

源自天然席夫碱的过渡金属配合物在分光光度法测 天然水中的 Fe(III)的应用

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摘要: 描述了一种新颖、简便的合成含五齿配位基的大环席夫碱配体的方法,制备和表征了该席夫碱的 1:1 包合物。用化学和光谱学方法测定了标题配合物的组成,认为在所有配合物中配位金属原子取八面体结构。数据表明:配体起 O₂N₄ 六齿结构而每个环绕金属原子在八面体环境中。配合物的红外和 ¹H NMR 光谱符合中心金属原子的配位结果。用分光光度法测定了配合物的稳定常数。用共轭余量法(CR method) 计算了在热分解的不同阶段配合物活化的动力学和热力学参数。此外,用抑菌圈直径法筛选了配体及其金属配合物抑制细菌和真菌的能力。用回收率试验研究了天然螯合配体在不同天然水体中对 Fe(III)离子配合作用的影响。

关键词: 席夫碱配合物; 光谱学技术; 生物活性; 回收率

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Transition Metal Complexes Derived from Natural Schiff Bases for Determination of Fe(III) Spectrophotometrically in Natural Water

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Abstract: A novel, simple approach to the synthesis of macrocyclic Schiff base ligand bearing pendent coordinating groups is described and its 1:1 inclusion complexes are prepared and characterized. The composition of the title material was determined by the chemical and spectroscopic methods and the surrounding of metal with the octahedral structure for the all complexes was suggested. The data reveal that the ligand acts as O₂N₄ hexadentate structure with each metal atom in an octahedral environment. Infrared and ¹HNMR spectra of the complexes agree with the coordination to the central metal atom. The stability constants of the complexes are calculated spectrophotometrically. The activation kinetic and thermodynamic parameters are calculated in different stages of thermal decomposition using the conjugate residual method (CR method). Moreover, the ligand and its metal complexes are screened against bacteria and fungi using the inhibitory zone diameter. The effect of a neutral chelating ligand on the complexation with iron in different types of natural water was studied by using recovery test.

Key words: Schiff base complexes; spectroscopic techniques; biological activity; recovery

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0 Introduction

Considerable attention has been paid to the chemistry of the transition metal complexes of the Schiff bases containing nitrogen and oxygen donors^[1-4]. Schiff bases are a class of important compounds in medicinal, pharmaceutical^[5-8], antifungal^[9-10], anticancer^[11] and herbicidal^[12] activities. The formation of macrocyclic complexes depends significantly on the dimension of internal cavity, on the rigidity of the macrocycles, on the nature of its donor atoms and on the complexing properties of the anion involved in the coordination^[13]. Schiff bases derived from condensation of various aldehydes with triethylenetetraamine and their complexes were reported^[14-17]. We wish to report here octahedral complexes synthesis from Schiff base, H₂L ligand derived from condensation of the triethylenetetraamine and 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde in the molar ratio of 1:1 and characterization by different physicochemical techniques and the computational results are used to interpret the actual structural and spectroscopic data.

1 Experimental

All chemicals used were of chemical or analytical pure grade with the highest purity available and used without further purification.

1.1 Synthesis of Schiff base ligand (H₂L)

Hot solution (60 °C) of triethylenetetraamine (0.973 g, 6.67 mmol) was mixed with hot solution (60 °C) of 2-[2-(2-formylphenoxy)ethoxy]benzaldehyde (1.6 g, 6.67 mmol) in 50 mL ethanol. The formed solid product was separated by filtration, purified by crystallization from ethanol, washed and dried in a vacuum over anhydrous calcium chloride. The yellowish brown ligand; H₂L, was produced in 81% yield.

1.2 Synthesis of metal complexes

The solid complexes of some selected metal ions were prepared by mixing (1 mmol) of the metal ions solutions with a hot alcoholic/DMF solution of ligand (1 mmol). The mixture was heated for 30 min and magnetically stirred whereupon the complexes precipitated then collected by filtration, then washed

several times with ethanol and diethyl ether for further purification.

1.3 Solution preparations

Stock solute ion of the Schiff base (0.01 mol·L⁻¹) was prepared and metal chloride ion {Cr(III), Fe(III), Ni(II), Co(II), Cu(II) and Zn(II)} was prepared by dissolving the calculated amount of each one in a definite volume of distilled water and 1.0 mol·L⁻¹ stock sodium hydroxide solution was prepared. For pH value adjustment; a mixture of 0.04 mol·L⁻¹ phosphoric, acetic and boric acids was prepared to obtain universal buffer solution of the required pH values from 2 to 13. Mixed 54 g of ammonium chloride with 350 mL of ammonia solution (33%, V/V). This mixture was diluted up to one liter to prepare an ammoniacal buffer of pH=10^[18]. 0.05 mol·L⁻¹ Zinc oxide solution was prepared as a standard solution by dissolving 4.068 5 g·L⁻¹ in 2 mol·L⁻¹ nitric acid then diluted with deionized water. The 0.05 mol·L⁻¹ disodium salt of EDTA solution was prepared by dissolving 4.557 g in 250 mL bidistilled water. This solution was standardized compleximetrically^[19].

