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Synthesis, spectroscopic and structural characterization, and antimicrobial studies of metal complexes of a new hexadentate Schiff base ligand. Spectrophotometric determination of Fe(III) in water samples using a recovery test

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Abstract New Schiff base complexes were prepared using the bioactive antimicrobial bis-Schiff base ligand synthesized by condensation of 2-aminobenzoic acid and 2,2'-(ethylenedioxy)bis(benzaldehyde). The pK_A value of the bis-Schiff base was determined through visible spectrophotometric experiments and the stability constants of its complexes were also studied. The structural features of the complexes were determined from their elemental analyses, magnetic susceptibility, molar conductance, and spectral (IR and ¹H NMR) studies. Powder XRD indicates that all the complexes are amorphous except the Cr(III) and Cu(II) chelates which are crystalline. The data revealed that the stoichiometries of all prepared complexes are of 1:1 M/L type. The UV-vis absorption spectral data for the complexes suggest an octahedral geometry around the central metal ion. Thermogravimetric data (TG and DTG) were also studied. The kinetic and thermodynamic parameters for thermal decomposition of the complexes were calculated by graphical methods using the Coats-Redfern approach. The antimicrobial activity of the bis-

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G. G. Mohamed (⊠) · A. B. Kamel Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt e-mail: ggenidy68@hotmail.com Schiff base and its complexes was tested against a number of bacteria and fungi to assess their inhibiting potential. Most of the complexes exhibit antibacterial activity more than the parent bis-Schiff base. Also Cr(III), Co(II), and Ni(II) complexes have antifungal activity against *Candida albicans* whereas the parent bis-Schiff base is inactive. A recovery test was also applied for the spectrophotometric determination of Fe(III) in different natural water samples.

Keywords Bis-Schiff base · Metal complexes · Biological activity · Recovery test · Spectroscopic studies

Introduction

Schiff bases are important in molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc. [1–5]. Macrocyclic ligands with additional donor atoms appended to the ring have attracted considerable interest owing to their capacity to bind and transport metal ions, for the potential to prepare and study their mixed-valence forms, and as models for metalloproteins [6, 7]. There is a continued interest in synthesizing macrocyclic complexes [2, 8-11] because of their potential applications in fundamental and applied sciences [11-13] and importance in the area of coordination chemistry [14, 15]. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth in interest in macrocyclic compounds [16]. An effective way to use the molecular recognition capability of macrocycles for metal ion separation is to incorporate such ligands into solvent extraction and liquid membrane systems [17]. During the past few years, the separation of heavy metals and organic substances has become more important in water purification applications owing to the drastic strengthening of environmental protection laws. A macrocyclic Schiff base prepared by reaction of 2,6-diaminopyridine and 2,2'-(ethylenedioxy)bis(benzaldehyde) has been reported. Its Cu(II), Ni(II), Pb(II), Co(III), and La(III) complexes were synthesized by exploiting the template effect. Spectral, magnetic, and electrochemical properties of the new compounds were studied in detail [18].

This work focuses on the use of a hexadentate bisaldehyde-type ligand having selective ability to coordinate transition ions, protect them from deactivation due to interaction with solvent molecules, and enhance their biological activity. Structurally characterized bisaldehydetype complexes of the 3d block elements are rare and the coordination mode of the Schiff base ligand (Scheme 1) is usually proposed on the basis of the composition and spectroscopic data. Depending on the preparative procedures, different compositions have been reported for bisaldehyde-type complexes, including [M(L)]Cl (M = Cr and Fe) and [M(L)] [M = Co, Ni, Cu, and Zn]. In this context, we have studied the interaction of M(II) or M(III) chloride (Cr, Fe, Co, Ni, Cu, and Zn ions) with a

Scheme 1

hexadentate Schiff base ligand derived from the condensation of 2,2'-(ethylenedioxy)bis(benzaldehyde) and 2-aminobenzoic acid. The coordination behavior of the bis-Schiff base ligand towards metal chlorides was investigated and the data obtained were correlated with their elemental analysis, thermal properties, ¹H NMR, FT-IR, UV–vis, and molar conductivity measurements. The antimicrobial efficiency of the bis-Schiff base and its complexes was screened against different microorganisms.

Results and discussion

The bis-Schiff base ligand has several potential coordination sites, of which the two carboxylate oxygen, two azomethine nitrogen, and two ether oxygen atoms can bond to one metal ion to produce a 6-membered chelate ring. This work describes the preparation of a new macrocyclic bis-Schiff base ligand via the condensation of 2,2'-(ethylenedioxy)bis(benz-aldehyde) with 2-aminobenzoic acid (Scheme 1).

