$$
= \log\left[AR/q\theta E^*\left(1 - 2RT/E^*\right)\right] - E^*/2.303RT
$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T; R is the gas constant, E^* is the activation energy in KJ/mol and θ is the heating rate. Since, $1 - 2RT/E^* \cong 1$, a plot of the left hand side of the equation against $1/T$ was drawn and the data obtained are given in **Table 5**. The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation is found to have negative values in all the complexes which indicate that the decomposition reactions proceed with a lower rate than the normal ones.

3.7. X-Ray Diffraction

The trend of the curves decreases from maximum to minimum intensity indicating that all the metal complexes are amorphous in nature in the present metal-ligand formation except the Cr(III), Ni(II), Cu(II) and Zn(II) chelates they have crystalline phase.

3.8. Structures Interpretation

On the basis of the above observations, octahedral geometry is suggested for the investigated complexes. The structures of the complexes are shown in **Figure 4**.

Table 5. Thermodynamic data of the thermal decomposition of the Schiff base ligand and its metal complexes.

Complex	Decomp. Temp. ˚C	A s^{-1}	E* kJ·mol^{-1}	ΔS* J·mol^{-1}	ΔH* kJ·mol^{-1}	ΔG* kJ·mol^{-1}
L	25 - 140	1.34×10^5	72.60	−33.00	72.10	80.40
	140 - 220	8.53×10^6	26.20	−52.00	93.80	133.4
	220 - 445	7.78×10^5	82.20	−104.0	128.8	152.0
	445 - 630	6.75×10^{10}	95.30	−141.0	191.1	212.0
	630 - 750	2.91×10^{11}	90.80	−181.0	239.9	262.0
[Fe(L)Cl₂]Cl	35 - 185	6.15×10^4	43.60	−46.00	72.60	90.30
	185 - 220	2.69×10^{11}	79.90	−83.00	106.9	115.0
	220 - 470	1.90×10^7	42.00	−106.0	139.1	160.0
	470 - 775	2.91×10^6	82.40	−146.0	177.4	202.0
[Co(L)Cl₂]	25 - 160	2.27×10^9	141.0	−46.00	63.80	82.00
	160 - 270	6.28×10^{10}	172.0	−75.00	95.50	122.7
	270 - 415	2.69×10^8	156.0	−125.0	152.6	163.4
	415 - 650	2.26×10^8	114.0	−191.0	210.9	266.0
	650 - 705	2.09×10^5	180.0	−252.0	280.2	318.3
[Cu(L)Cl₂]	50 - 245	3.19×10^9	68.30	−59.0	82.70	106.3
	245 - 520	1.31×10^{11}	106.0	−134.0	174.5	205.0
	520 - 790	1.74×10^5	116.0	−181.0	211.0	243.0
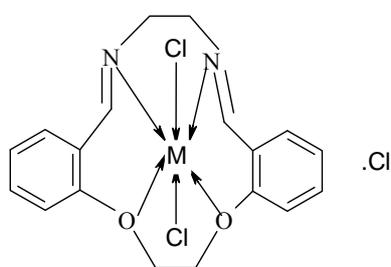
M = Ni(II), Co(II), Cu(II) and Zn(II).　　　　　M = Cr(III) and Fe(III).
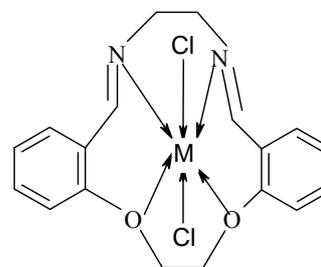
Figure 4. Structural formula of the metal complexes.

3.9. Biological Activity

The main aim of the production and synthesis of any antimicrobial compound is to inhibit the causal microbe without any side effects on the patients. In addition, it is worthy to stress here on the basic idea of applying any chemotherapeutic agent which depends essentially on the specific control of only one biological function and not multiple ones. The antibacterial activity of the parent Schiff base and its metal complexes against *Aspergillus flavus* and *Canidia albicans* fungi and, *Staphylococcus* (G$^+$) and *E. coli* (G$^-$) bacteria was tested in order to asses their potential antimicrobial agents. The biological activeity of the Schiff base ligand and its metal complexes were also compared with tetracycline (Antibacterial agent) and Amphotericin B (Antifungal agent). The data are listed in **Table 6** and **Figure 5**. According to the data it can be seen that the ligand did not show any biological activity, while all the complexes showed activity against *Staphylococcus* (G$^+$) and *E. coli* (G$^-$) bacteria and *Canidia albicans* fungi. On the other hand, no activity is observed for *Aspergillus flavus* fungi by the ligand or the complexes [31]. This means that the activity of the newly prepared Schiff base against different microorganisms is enhanced with chelation with different biological active metals.

4. APPLICATION

A New Spectrophotometric Determination to Fe(III) Ions in Natural Water

The UV-vis spectrum of the Fe(III) solution in the presence of the Schiff base ligand was measured from 250 to 900 nm at an interval of 1 nm and an average measuring time of 1 s per wavelength and the maximum wavelength is found at 313 nm. Several factors influence on the recovery method are studied for [Fe(III)-L] system in order to achieve maximum recovery. The optimum factors are pH = 3, 25˚C, 1:1 (M:L) metal to ligand ratio and 30 min. In order to assess the applicability of the proposed method to recover Fe(III) from spiked water samples, the effect of some foreign ions was also investigated. These foreign ions were selected on the basis that they are normally present in natural water samples. Solutions containing various amounts of foreign ions, Fe(III), and the ligand were subjected to the described spectrophotometric procedure. The tolerable amounts of each ion, given a maximum error up to 1.23% in the recovery, are summarized in **Table 7**. As can be seen, all the investigated foreign ions with a relatively high concentration have no adverse effect on the ferric ions determinate.