1.4 Physical measurements

IR spectra were recorded as KBr discs using Matson FTIR spectrophotometer in the 4 000~200 cm⁻¹ range. The molar conductance using Sybron-Barnstead conductometer (Meter-PM.6, $E=3406$). The ¹H NMR spectra were recorded using 300MHz Varian-Oxford Mercury. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument. The UV-Vis absorption spectra were measured on a Shimadzu 3101pc spectrophotometer and performed using a Unicam UV-2 spectrophotometer in 10 mm quartz cell and a blank solution as a reference. The microanalysis for C, H, N and Cl were performed in the Microanalytical Center, Faculty of Science, Cairo University. The pH value measurements were made using HANNA pH meter. Thermogravimetric analysis (TGA) was performed on a TA Instruments, SDT2960). The precursor was carried out at a heating rate of 10 °C·min⁻¹ in nitrogen atmosphere. The X-ray powder diffraction analyses were

carried out by using Philips Analytical X-Ray BV, diffractometer type PW 1840 in the $2\theta=0^\circ\sim 80^\circ$ range. Radiation was provided by copper target (Cu anode 2 000 W, $\lambda=0.154\ 18\ \text{nm}$) operated at 40 kV and 25 mA. Divergence and the receiving slits were 1 and 0.2 mm, respectively.

1.5 Spectrophotometric determination studies

The absorption spectra of Schiff base ligand under study were scanned within the wavelength up to 800 nm using $1\times 10^{-4}\ \text{mol}\cdot\text{L}^{-1}$ solution of Schiff base measured in a universal buffer of different pH values from 2~13 to show the pH value effect on the absorption spectra of the ligand and the determination of its dissociation constants under investigation^[20]. The stability constant was calculated using the method developed by Taneja^[21].

1.6 Spectrophotometric procedure for Fe (III) in natural water

Water samples were collected according to the recommended standard methods^[22]. They were spiked with a definite concentration of Fe(III) ion solution and 1 mL of $10^{-4}\ \text{mol}\cdot\text{L}^{-1}$ of the Schiff base was added. The spectrophotometric measurements of Fe (III) in natural water were taken in pH value range of 2~13 by using universal buffer.

1.7 Biological activity

The new complex was tested in vitro to assess growth inhibitory activity against the bacterial and fungal species with standard antibacterial and antifungal agents according to the recommended procedure^[23]. The statistic analysis was done by using soft ware program SPSS version 16 (IBM).

2 Results and discussion

Condensation of 2-[2-(2-formylphenoxy) ethoxy] benzaldehyde with triethylenetetraamine gives the corresponding cyclic Schiff base as identified by IR, ¹HNMR and mass spectra.

An attempt to gain a better insight on the molecular structure of the ligand (using Chem3D ultra 8.0 program) was made. The results show 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

and all bond angles predict sp^3 and sp^2 hybridization in addition to no formation of hydrogen bonds due to the presence of the corresponding NH in the two direction sides far away from each other.

The mass spectra are given molecular ion peak (m/z) of 380 at 5% relative abundance and the basic beak (m/z) =86 at 100% relative abundance attributed to $\text{C}_{22}\text{H}_{28}\text{N}_4\text{O}_2$ and $\text{C}_4\text{H}_9\text{O}_2$ ion, respectively, and the other molecular ion peaks in the mass spectra are attributed to the fragmentation of H_2L molecule obtained from the rupture of different bonds inside the ligand molecule (Fig.1 and Scheme 1).

The UV-Vis absorption spectra of H_2L ligand show sharp bands at 405 nm ($\epsilon=5\ 224\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 415 nm ($5\ 642\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) which can be assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions within the Schiff base ligand molecule, respectively, and due to the presence of two identical groups in the Schiff base ligand, one value of dissociation constant appears at the same value ($\text{p}K_a=8.88$), which can be attributed to the ionization of NH proton and indicates the presence of one hydrogen that can be ionized, and the positive values of its free energy change indicate the nonspontaneous character of dissociation reaction.

2.1 Metal-ligand stability constant^[21]

The order of stability constants is $\text{Co}^{2+}<\text{Ni}^{2+}<\text{Cu}^{2+}>\text{Zn}^{2+}$ in accordance with the Irving and Williams order^[24] for divalent metal ions of the 3d series. It is clear from Table 1 that the stability of Cu (II) complex is considerably larger as compared to other metals of the 3d series. Under the influence of the ligand field, Cu(II) ($3d^9$) will receive some extra stabilization^[25] due to tetragonal distortion of octahedral symmetry in their complexes in addition to further stabilization due to the Jahn-Teller effect^[26]. The negative values of ΔG^\ominus show that the driving tendency of the complexation reaction is from left to right and the reaction proceeds spontaneously.