The new bis-Schiff base was characterized on the basis of elemental analysis, IR, ¹H NMR, UV-vis, and mass spectra. The mass spectrum provides a vital clue for





Fig. 1 Mass spectrum of bis-Schiff base ligand

elucidating the structures of the Schiff base. The fragment ion peak at m/z = 506 (relative intensity 8 %) corresponds to the molecular weight of the Schiff base under investigation. The Schiff base shows a peak at m/z = 78 (100 %) corresponding to the C₆H₆ ion, and other fragments observed were in good agreement with the proposed formula given in Scheme 1 and Fig. 1. The molecular modeling of the Schiff base ligand shows that the bond lengths of all bonds in the left- and right-hand sides are typical. The structure is considered symmetrical and all bond angles are predicted to be sp³ and sp² hybridized according to Chem3D ultra 8.0.

The absorption spectra of the bis-Schiff base ligand (10^{-4} M) under investigation in buffer solutions of different pH values ranging from 2 to 13 were scanned in the wavelength range from 200 to 700 nm, against the same solvent as a blank. The experimental spectrum features shows two sharp peaks centered at 350 nm ($\varepsilon = 23,820 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 390 nm ($\varepsilon = 7,186 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) which can be attributed to π – π * and n– π * transitions within the bis-Schiff base molecule. The characteristic IR and ¹H NMR spectral bands of the bis-Schiff base will be discussed in detail with the respective metal complexes.

Ligand dissociation and metal-ligand stability constants

The ligand dissociation constant was calculated spectrophotometrically using the half height and limiting absorbance methods [19]. It is obvious from the data that one pK_a value is obtained, amounting to 5.20, which can be attributed to the dissociation of the COOH proton. The positive value of ΔS° indicates the nonspontaneous character of dissociation reaction.

Calculation of metal complex formation constants

The stability constants of M(II)/(III) complexes with the bis-Schiff base ligand were determined spectrophotometrically using Taneia and Srivastova's method [20] by measuring the absorbance of solutions of ligand and metal at fixed concentration but at distinct pH values ranging from 2 to 12. The complex-forming abilities of the transition metal ions are frequently characterized by stability orders of Irving and Williams series [21]. The order of stability constants is found to be Co(II) < Ni(II) < Cu(II) > Zn(II)for divalent metal ions of the 3d series. Under the influence of the ligand field and Jahn–Teller effect [22], Cu(II) (3d⁹) will receive some extra stabilization [23] due to tetragonal distortion of octahedral symmetry in their complexes. The free energy of formation, ΔG° , accompanying the complexation reaction was determined at 25 °C; negative values of ΔG° show that the driving force of the complexation reaction is from left to right and the reaction proceeds spontaneously.

Elemental analyses of complexes

The elemental analysis results for the metal complexes are in good agreement with the calculated values. It is clear that the complexes have 1:1 metal–ligand stoichiometry of the type ML. The formation of these complexes may proceed according to the following equations (H_2L = bis-Schiff base ligand):

(a)
$$MCl_2 + H_2L \rightarrow [M(L)] + 2HCl$$

 $M = Ni(II), Co(II), Cu(II), Zn(II)$

(b) $MCl_3 + H_2L \rightarrow [M(L)]Cl + 2HCl$ M = Cr(III), Fe(III)

Molar conductance measurements

The metal(II)/(III) complexes were dissolved in DMF and the molar conductivities of their solutions (10^{-3} M) at room temperature were measured. The low conductance values of the bivalent metal complexes support the nonbonding of the chloride anions to the metal ions and their non-electrolytic nature. The Cr(III) and Fe(III) complexes have molar conductance values of 56.27 and $63.86 \ \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, respectively, indicating their electrolytic nature and they are of the type 1:1.

IR spectral studies

The spectrum of the free bis-Schiff base ligand showed a band in the region at $1,597 \text{ cm}^{-1}$ characteristic of the azomethine stretching mode indicating the formation of the bis-Schiff base product. This band was shifted toward lower/higher frequencies in the spectra of metal complexes (1,590–1,689 cm⁻¹) compared with the parent bis-Schiff base. This phenomenon appears to be due to the coordination of the azomethine nitrogen to the metal ion [19, 24].

The intense band at $1,686 \text{ cm}^{-1}$ present in the IR spectrum of the free bis-Schiff base ligand may be assigned to the carboxylic group. However, the spectra of all the complexes showed variety in the characteristic band accompanied by the appearance of the two characteristic bands at 1,469-1,501 and $1,369-1,404 \text{ cm}^{-1}$ attributed to $(\text{COO}^{-})_{(asym)}$ and $(\text{COO}^{-})_{(sym)}$, respectively, indicating the participation of the carboxylate oxygen atom in the complex formation. The IR spectra of the complexes clearly demonstrated that the C–O–C and C–C–O stretching vibrations are altered compared to those of the bis-Schiff base ligand owing to conformational changes. The fact that the C–O–C absorptions of the complexes are shifted to higher wavenumbers compared to those of the ligand also confirms the complex formation [19, 25, 26].