Recovery tests were carried out on different types of water samples in order to assess its accuracy. The selection of these samples was done in a way to provide a wide variety of sample matrices characterized by different types of interferents. Solutions of water samples containing Fe(III) with varying a concentration were recovered with the newly Schiff base synthesized under the recommended conditions and the data listed in **Table 8** showed satisfactory recovery of Fe(III). The standard deviation and relative standard deviation of the method were also calculated and their values indicate that, this method has a greater accuracy where the small values for the standard deviation attest to the procedure's fairly high degree of precision. Therefore, the synthesis of these complexes might be established a new line for search to new ligand for determination of ferric ion in natural water.

Table 6. Biological activity of L and its metal complexes.

	Sample	Inhibition Zone Diameter (mm)			
		Escherichia coli (G$^-$) Mean ± RSD	*Staphylococcus aureus* (G$^+$) Mean ± RSD	*Aspergillus favus* (Fungus) Mean ± RSD	*Candida albicans* (Fungus) Mean ± RSD
	Control: DMSO	0.0	0.0	0.0	0.0
Standard	Tetracycline (Antibacterial agent)	33	30	----	----
	Amphotericin B (Antifungal agent)	----	----	18	19
	L	0.00	0.00	0.0	0.00
	[Cr(L)Cl$_2$]Cl	14.33 ± 0.011	14.43 ± 0.041	0.0	12.433 ± 0.191
	[Fe(L)Cl$_2$]Cl	13.23 ± 0.019	13.067 ± 0.069	0.0	11.500 ± 0.157
	[Co(L)Cl$_2$]	21.16 ± 0.007	21.667 ± 0.071	0.0	14.000 ± 0.286
	[Ni(L)Cl$_2$]	16.40 ± 0.022	22.333 ± 0.068	0.0	16.000 ± 0.250
	[Cu(L)Cl$_2$]	13.13 ± 0.012	14.000 ± 0.143	0.0	13.000 ± 0.428
	[Zn(L)Cl$_2$]	20.23 ± 0.010	25.667 ± 0.098	0.0	12.333 ± 0.528
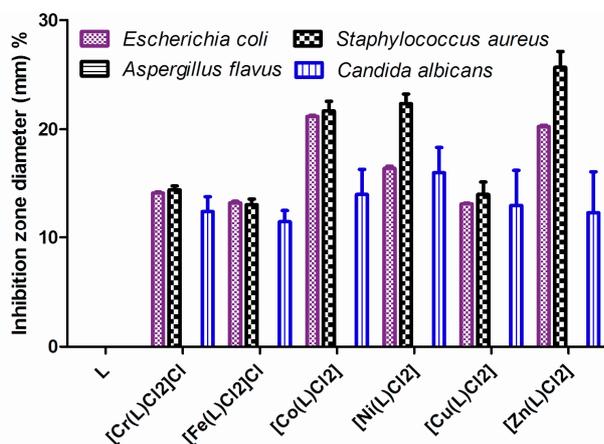
Figure 5. Percent of inhibition zone diameter (mm) relative to used standard vs. the Schiff base ligand (L) and its metal complexes.

Table 7. Effect of some foreign ions on the recovery of 5×10^{-4} mol·L^{-1} Fe(III) using 5×10^{-4} mol·L^{-1} of L ligand at pH = 3, t = 30 min, T = 25°C and λ_{max} = 313 nm.

Foreign Ion Added	[Foreign Ion]/[Fe(III)]	R(%)
Ag(I)	2000	98.77
Cd(II)	0.200	99.45
NH(I)	20.00	99.62
Sn(IV)	2000	98.89
Al(III)	200.0	99.50
K(I)	20.00	99.43
Hg(I)	20.00	99.49
Ca(II)	20.00	99.47
Na(I)	200.0	99.50
Cu(II)	20.00	99.44
Co(II)	0.200	99.68
Ni(II)	20.00	99.38
Zn(II)	200.0	99.50
Cl$^-$	200.0	99.10
Mg(II)	2000	99.77

Table 8. Recovery percent (%) of Fe(III) in spiked natural water samples using 5×10^{-4} mol·L^{-1} at pH = 3, t = 30 min, T = 25°C and λ_{max} = 313 nm.

Water Samples (location)	Fe(III)$_{spiked}$ (mg·L^{-1})	Fe(III)$_{recovered}$ (mg·L^{-1})	Recovery Percent (%)	SD $\times 10^{-3}$	RSD (%)
Distilled water	4.65	4.641	99.81	1	14.14
	8.42	8.409	99.87		
Tap water (our Lab.)	4.65	4.628	99.53	1	6.734
	8.42	8.400	99.76		
Nile water (Egypt)	4.65	4.631	99.59	4	16.44
	8.42	8.396	99.71		
Sea water (Gamasah)	4.65	4.638	99.74	1	10.88
	8.42	8.406	99.83		
Underground water (Belqas)	4.65	4.629	99.55	3	14.89
	8.42	8.403	99.80		
Well water (6th October City)	4.65	4.620	99.35	5	18.68
	8.42	8.397	99.73		

SD = standard deviation and RSD = relative standard deviation.

5. CONCLUSION

Synthesis and characterization of complexes containing N$_2$O$_2$-donor tetradentate Schiff base ligand have been described in this paper. The spectroscopic data of the complexes give good evidence of proposed structure. The results of the antibacterial screening of the test compounds indicate mild to moderate bactericidal activities and *Canidia albicans* fungi. Spectrometry procedure used to determine of iron (III) in different types of natural water within recovery test including with stable solution of the newly synthetic Schiff base as selective reagent by highly sensitive, selective and simple method than others.

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