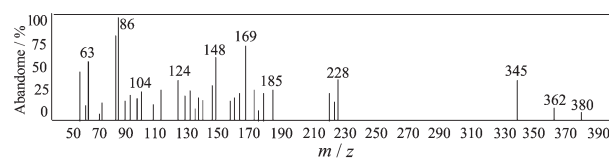


Fig.1 Mass spectrum of Schiff base ligand

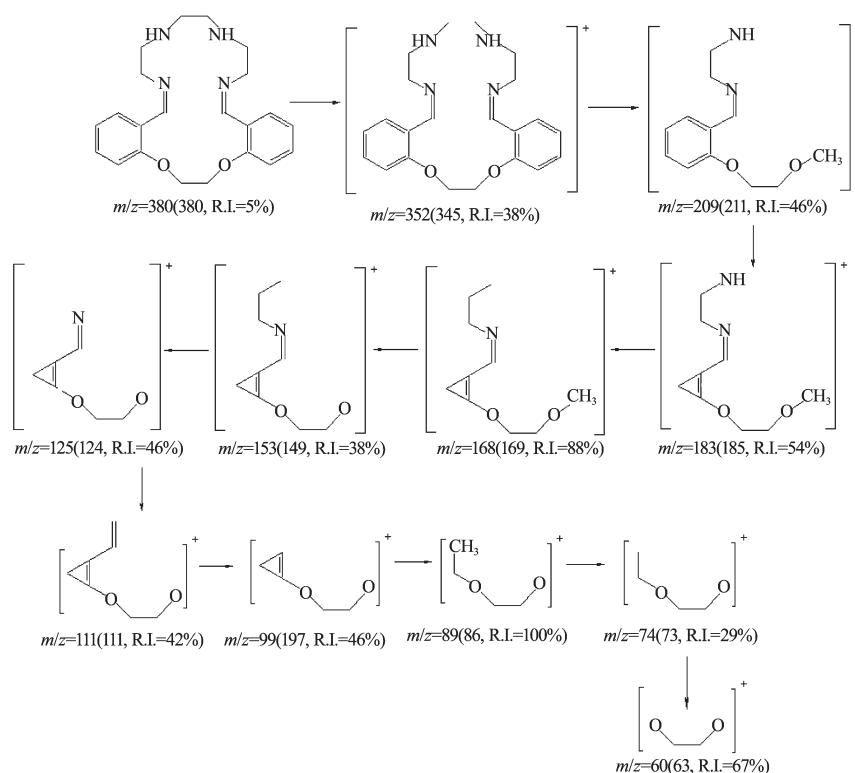
Scheme 1 Mass fragmentation pattern of H_2L ligand

Table 1 Calculated stability constant for Schiff base metal complexes,
 $(c_{\text{H}_2\text{L}}=1\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}, c_{\text{M}}=1\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}, \lambda_{\text{max}}=415 \text{ nm})$

Complex	$[\text{Cr}(\text{H}_2\text{L})]\text{Cl}_3$	$[\text{Fe}(\text{H}_2\text{L})]\text{Cl}_3$	$[\text{Co}(\text{H}_2\text{L})]\text{Cl}_2$	$[\text{Ni}(\text{H}_2\text{L})]\text{Cl}_2$	$[\text{Cu}(\text{H}_2\text{L})]\text{Cl}_2$	$[\text{Zn}(\text{H}_2\text{L})]\text{Cl}_2$
$\lg \beta$	1.99	2.32	2.4	2.59	2.82	2.79
$-\Delta G^\ominus / (\text{kJ}\cdot\text{mol}^{-1})$	740.1	905.1	941.5	1 023.5	1 115.0	1 103.5

2.2 Elemental analyses and molar conductance measurements for the complexes

The results of elemental analyses are in good agreement with those required by the proposed formulae given in Table 2. The electrolytic nature of the clear solutions metal complexes ($10^{-3} \text{ mol}\cdot\text{L}^{-1}$) dissolved in DMF at $(25 \pm 2)^\circ\text{C}$ leads us to conclude that the

coordination geometry of the divalent ions is distorted octahedral involving four nitrogen donors of the macrocyclic ring and the two oxygen of the Schiff base ligand, thus suggesting that the Schiff base acts as hexadentate structure. The $\text{M}(\text{III})\text{-H}_2\text{L}$ complexes are ionic in nature and they are considered as 1 :3 electrolyte, indicating the bonding of the chloride