Conclusive evidence of the bonding was also shown by the observation that new bands in the spectra of all metal complexes appear in the low frequency regions at 463–475 and 513–532 cm⁻¹ characteristic of M–N and M–O stretching vibrations, respectively, that were not observed in the spectrum of the free bis-Schiff base ligand. So, it can be concluded that the bis-Schiff base ligand behaves as a double negatively charged hexadentate ligand coordinated to the metal ions via azomethine N, deprotonated carboxylic O, and ether O.

¹H NMR spectra

The formation of the bis-Schiff base ligand was conveniently monitored by peak ratios in the ¹H NMR spectra recorded in DMSO-d₆ using tetramethylsilane (TMS) as internal standard. The azomethine proton signal in the spectrum of the zinc complex ($\delta = 7.95$ ppm) was shifted upfield compared to the free bis-Schiff base ligand (7.68 ppm), suggesting deshielding of the azomethine group as a result of the coordination with the metal ion. The disappearance of the COOH signal in the spectrum of the Zn(II) complex relative to free bis-Schiff base (10.31 ppm) indicates the involvement of the COOH group in chelation with proton displacement. In addition, multiple signals observed at 4.59 and 6.49-7.67 ppm (free bis-Schiff base ligand) and 4.58 and 7.10-7.67 ppm (Zn(II) complex) are assignable to the aromatic and OCH₂ protons, respectively.

Magnetic susceptibility and electronic spectral studies

The electronic absorption spectra of the chelates were recorded at room temperature using DMF/ethanol mixture as solvent. The electronic spectra of the free ligand in this solvent showed strong absorption bands in the ultraviolet region that could be attributed to the π - π^* and n- π^* transitions in the benzene ring or azomethine or C=O groups



Fig. 2 UV-vis absorption spectra of the bis-Schiff base ligand and its metal chelates. [M] = [bis-Schiff base ligand] = 5×10^{-4} M, T = 25 °C

for the free bis-Schiff base. The absorption spectra of the complexes are given in Fig. 2.

The diffused reflectance spectral data of the complexes, position of bands, and their transition assignments are of particular importance as they are highly dependent on the geometry of the molecule [27]. The electronic spectrum of the Cr(III) complex shows three absorption bands at 15,556, 21,969, and 27,700 cm^{-1} . The three spin-allowed transitions for Cr(III) in an octahedral field are as follows: ${}^{4}A_{2g}~(F) \rightarrow {}^{4}T_{2g}~(F),~{}^{4}A_{2g}~(F) \rightarrow 4T_{1g}~(F),~and~{}^{4}A_{2g}$ $(F) \rightarrow {}^{4}T_{1g}$ (P). The band at 15,556 cm⁻¹ is a direct measurement of the ligand field parameter 10Dq. In addition, the magnetic moment value (3.61 BM) can be taken as additional evidence for the octahedral geometry [27]. From the diffused reflectance spectrum of the Fe(III) complex, the bands at 14,096, 18,625, and 24,585 cm⁻¹ may be assigned to the ${}^{6}A_{1g} \rightarrow T_{2g}(G)$ and ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$ transitions in octahedral geometry of the complex [28]. The spectrum shows also a band at 27,777 cm^{-1} which may be attributed to ligand to metal charge transfer [27, 29].

The diffused reflectance spectrum of the Cu(II) complex displayed the *d*-*d* transition band in the region 13,606 cm⁻¹ which is due to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition. This d-d transition band strongly favors a distorted octahedral geometry around the metal ion. The spectrum of the Ni(II) complex displayed three d-d bands at 13,150, 14,749, and 23,310 cm⁻¹. These correspond to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F), {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$, and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transitions, respectively, being characteristic of an octahedral geometry [27, 29]. This geometry is further supported by its magnetic susceptibility value (2.76 BM). The diffused reflectance spectrum of the Co(II) complex displayed the d-d transition bands in the region 15,017, 16,723, and 23,566 cm⁻¹ which are assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F), {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(F)$



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

TG range/°C	DTG _{max} /°C	п	Mass loss Calcd (estim)/%	Total mass loss	Assignment	Metallic residue
150-375	291	1	29.33 (30.09)	100 (100)	Loss of 3CO ₂ and NH ₃	_
375–970	414, 711	2	70.67 (69.91)		Loss of C ₂₇ H ₂₁ N	
25-175	160	1	18.72 (18.72)	89.28 (89.73)	Loss of 3HCl and 1/2O ₂	FeO
175-370	372	1	9.55 (9.53)		Loss of 2NO and 2H ₂	
370-475	472	1	6.56 (6.53)		Loss of CO ₂	
475–765	619	1	54.45 (54.95)		Loss of C ₂₉ H ₁₇	
30-285	110, 219	2	25.24 (24.86)	88.26 (88.31)	Loss of 2HCl, 2NO and CO	CoO
285-480	291	1	14.42 (14.69)		Loss of CO ₂ and 3CH ₄	
480-810	655	1	48.60 (48.76)		Loss of C ₂₅ H ₁₀	
25-465	161, 388	2	22.57 (22.84)	87.63 (87.57)	Loss of 2HCl, CO ₂ and CO	CuO
465–760	505, 639	2	65.06 (64.73)		Loss of O_2 , 2NH ₃ and $C_{28}H_{16}$	
	TG range/°C 150–375 375–970 25–175 175–370 370–475 475–765 30–285 285–480 480–810 25–465 465–760	TG range/°C DTG _{max} /°C 150–375 291 375–970 414, 711 25–175 160 175–370 372 370–475 472 475–765 619 30–285 110, 219 285–480 291 480–810 655 25–465 161, 388 465–760 505, 639	TG range/°C DTG _{max} /°C n 150–375 291 1 375–970 414, 711 2 25–175 160 1 175–370 372 1 370–475 472 1 475–765 619 1 30–285 110, 219 2 285–480 291 1 480–810 655 1 25–465 161, 388 2 465–760 505, 639 2	TG range/°CDTG $_{max}/°C$ nMass loss Calcd (estim)/%150-375291129.33 (30.09)375-970414, 711270.67 (69.91)25-175160118.72 (18.72)175-37037219.55 (9.53)370-47547216.56 (6.53)475-765619154.45 (54.95)30-285110, 219225.24 (24.86)285-480291114.42 (14.69)480-810655148.60 (48.76)25-465161, 388222.57 (22.84)465-760505, 639265.06 (64.73)	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 1 Thermoanalytical results (TG and DTG) of bis-Schiff base ligand and its metal complexes

n number of decomposition steps

(P) transitions, respectively [27, 29]. The transitions correspond to the octahedral geometry of the complex, which is also supported by its magnetic susceptibility value (5.25 BM). The complex of Zn(II) is diamagnetic. According to the empirical formula, an octahedral geometry is proposed for this complex.

Thermal analysis studies (TG and DTG)

Figure 3 and Table 1 show the TG and DTG results introducing a new possibility for investigation of the bis-

Schiff base and their metal(II)/(III) complexes. The thermogravimetric analysis (TG) (Table 1) and curves were obtained at a heating rate of 10 °C/min in a nitrogen atmosphere over a temperature range of 20–900 °C. The bis-Schiff base ligand was stable up to 150 °C and its decomposition started at this temperature. In the decomposition process of the ligand, the mass losses corresponded to $3CO_2$, NH₃, and $C_{27}H_{21}N$ molecules. The decomposition of the bis-Schiff base ligand is irreversible.

The Fe(III) complex starts its decomposition at 25 $^{\circ}$ C. In the decomposition process of the Fe(III) complex, the

mass losses corresponded to 3HCl, $1/2O_2$, 2NO, 2H₂, CO₂, and C₂₉H₁₇ molecules leaving FeO in the last stage of the decomposition. Sharp peaks were found at 160, 372, 472, and 619 °C in the DTG curve which demonstrated the decomposition of the complex in four steps. The overall weight loss of 89.73 % (theoretically 89.28 %) may be in accordance with the proposed structure of the complex shown in Scheme 1.

The Co(II) complex starts decomposition at 30 °C. In the decomposition process of the Co(II) complex, the mass losses corresponded to 2HCl, 2NO, CO, CO₂, 3CH₄, and C₂₅H₁₀ molecules leaving CoO at the end of the decomposition. The Cu(II) complex was stable up to 25 °C and its decomposition started at this temperature. In the decomposition process of the Cu(II) complex, the mass losses corresponded to 2HCl, CO₂, CO, O₂, 2NH₃, and C₂₈H₁₆ molecules leaving CuO in the fourth stages of the decomposition. The decompositions of the Fe(III), Co(II), and Cu(II) complexes are irreversible. The total weight losses for Fe(III), Co(II), and Cu(II) complexes were found to be approximately the same, when expressed as the percentages calculated stoichiometrically from their chemical formulas given in Table 1.

X-ray diffraction

X-ray powder diffraction crystallographic investigation is the most precise source of information regarding the structure of the bis-Schiff base and its complexes. The data were recorded over the $2\theta = 0^{\circ}-80^{\circ}$ range. The trend of the curves gives a clear idea about the crystallinity of the complexes. It indicates that all the metal complexes are amorphous except the Cr(III) and Cu(II) chelates, which are crystalline.

Calculation of activation thermodynamic parameters

The thermodynamic activation parameters of decomposition processes of dehydrated complexes are evaluated graphically by employing the Coats–Redfern relation [30] and the data are summarized in Table S1 (Supplementary Material). 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 indicates that the decomposition reactions proceed with a lower rate than the normal ones.

Structural interpretation

Single crystals of the complexes could not be isolated from any solutions; thus no definitive structure could be described. However, the analytical, spectroscopic, and magnetic data enable us to propose the possible structures. On the basis of the above observations, the strucutres of the complexes are shown in Scheme 1.