Table 2 Analytical and physical data of Schiff base and its metal complexes

Compound	Colour (yield / %)	M.P. / °C	Found / % (calcd. / %)					$\mu_{\text{eff.}} /$ B.M.	$\Lambda_{\text{m}} /$ ($\Omega^{-1}\cdot\text{mol}^{-1}\cdot\text{cm}^2$)
			C	H	N	M	Cl		
$\text{H}_2\text{L}=\text{C}_{22}\text{H}_{28}\text{N}_4\text{O}_2$	Yellowish Brown(81)	110	70.03(69.47)	7.11(7.37)	14.41(14.74)	—	—	—	—
$[\text{Cr}(\text{H}_2\text{L})]\text{Cl}_3$	Brown(83)	118	49.34(49.03)	5.46(5.21)	10.37(10.40)	9.50(9.63)	19.56(19.78)	4.18	271.1
$[\text{Fe}(\text{H}_2\text{L})]\text{Cl}_3$	Black(80)	106	48.75(48.68)	5.43(5.16)	10.92(10.33)	10.78(10.29)	19.36(19.63)	5.34	220.3
$[\text{Co}(\text{H}_2\text{L})]\text{Cl}_2$	Dark Green(96)	280	51.37(51.77)	5.55(5.49)	10.39(10.98)	11.02(11.55)	13.66(13.92)	4.54	108.8
$[\text{Ni}(\text{H}_2\text{L})]\text{Cl}_2$	Silversh Brown(80)	104	51.67(51.79)	5.24(5.49)	10.47(10.99)	11.10(11.52)	13.11(13.93)	2.71	146.6
$[\text{Cu}(\text{H}_2\text{L})]\text{Cl}_2$	Brown(89)	250	51.98(51.31)	5.17(5.44)	10.72(10.88)	12.61(12.34)	13.28(13.80)	2.54	141.5
$[\text{Zn}(\text{H}_2\text{L})]\text{Cl}_2$	Honey Brown(82)	170	51.44(51.13)	5.05(5.42)	10.41(10.84)	12.08(12.66)	13.29(13.75)	—	120.1

anions to the M(III) ions, in which the molar conductance values of M(II) chelates are ionic in nature and of the type 1:2 electrolytes^[27].

2.3 IR and ¹H NMR spectra

The IR spectra of the metal complexes are similar to each other, except for some slight shifts and intensity changes of a few vibration peaks caused by different metal (II/III) ions, indicating that the metal complexes have similar structure. The most important IR bands of Schiff base and its metal complexes with probable assignments are given in Table 3. The ligand has multi coordination sites which gave variable coordination modes. The IR spectra of all complexes show a shift for the band of $\nu(\text{C}=\text{N})$, $\nu(\text{-O-})$ and $\nu(\text{NH})$ towards lower

and higher or disappearance frequencies compared to the free ligand, indicating the participation of the azomethine nitrogen, the ether oxygen and amine nitrogen in the coordination, respectively^[28], in addition the new bands between 511~540 cm^{-1} and 417~471 cm^{-1} regions can be assigned to $\nu(\text{M-N})$ and $\nu(\text{M-O})$, respectively^[29].

The ¹H NMR spectrum of Schiff base, in d₆-DMSO, shows signals at 3.545 and 8.529 ppm due to NH and CH=N, respectively, which shifts about their position in the Zn (II) complex within chelation mode, also the multiple signals are assigned to aromatic ring protons, Table 4.

Table 3 IR data (cm^{-1}) of Schiff base and its metal complexes

Compound	$\nu(\text{NH})$	$\delta(\text{NH})$	$\nu(\text{HC}=\text{N})_{\text{azomethine}}$	$(\text{C-O-C})_{\text{ether}}$	$\nu(\text{M-N})_{\text{NH}}$	$\nu(\text{M-N})_{\text{azo}}$	$\nu(\text{M-O})_{\text{ether}}$
H ₂ L	3 036m	829s	1 597sh	1 049m	—	—	—
[Cr(H ₂ L)]Cl ₃	Disappear	815m	1 604sh	1 040m	519w	540s	467s
[Fe(H ₂ L)]Cl ₃	2 932sh	833m	1 610sh	1 039sh	462w	520s	470s
[Co(H ₂ L)]Cl ₂	Disappear	800s	1 643sh	1 056m	443m	513s	417s
[Ni(H ₂ L)]Cl ₂	2 928m	822s	1 590sh	1 055sh	418m	522s	444s
[Cu(H ₂ L)]Cl ₂	3 067m	810s	1 601sh	1 045m	517m	530s	470s
[Zn(H ₂ L)]Cl ₂	2 928sh	830s	1 605m	1 053m	465w	511s	471s

sh=sharp; m=medium; br=broad; s=small; w=weak

Table 4 ¹H NMR spectral data of Schiff base and its metal complexes

Compound	Chemical shift (δ) / ppm	Assignment
H ₂ L	2.654-2.975	(m, 6H, -NH-CH ₂)
	4.429	(m, 2H, -OCH ₂)
	3.545	(m, 1H, NH)
	6.840-7.977	(m, 4H, ArH)
	8.529	(m, 1H, CH=N azomethine)
[Zn(H ₂ L)]Cl ₂	2.655-2.886	(m, 6H, -NH-CH ₂)
	4.346	(m, 2H, -OCH ₂)
	3.319	(m, 1H, NH)
	7.012-7.150	(m, 4H, ArH)
	7.947	(m, 1H, CH=N azomethine)

2.4 Electronic absorption spectra and magnetic moments of the metal complexes

Octahedral geometry is assumed for all the complexes based on their magnetic data (Table 2) and the (UV-Vis) spectra of $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ of the free ligand and $10^{-4} \text{ mol} \cdot \text{L}^{-1}$ of its metal complexes are measured in (Fig.2). The electronic spectra of the free ligand in DMFs

how strong absorption bands at 405 and 420 nm, that could be attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, in the benzene ring or azomethine groups^[30] for free ligand and the bands shift in wavelength for its metal complexes due to complexation which change the conjugation and delocalization of the whole electronic system. Also the d-d transition in these complexes may