Biological activity

Because of the many biological roles played by these metal ions efforts have been made to synthesize metal complexes to study their structure, spectral, electrochemical, and magnetic properties. The synthesized ligand and the complexes were tested for their in vitro antimicrobial activity against bacteria (Staphylococcus aureus and Escherichia coli) and fungi (Aspergillus flavus and Candida albicans). The inhibition zone diameter (mm/mg sample) values of the investigated compounds are summarized in Table 2. A comparative study of inhibition zone diameter (mm/mg sample) values of the bis-Schiff base ligand and the complexes indicates that the metal complexes exhibit higher antimicrobial activity than the free bis-Schiff base ligand (Table 2; Fig. 4). Such increased activity of the complexes can be explained on the basis of Tweedy's chelation theory [31, 32]. Chelation reduces the polarity of the metal ion considerably because of the partial sharing of its positive charge with the donor group and also due to p-electron delocalization on the whole chelate ring. The lipids and polysaccharides are some important constituents of the cell wall and membranes which are preferred for metal ion interaction. Apart from this, the cell walls also contain many phosphates, carbonyl, and cysteinyl ligands which maintain the integrity of the membrane by acting as a diffusion barrier and also provide suitable sites for binding. Furthermore, the reduction in polarity increases the lipophilic character of the chelates and an interaction between the metal ion and the lipid is favored. This may lead to the breakdown of the permeability barrier of the cell resulting in interference with the normal cell processes. Besides this, the complexes may also form hydrogen bonds through the coordinated anions and azomethine group with the active centers of the cell constituents [31, 32]. Factors capable of increasing the lipophilic nature are expected to enhance the antimicrobial properties. The synthesized Schiff base ligand has moderate inhibitory effects on the growth of the tested microorganisms. This is due to the presence of azomethine groups which have chelating properties. These properties may be used in metal transport across the bacterial membranes or to attach to the bacterial cells at a specific site from which it can interfere with their growth. The antimicrobial activity of metal complexes shows greater bactericidal and fungicidal activities as compared to their corresponding Schiff base. It is clear from Table 2 that the Cr(III), Co(II), and Ni(II) complexes show antifungal activity against C. albicans in comparison with the free bis-Schiff base ligand which has no activity. Also, the Zn(II) complex shows a higher antibacterial activity than

Table 2 Biological activity of the bis-Schiff base ligand and its metal complexes

Sample	Inhibition zone diameter/mm/mg sample ⁻¹						
	Escherichia coli (G ⁻)	Staphylococcus aureus (G ⁺)	Aspergillus flavus (fungus)	Candida albicans (fungus)			
Control: DMSO Standard	0.0	0.0	0.0	0.0			
Tetracycline (antibacterial agent)	33	30	-	-			
Amphotericin B (antifungal agent)	-	-	18	19			
2	13	14	0	0			
3a	12	12	0	11			
3b	11	11	0	0			
3c	16	15	0	12			
3d	14	15	0	14			
3e	13	14	0	0			
3f	20	28	0	0			





the free bis-Schiff base ligand and the remaining complexes.

The present investigations of antimicrobial activity data indicated that all of the newly synthesized complexes exhibited different antimicrobial activity as compared to that of the control drugs. According to these data, it can be concluded that these complexes might be recommended and/or established as new candidates for the search for new antibacterial and antifungal agents [28, 33].

Application: spectrophotometric determination of Fe(III) ions in natural water

In this work, the bisaldehyde-type ligand was utilized for the spectrophotometric determination of Fe(III) in different natural water samples. This reaction produces a stable colored product which can be measured spectrophotometrically at 335 nm. Different analytical parameters were optimized in order to achieve maximum recovery under the recommended conditions. They are pH 3.5, temperature 25 °C, time 45 min, and 1:1 [Fe(III)]/[L] ratio.

Effect of foreign ions

In order to assess the applicability of the proposed method to recover Fe(III) added to water samples, the effect of some foreign ions was investigated. These foreign ions were selected on the basis that they are normally present in fresh and saline waters. 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 of $\pm 2 \%$ in the recovery, are summarized in Table S2 (Supplementary Material). As can be seen, all the investigated foreign ions with a relatively high concentration have no adverse effect on the ferric ions to be determined. Therefore, the recommended procedure may be applied to natural water samples.

Table 3 Recovery percent of Fe(III) in spiked natural water samples

Water samples (location)	[Fe(III)] spiked/ mg cm ⁻³	[Fe(III)] found/ mg cm ⁻³	Recovery/ %	SD	RSD/ %
Distilled water	2.63	2.58	98.10	0.060	2.33
(Cairo University)	6.44	6.41	99.53	0.078	1.22
Tap water (Cairo	2.63	2.55	96.96	0.047	1.84
University)	6.44	6.40	99.38	0.062	0.97
Nile water (Egypt)	2.63	2.60	98.86	0.055	2.12
	6.44	6.37	98.91	0.042	0.66
Sea water	2.63	2.59	98.48	0.064	2.47
(Gamasah)	6.44	6.39	99.22	0.036	0.56
Underground water	2.63	2.57	97.72	0.028	1.09
(Belqas)	6.44	6.39	99.22	0.058	0.91
Well water (sixth	2.63	2.61	99.24	0.031	1.19
October City)	6.44	6.38	99.07	0.064	1.00