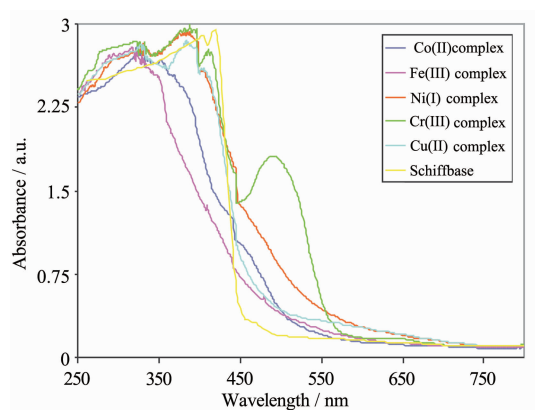


Fig.2 UV-Vis absorption spectra of the Schiff base and its metal chelates

appear above 550 nm and may not due to the low intensity of the $d-d$ transition which is attributed to the low solubility of these complexes. The absorptions are of particular importance as they are highly dependent on the geometry of the molecule where the resulting wavelength of the bands corresponding to the transitions makes a good resemblance between the geometry of the complexes and that of octahedral complexes, especially in Cr complex with shoulder band at 491 nm. Magnetic susceptibility data coupled with electronic spectra suggest a distorted octahedral structure for the metal complexes (Table 2).

2.5 Thermal analyses and kinetic data

The experimental results reveal that the ligand decomposition occurs in multiple stages following a complex mechanism. For the Schiff base, the first two estimated mass losses of 13.50% (calcd. 13.42%) in the range of 175~405 °C may be attributed to the liberation of 3NH_3 as gases, and in the following stages the remaining organic part ($\text{C}_{21}\text{H}_{19}$ molecule), CO_2 and $1/2\text{N}_2$ gases are lost with an estimated mass loss of 86.50% (calcd. 86.58%) with a complete decomposition within the temperature range from 410~935 °C. On the other hand, the Fe(III), Co(II) and Cu(II) chelates show four stages of decomposition within the temperature range 25~790 °C, 45~630 °C and 35~830 °C, with overall weight loss of 86.90% (calcd. 86.76%), 84.91% (calcd. 85.31%) and 84.71% (calcd. 84.54%), respectively (Fig.3 and Table 5).

By employing the Coats-Redfern relation ^[31] the high values of the activation energies reflect the thermal stability of the complexes and the entropy of the activation is in negative value in all complexes indicating that the decomposition reactions proceed with a lower rate than the normal ones. The data are listed in Table 6.

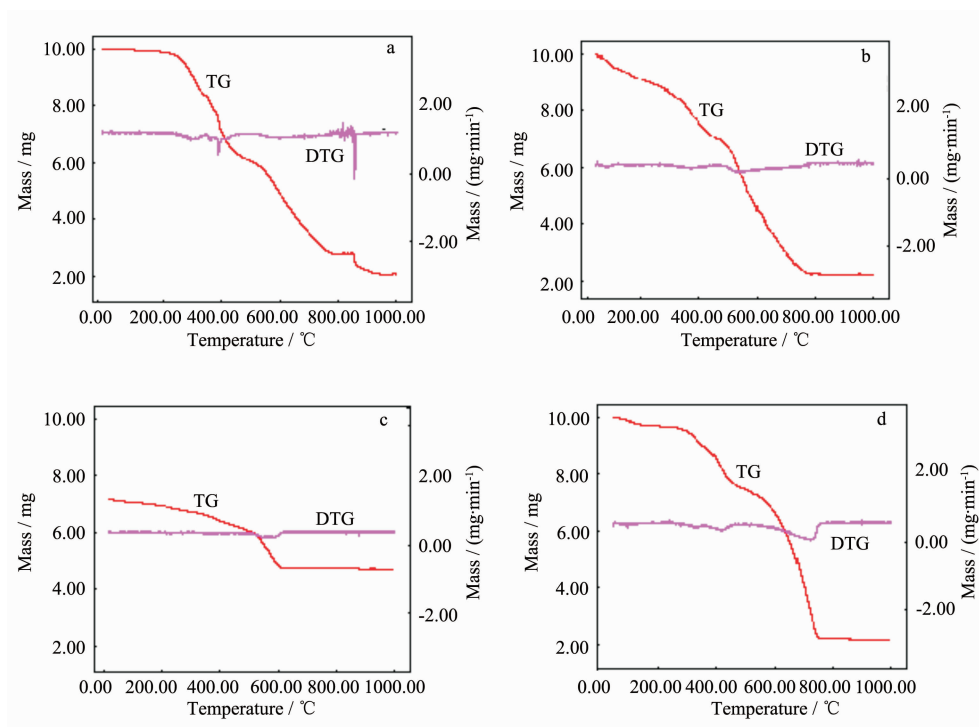


Fig.3 Thermal analyses of (a) Schiff base ligand, (b) Fe(III)-H₂L, (c) Co(II)-H₂L and (d) Cu(II)-H₂L complexes

Table 5 Thermoanalytical results (TG and DTG) for Schiff base and its metal complexes

Compound	TG range / °C	DTG _{max} / °C	<i>n</i> *	Mass loss (Total mass loss)	Assignment	Metallic Residue / %
H ₂ L	175-405	320,383	2	13.42(13.50)	-Loss of 3NH ₃	—
	410-935	421,640,861	3	86.58(86.50), 100(100)	-Loss of CO ₂ , 1/2N ₂ and C ₂₁ H ₁₉	
[Fe(H ₂ L)]Cl ₃	25-350	76,296	2	12.82(12.76)	-Loss of HCl, NO and 1/2H ₂	FeO
	350-465	394	1	16.04(15.99)	-Loss of 2HCl and 1/2N ₂	13.24(13.10)
	465-790	671	1	57.90 (58.15), 86.76(86.90)	-Loss of C ₂₂ H ₂₂ N ₂	
[Co(H ₂ L)]Cl ₂	45-350	81,317	2	18.43(18.42)	-Loss of 2HCl, CH ₄ and 1/2H ₂	CoO
	350-630	433,568	2	66.88(66.49), 85.31(84.91)	-Loss of 4NH ₃ , CO and C ₂₀ H ₅	14.69(15.09)
[Cu(H ₂ L)]Cl ₂	35-125	62	1	5.44(5.59)	-Loss of N ₂	CuO
	125-320	212	1	10.20(10.01)	-Loss of HCl, 1/2O ₂	15.45(15.29)
	320-480	346	1	17.98(18.04)	-Loss of HCl, 2NH ₃ , CH ₄ and 3H ₂	
	480-830	590	1	50.92(51.07), 84.54(84.71)	-Loss of C ₂₁ H ₁₀	

*n**=number of decomposition steps**Table 6 Thermodynamic data for the thermal decomposition of the Schiff base and its metal complexes**

Complex	Decomp. Temp. / °C	<i>A</i> / s ⁻¹	<i>E</i> * / (kJ·mol ⁻¹)	Δ <i>S</i> * / (J·mol ⁻¹ ·K ⁻¹)	Δ <i>H</i> * / (kJ·mol ⁻¹)	Δ <i>G</i> * / (kJ·mol ⁻¹)
H ₂ L	175~245	2.52×10 ¹¹	57.60	-27.00	49.1	66.00
	245~405	6.47×10 ⁶	92.00	-56.00	89.10	133.0
	410~500	6.84×10 ⁶	106.0	-96.00	113	152.0
	500~725	1.70×10 ¹³	146.0	-132.0	151	170.0
	725~935	1.20×10 ¹²	189.0	-172.0	243	268.0
[Fe(H ₂ L)]Cl ₃	35~125	4.45×10 ⁷	55.10	-45.00	64.60	99.05
	125~320	4.01×10 ⁸	155.0	-77.00	103.70	133.0
	320~480	3.31×10 ⁶	193.0	-121.0	153.40	195.40
	480~830	7.19×10 ⁷	264.0	-151.0	191.50	221.0
[Co(H ₂ L)]Cl ₂	45~350	1.14×10 ¹¹	74.00	-22.00	42.70	66.60
	350~430	1.11×10 ⁷	151.0	-60.00	88.30	104.0
	430~520	9.28×10 ¹²	221.0	-92.00	121.60	147.0
	520~630	1.70×10 ¹¹	286.0	-135.0	161.30	191.0
[Cu(H ₂ L)]Cl ₂	25~350	1.06×10 ¹¹	92.80	-32.00	62.90	90.60
	350~465	2.10×10 ¹¹	157.0	-88.00	115.50	133.0
	465~515	3.33×10 ⁶	204.0	-122.0	167.20	195.0
	515~790	6.18×10 ¹⁰	271.0	-145.0	171.50	218.0

2.6 X-Ray diffraction

X-ray powder diffraction pattern of the Schiff base ligand and its complexes were carried out in order to give an insight about the lattice dynamics of these complexes. It is observed from the trend of their curves decrease from maximum to minimum intensity indicating that all the metal complexes are amorphous in nature except Cr(III) and Fe(III) complexes are found to have crystalline structures (Fig.4). The identification of the complexes was done by the known method^[32].

2.7 Biological activity

The results of the biological activity screening indicate that all the complexes exhibit broad spectrum antimicrobial activity against the reference bacteria and Fungi as compared to that of the Schiff base. The ligand exhibits biological activity against *Escherichia coli* (G⁻) and *Staphylococcus aureus* (G⁺) bacteria in addition to *Aspergillus flavus* and *Candida albicans* fungus. On the other hand, the metal complexes show biological activity against bacteria higher than the ligand. From all