Conditions: 5×10^{-4} mol/cm³ bis-Schiff base ligand, t = 45 min, pH 3.5, T = 25 °C, and $\lambda_{max} = 315$ nm

Application

The proposed analytical procedure was applied to different types of water samples in order to assess its accuracy. Recovery tests were carried out on different types of water samples. 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 pre-filtered water samples (10 dm³ each) containing Fe(III) with a concentration of 5 or 10 mg/cm³ were recovered under the recommended conditions. The data in Table 3 show a satisfactory recovery of Fe(III). So, the synthesis of these complexes might provide a new approach for the search for organic ligands for the removal of ferric ions from natural water.

Conclusions

The new metal(II)/(III) complexes synthesized in this work were characterized using different physicochemical and spectroscopic methods. The interaction of the metal ions with the bis-Schiff base ligand was studies with UV–vis spectroscopy. The geometry can be described as octahedral and the thermal study indicates the coordination with the metal ion. Magnetic moment, electronic spectra, and conductance studies provide further evidence of the geometry of the complexes. All these studies support the proposed structures. The results of ¹H NMR studies were in good agreement with those obtained from IR studies. XRD analysis established the crystalline and morphological nature of the complexes. The proton dissociation constants of the bis-Schiff base ligand and the stability constant of their complexes were determined. The activation kinetic and thermodynamic parameters were calculated in different stages of thermal decomposition. We also evaluated the in vitro activities of the new bis-Schiff base and its metal complexes; the results demonstrated that the compounds have good to moderate antibacterial and antifungal activity against the bacterial and fungal strains tested.

A new analytical application was developed to measure Fe(III) in aqueous solution, based on the reaction of Fe(III) with 2,2'-[1,2-ethanediylbis[oxy(2,1-phenylenemethylidyn enitrilo)]]bis(benzoic acid). This reaction produces a stable color, which can be measured by absorbance at 330 nm. The selectivity of the proposed method for the determination of Fe(III) was studied in the presence of various concentrations of cations and anions. The tolerance limits of the ions do not cause a deviation of more than ± 2 % in the absorbance of the Fe(III) complex. The method is simple and does not require any difficult or time-consuming operations. It can be performed by using standard laboratory instruments (spectrophotometer). Therefore, the synthesis of these complexes might provide a new approach for the determination of Fe(III) ions in natural water.

Experimental

All the chemicals used were of high purity analytical grade. $CuCl_2 \cdot 2H_2O$ (Sigma), $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$ (BDH), $CrCl_3 \cdot 6H_2O$ and $ZnCl_2 \cdot 2H_2O$ (Ubichem), and $FeCl_3 \cdot 6H_2O$ (Prolabo) were used. Organic solvents like absolute ethyl alcohol, diethyl ether, and dimethylformamide were supplied by BDH. 2-Aminobenzoic acid was supplied by Aldrich. 2,2'-(Ethylenedioxy)bis(benzaldehyde) was prepared as previously described [34].

Stock solution of the bis-Schiff base ligand $(5 \times 10^{-4} \text{ M})$ was prepared by dissolving the appropriate amount of 0.395 g in 100 cm³ of doubly distilled water. Working solutions were obtained from the stock solution by further dilution with doubly distilled water. Stock solutions (5 \times 10⁻⁴ M) of the metal salts (Cr(III) 0.341 g/ dm³, Fe(III) 0.117 g/dm³, Co(II) 0.119 g/dm³, Ni(II) 0.119 g/dm³, Cu(II) 0.085 g/dm³, and Zn(II) 0.086 g/dm³) were prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of doubly distilled water. A mixture of 0.04 M phosphoric, acetic, and boric acids was prepared to obtain universal buffer solutions of the required pH values from 2 to 13 adjusting using NaOH or HCl (0.1 M) prior to dilution of the mixture to 100 cm³ with water. The reference buffer was prepared analogously. Zinc oxide stock solution (0.05 M) was prepared and the 0.01 M dilute solution was prepared by accurate dilution. The 0.049 M disodium salt of EDTA solution (MW = 372 g/mol) was prepared by dissolving 4.557 g in 250 cm³ doubly distilled water. This solution was standardized compleximetrically. Ammonium chloride (54 g) was mixed with 350 cm³ of ammonia solution (33 % v/v). This mixture was diluted up 1 1 to prepare an ammoniacal buffer of pH 10. Sodium hydroxide solution (10 %) was prepared by dissolving 25 g in 250 cm³ doubly distilled water.

Elemental microanalyses of the separated solid chelates for C, H, N, and Cl were performed at the Microanalytical Center, Cairo University using a CHNS-932 (LECO) Vario Elemental analyzer. The molar conductance of the complexes in DMF was measured using a Sybron-Barnstead conductometer (Meter-PM.6, E = 3,406). Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1,650 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 an MS-5988 GS-MS Hewlett-Packard instrument. The ¹H NMR spectra were recorded using a 300-MHz Varian-Oxford Mercury. The thermal analyses were carried out in a dynamic nitrogen atmosphere (20 $\text{cm}^3 \text{min}^{-1}$) with a heating rate of 10 °C min⁻¹ using a Shimadzu TG-60H thermal analyzer. XPD analyses were carried out by using a Philips Analytical X-ray BV, diffractometer type PW 1840. Radiation was provided by a copper target (Cu anode 2,000 W) high intensity X-ray tube operated at 40 kV and 25 mA. All spectrophotometric measurements were performed using a Unicam UV-2 spectrophotometer using 10-mm quartz cell and a blank solution as a reference. The pH measurements were made using a HANNA pH meter.

Spectrophotometric determination of ionization constant

The absorption spectra of the bis-Schiff base ligand $(1.0 \times 10^{-4} \text{ M})$ were scanned within the wavelength range from 200 to 700 nm in a universal buffer of different pH values ranging from 2 to 13. From the absorption spectra of the bis-Schiff base ligand, the dissociation constants were calculated by applying half height and limiting absorbance methods [19].

Calculation of metal complex formation constants

Chelate stability constants were obtained spectrophotometrically [20, 35] by measuring the absorbance of solutions of ligand and metal at fixed concentration but at distinct pH values ranging from 2 to 12. The degree of formation of the complex is obtained from the relationship

$$n^{\sim} = (A_{\rm x} - A_{\rm L})/(A_{\rm ML} - A_{\rm L})$$
 (1)

where A_x , A_L , and A_{ML} are the absorbances of the partially formed complex at a specific pH, the free ligand, and the fully formed complex, respectively. Then, the negative logarithm of the concentration of non-protonated ligand (pL) was obtained using Eq. 2:

$$pL = \log \left[(1 + B_1^H [H^+] + B_2^H [H^+]^2 + \cdots) / (T_L - nT_M) \right]$$
(2)

where $B_1^{\rm H}$ and $B_2^{\rm H}$ are the reciprocals of the acid dissociation constants of the ligand, i.e., $[LH_1]/[L][H]$ and $[LH_2]/[L][H]^2$, respectively. $T_{\rm L}$ and $T_{\rm M}$ represent the stoichiometric concentration of the ligand and metal. The stability constant (*K*) can be calculated from Eq. 3:

$$n^{\sim} + (n^{\sim} - 1)K(L) = 0 \tag{3}$$

2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoic acid) (**2**, C₃₀H₂₄N₂O₆)

The bis-Schiff base was prepared by refluxing a mixture of 3.654 g 2-aminobenzoic acid (13.34 mmol) and 1.6 g 2,2'-(ethylenedioxy)bis(benzaldehyde) (6.67 mmol) in ethanolic medium on a water bath for 3 h. The resulting yellow precipitate was filtered and purified by crystallization from ethanol, then dried in vacuum to give the desired bis-Schiff base ligand. Yellowish brown solid; yield 95 %; m.p.: 96 °C; IR: $\bar{v} = 1,686$ (C=O), 1,485 (COO)_(asym), 1,388 (COO)_(sym), 1,597 (HC=N)_{azomethine}, 1,045 (C-O-C)_{ether} cm⁻¹; ¹H NMR (DMSO- d_6): $\delta = 4.59$ (m, 2H, OCH₂), 6.49–7.67 (m, 4H, ArH), 7.68 (s, 1H, CH=N), 10.31 (s, 1H, COOH) ppm; ${}^{13}C$ NMR (DMSO- d_6): $\delta = 68.9$ (O-CH₂-CH₂-O), 112.0, 120.4, 125.1, 127.3, 131.6, 158.5 (O-C₆H₄), 128.6, 130.2, 130.3, 133.9 (N-C₆H₄), 160.8 (-CH=N), 169.3 (-COOH) ppm; pK_a $(-\Delta G^{\circ}) = 5.20 \ (31.52 \text{ kJ mol}^{-1}).$

Synthesis of metal complexes

To a solution of 0.395 g Schiff base ligand (1 mmol) in 30 cm^3 ethanol a solution of metal(II)/(III) chlorides (1 mmol) in 30 cm^3 ethanol was added. The resulting mixture was refluxed for 2.5 h on a water bath whereupon the complexes precipitated, which were then filtered off and washed thoroughly with ethanol and diethyl ether for further purification and dried in vacuum. The metal content of the complexes was analyzed complexometrically [29, 36].

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)] chromium(III) chloridetetrahydrate (**3a**, C₃₀H₂₂ClCrN₂O₆)

Dark green solid; yield 80 %; m.p.: 130 °C; $\mu_{eff} = 3.61$ BM; $\Lambda_m = 56.27 \ \Omega^{-1} \ mol^{-1} \ cm^2$; IR: $\bar{\nu} = 1,640$ (C=O), 1,489 (COO_{asym}), 1,369 (COO_{sym}), 1,689 (HC=N_{azomethine}), 1,049 (C–O–C_{ether}), 532 (M–O), 463 (M–N) cm⁻¹; log β ($-\Delta G^\circ$) = 2.56 (155.2 kJ mol⁻¹).