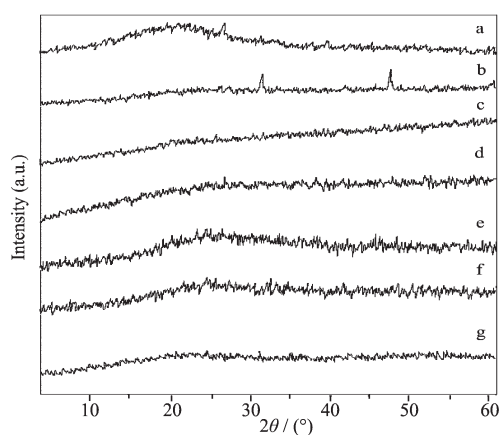


Fig.4 XRD patterns of (a) Schiff base, (b) Cr(III), (c) Fe(III), (d) Co(II), (e) Ni(II), (f) Cu(II) and (g) Zn(II) complexes

complexes, only Ni (II) and Cu (II) complexes have activity against *A. flavus* whilst for *Candida albicans* all the complexes were active except Fe (III) and Zn (II) complexes, Table 7 and Fig.5.

Table 7 Biological activity of the Schiff base and its metal complexes

Sample	Inhibition zone diameter (mm)			
	<i>Escherichia coli</i> (G ⁻)	<i>Staphylococcus aureus</i> (G ⁺)	<i>Aspergillus flavus</i> (Fungus)	<i>Candida albicans</i> (Fungus)
	Mean±RSD*	Mean±RSD*	Mean±RSD*	Mean±RSD*
Control: DMSO	0.0	0.0	0.0	0.0
Tetracycline (Antibacterial agent)	33	30	—	—
Amphotericin B (Antifungal agent)	—	—	18	19
H ₂ L	12.333±0.204	12.667±0.3191	0.0000	0.0000
[Cr(L)Cl ₂]Cl	14.000±0.214	15.000±0.200	0.0000	12.000±0.333
[Fe(L)Cl ₂]Cl	13.333±0.229	13.000±0.154	0.0000	0.0000
[Co(L)Cl ₂]	16.333±0.215	14.667±0.239	0.0000	12.667±0.250
[Ni(L)Cl ₂]	14.667±0.276	14.000±0.286	12.667±0.164	15.000±0.319
[Cu(L)Cl ₂]	15.000±0.333	15.000±0.000	10.333±0.391	11.000±0.200
[Zn(L)Cl ₂]	21.000±0.238	25.333±0.160	0.0000	0.0000

RSD*: relative standard deviation

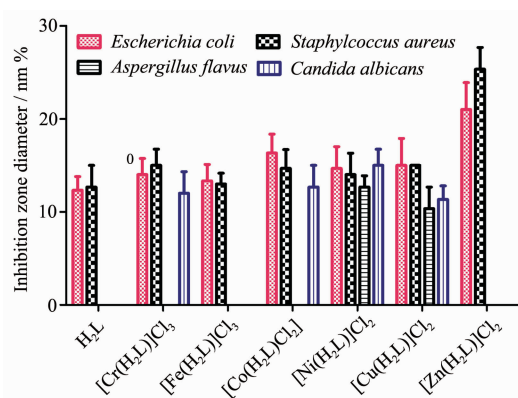


Fig.5 Percent of inhibition zone diameter (mm·mg⁻¹ sample) relative to standard vs. the Schiff base ligand (H₂L) and its metal complexes

3 Application

A new spectrophotometric determination of 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 and the maximum wavelength is found at 410 nm (Fig.2). The optimum factors such as pH value, temperature, molar ratio, time and effect of some foreign ions were studied in order to achieve maximum recovery and assess the applicability of the proposed method to recover Fe(II) from spiked water samples (Fig.6). The tolerable amounts of each ion,

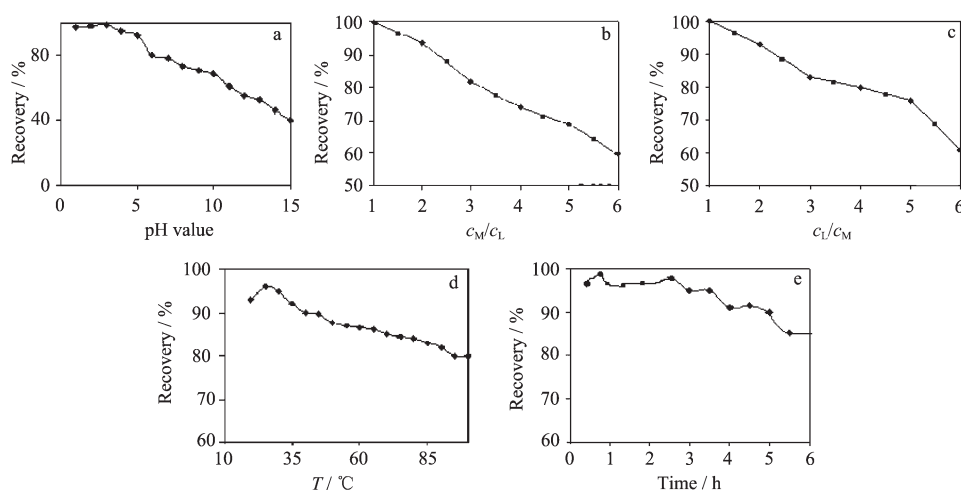


Fig.6 Recovery (R%) of $5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \text{ Fe(III)}$ vs. (a) pH value, (b) different concentrations of H_2L ligand, (c) Fe(III) using H_2L ligand, (d) temperature, (e) time effect