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)]iron(III) chloride trihydrate (**3b**, C₃₀H₂₂ClFeN₂O₆)

Dark green solid; yield 83 %; m.p.: 196 °C; $\mu_{\rm eff} = 5.30$ BM; $\Lambda_{\rm m} = 63.86 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$; IR: $\bar{\nu} =$ 1,655 (C=O), 1,496 (COO_{asym}), 1,383 (COO_{sym}), 1,600 (HC=N_{azomethine}), 1,055 (C–O–C_{ether}), 529 (M–O), 474 (M–N) cm⁻¹; log β ($-\Delta G^{\circ}$) = 3.15 (190.9 kJ mol⁻¹).

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)]cobalt(II) tetrahydrate(**3c**, C₃₀H₂₂CoN₂O₆)

Green solid; yield 97 %; m.p.: 184 °C; $\mu_{eff} = 5.25$ BM; $\Lambda_{m} = 12.40 \ \Omega^{-1} \ mol^{-1} \ cm^{2}$; IR: $\bar{\nu} = 1,639$ (C=O), 1,474 (COO_{asym}), 1,393 (COO_{sym}), 1,610 (HC=N_{azomethine}), 1,049 (C-O-C_{ether}), 520 (M-O), 475 (M-N) cm⁻¹; log β ($-\Delta G^{\circ}$) = 3.21 (194.6 kJ mol⁻¹).

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)]nickel(II) trihydrate (**3d**, C₃₀H₂₂N₂NiO₆)

Olive solid; yield 86 %; m.p.: 112 °C; $\mu_{eff} = 2.76$ BM; $A_{m} = 14.96 \ \Omega^{-1} \ \text{mol}^{-1} \ \text{cm}^{2}$; IR: $\bar{\nu} = 1,692$ (C=O), 1,501 (COO_{asym}), 1,385 (COO_{sym}), 1,621 (HC=N_{azomethine}), 1,061 (C-O-C_{ether}), 513 (M-O), 467 (M-N) cm⁻¹; log β ($-\Delta G^{\circ}$) = 3.39 (205.5 kJ mol⁻¹).

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)]copper(II) dihydrate (**3e**, C₃₀H₂₂CuN₂O₆)

Brown solid; yield 78 %; m.p.: 96 °C; $\mu_{eff} = 1.84$ BM; $\Lambda_{m} = 15.10 \ \Omega^{-1} \ mol^{-1} \ cm^{2}$; IR: $\bar{\nu} = 1,692$ (C=O), 1,469 (COO_{asym}), 1,404 (COO_{sym}), 1,590 (HC=N_{azomethine}), 1,049 (C–O–C_{ether}), 513 (M–O), 466 (M–N) cm⁻¹; log β (– ΔG°) = 3.71 (224.9 kJ mol⁻¹).

[2,2'-[1,2-Ethanediylbis[oxy(2,1-phenylenemethylidynenitrilo)]]bis(benzoato)]zinc(II) 2.5-hydrate(**3f**, C₃₀H₂₂N₂O₆Zn)

Yellow solid; yield 80 %; m.p.: 120 °C; μ_{eff} = diamagnetic; $\Lambda_{\rm m}$ = 12.20 Ω^{-1} mol⁻¹ cm²; IR: $\bar{\nu}$ = 1,659 (C=O), 1,480 (COO_{asym}), 1,373 (COO_{sym}), 1,606 (HC=N_{azomethine}), 1,052 (C–O–C_{ether}), 524 (M–O), 464 (M–N) cm⁻¹; ¹H NMR (DMSO-*d*₆): δ = 4.58 (m, 2H, OCH₂), 7.10–7.67 (m, 4H, ArH), 7.95 (s, 1H, CH=N) ppm; ¹³C NMR (DMSO-*d*₆): δ = 68.8 (O–CH₂–CH₂–O), 112.0, 120.5,

125.2, 127.3, 131.4, 158.4 (O–C₆H₄), 128.5, 130.3, 130.3, 133.8 (N–C₆H₄), 160.9 (–CH=N), 169.4 (–COO) ppm; log β (– ΔG°) = 3.67 (222.4 kJ mol⁻¹).

Biological activity

The standardized disk-agar diffusion method [37] was followed to determine the antibacterial and antifungal activity of the synthesized compounds. The tested compounds were dissolved in DMF (which has no inhibition activity) to get concentrations of 100 μ g/cm³. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (0.1 cm³) from the specific concentration of dissolved tested compounds and carefully placed on the incubated agar surface. After incubation for 48 h at 37 °C, inhibition of the organisms evidenced by a clear zone surrounding each disk was measured and used to calculate the mean inhibition zones.

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