Table 8 Effect of some foreign ions on the recovery of $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ Fe(III)}$ using $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ of Schiff base ligand at $\text{pH}=3.5$, $t=45 \text{ min}$, $T=25^\circ\text{C}$ and $\lambda_{\text{max}}=410 \text{ nm}$

Foreign ion added	NH_4^+	Al(III)	Cr(III)	Cd(II)	Ca(II)	Mn(II)	Co(II)
$c_{\text{Foreign ion}} / c_{\text{Fe(III)}}$	200	20	20	20	200	20	20
* R / %	99.78	99.71	99.61	98.4	98.65	98.88	99.78
Foreign ion added	Ni(II)	Cu(II)	Zn(II)	K(I)	Na(I)	Cl^-	F^-
$c_{\text{Foreign ion}} / c_{\text{Fe(III)}}$	20.00	20.00	20.00	200	200	200	2000
* R / %	99.71	99.75	98.28	98.12	99.49	98.73	99.89

*R is the recovery

given a maximum error up to 1.88% in the recovery, are summarized in Table 8. As can be seen, all the investigated foreign ions with a relatively high concentration have no adverse effect on the ferric ions determination especially for fluoride ion, a 1000 fold excess does not interfere in the determination.

4 Conclusions

The synthesis and characterization of new metal (II)/(III) complexes have been realized with physicochemical and spectroscopic methods. The study of the interaction of the selected metals with the Schiff base ligand has been performed with UV/Vis spectroscopy. Electronic spectra, magnetic moment and conductance study evidence the fact of the octahedral geometry of complexes. All these studies give good evidence for the proposed structure as suggested in Fig.7. The nuclear magnetic resonance studies are in good agreement with those obtained from IR studies proving that the ligand has multi

coordination sites and confirming the neutral behavior of the ligand. The in vitro activity evaluation results for newly synthesized compounds demonstrate that the compounds have well to moderate antibacterial and antifungal activity against the bacterial and fungal strains. In the analytical application, a new method was developed to recover Fe(III) in aqueous solution, based on the reaction of Fe(III) with synthesized Schiff base ligand. The quench fast reaction produces a stable colored sample which allows one to perform spectrophotometric measurements several hours after Fe(III) has reacted with the Schiff base ligand. The sensitivity of the method does not vary with Fe(III) concentration nor with the chemical composition of the natural water. The method demands low reagent consumption, thus reducing the contamination risk and increasing the sample throughput. The method does not require any difficult or time consuming operations and could be performed without any addition of active reagents.

Table 9 Recovery of Fe(III) spiked in natural water samples using $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{L}$ at $\text{pH}=3.5$, $t=45 \text{ min}$, $T=25 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}}=410 \text{ nm}$

Water samples (location)	Fe(III) spiked / ($\text{mg} \cdot \text{L}^{-1}$)	Fe(III) recovered / ($\text{mg} \cdot \text{L}^{-1}$) Mean \pm RSD*	SD*	Mean recovery / %
Distilled water	2.63	2.590 \pm 1.081	0.028	99.12
	4.54	4.507 \pm 0.999	0.045	
	6.44	6.397 \pm 0.954	0.061	
Tap water	2.63	2.580 \pm 1.202	0.031	98.79
	4.54	4.490 \pm 1.158	0.052	
	6.44	6.393 \pm 1.142	0.073	
Nile water(Egypt)	2.63	2.600 \pm 0.731	0.019	99.27
	4.54	3.833 \pm 0.939	0.036	
	6.44	6.397 \pm 0.813	0.052	
Sea water(Gamasah)	2.63	2.593 \pm 1.272	0.033	98.99
	4.54	4.500 \pm 0.844	0.038	
	6.44	6.403 \pm 0.656	0.042	
Underground water(Belqas)	2.63	2.590 \pm 0.849	0.022	98.94
	4.54	4.497 \pm 1.156	0.052	
	6.44	6.387 \pm 1.268	0.081	
Well water(6th October City)	2.63	2.607 \pm 0.882	0.023	99.50
	4.54	3.850 \pm 1.740	0.067	
	6.44	6.423 \pm 1.713	0.110	

SD*: standard deviation, RSD*: relative standard deviation

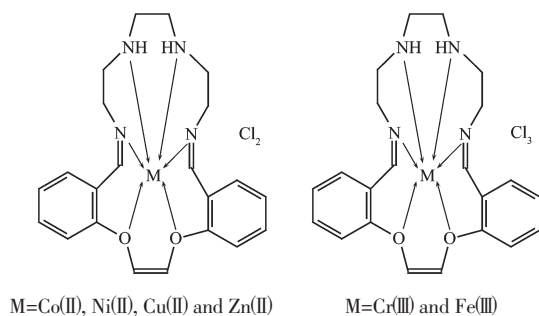


Fig.7 Suggested Structural formula of metal complexes

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