



Synthesis and characterization of bisaldehyde ligand with some transition metals and its application in spectrophotometric determination of Fe(III) in natural water samples using recovery test

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ARTICLE INFO

Article history:

Received 20 November 2011

Accepted 05 February 2012

Keywords:

Bisaldehyde ligand;

Metal complexes;

Elemental analysis;

Thermal analysis; Biological

activity; Recovery test.

ABSTRACT

The coordination behaviour of the bisaldehyde organic ligand with different coordination sites are investigated, towards some bi- and trivalent metal ions like Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). The solid chelates of the bisaldehyde are prepared and subjected to many analytical techniques such as elemental analyses, IR, ¹H NMR and solid reflectance spectra, magnetic moment, molar conductance, X-Ray diffraction (XRD) and thermal analyses. The chelates have octahedral geometry. The bisaldehyde ligand and its binary chelates were subjected to thermal analyses and the different activation thermodynamic parameters were calculated from their corresponding DTG curves. The biological activity of the bisaldehyde ligand and its complexes were also screened. The bisaldehyde ligand is utilized for spectrophotometric determination of spiked Fe(III) in natural water samples using recovery test under optimal experimental conditions.

Introduction

The design and application of new macrocyclic receptors capable of constitutional coordination of guest molecules and ions, had attracted a great deal of interest as these systems had many potential functions such as solubilization, extraction, membrane transport¹⁻⁶ with applications in separation, chromatography, electrochemistry and spectrophotometric methods⁷⁻⁹. New strategies in the design and synthesis of novel functionalized macrocyclic receptors capable of self-organization and self-assembly¹⁰⁻¹⁴ had been developed with the hope of improving the recognition and selective transport functions¹⁵⁻¹⁶. Crown ethers, cyclic peptides, oligoesters, bola-amphiphiles and heteroditopic receptors had been arisen, in this context¹⁷⁻²⁴. The chemistry of macrocyclic receptors and their supramolecular complexes²⁵⁻²⁸ had been extensively developed during last four decades with the hope of developing the "preorganization" concept for targeting inorganic and organic guests like cations, anions or molecules of specific interest²⁹⁻³¹. As a rule, the complexation of cations decreases³² due to the lower do-

nor capacity of benzo compared to aliphatic bonded heteroatoms and as a consequence of conformational hindrance. On the other hand, the complexation of uncharged organic molecules was promoted³³. In the present work, the synthesis and the coordination behaviour of the bisaldehyde organic ligand with different coordination sites are investigated, towards some bi- and trivalent metal ions like Cr(III), Fe(III) Co(II), Ni(II), Cu(II) and Zn(II) are described. The biological activity of the organic ligand and its metal complexes were also screened. The bisaldehyde is used for the spectrophotometric determination of iron in water samples using recovery test technique.

Experimental procedures

1. Materials and reagents:

The chemicals used included CuCl₂.2H₂O (Sigma), CoCl₂.6H₂O and NiCl₂.6H₂O (BDH), CrCl₃.6H₂O and ZnCl₂.2H₂O (Ubichem) and FeCl₃.6H₂O (Prolabo). Organic solvents (spectroscopic pure from BDH) used included absolute ethyl alcohol, diethylether and dimethylformamide (DMF).

2.2. Solutions

Fresh stock solutions of 5x10⁻⁴ M ligand was prepared by dissolving the accurately weighed amount of organic

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ligand (1.111 g/L) in the appropriate volume of absolute ethanol. A 5×10^{-4} M stock solutions of the metal salts (Cr(III) (0.341 g/L), Fe(III) (0.117 g/L), Co(II) (0.119 g/L), Ni(II) (0.119 g/L), Cu(II) (0.085 g/L), and Zn(II) (0.086 g/L)) 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 procedures³⁴. Dilute solutions of the metal ions and organic ligand under study were prepared.

2.3. Instruments

Elemental microanalyses of the separated solid chelates for C, H, N and Cl were performed at the Microanalytical center, Cairo University. The analyses were repeated twice to check the accuracy of the analyses data. The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, $E = 3406$). 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 HANNA pH meter. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wavenumber region $4000-200 \text{ cm}^{-1}$. The spectra were recorded as KBr pellets. The solid reflectance 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. The mass spectrum was recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument. The ^1H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) solution using tetramethylsilane (TMS) as internal standard and the spectra extended from 0 to 15 ppm. The thermal analyses were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ using Shimadzu TG-60H thermal analyzer. The X-ray powder diffraction 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 40KV and 25 mA. Divergence and the receiving slits were 1 and 0.2, respectively.

2.4. Synthesis of bisaldehyde ligand

Salicylaldehyde (20 mmol) was dissolved in hot ethanolic KOH solution (prepared by dissolving 1.12 g (20 mmol) of KOH in 20 ml of absolute ethanol), then the solvent was 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 crystallization³⁵.

2.5. Synthesis of metal complexes

The metal complexes of the bisaldehyde ligand were prepared by the addition of hot solution ($60 \text{ }^\circ\text{C}$) of the metal salts (1 mmol) to the hot solution ($60 \text{ }^\circ\text{C}$) of the bisaldehyde ligand (1.111 g, 1 mmol) in the same solvent (25 mL). The resulting mixture was stirred where upon the complexes precipitated. They were collected by filtration, washed several times with ethanol and diethyl ether.

2.6. Determination of the metal content of the chelates

The metal contents were determined complexometrically by titration against standard EDTA solution at a suitable pH value using the suitable indicator.

2.7. Biological activity

0.5 mL spore suspension (10^{-6} - 10^{-7} spore/mL) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 mL of the tested compounds dissolved in DMF (100 $\mu\text{g/mL}$) were poured into these holes. Finally, the dishes were incubated at $37 \text{ }^\circ\text{C}$ for 48 h where clear or inhibition zones were detected around each hole. A 0.1 mL DMF alone was used as a control under the same condition for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case³⁶.

2.8. Recommended spectrophotometer procedure

Water samples were collected according to the recommended standard methods³⁷. Use the recovery of known additions as part of a regular analytical protocol. After adjusting the pH with HNO_3 and/or NaOH, the mixture (water samples were spiked with a definite concentration of Fe(III) solution and 1 ml of 10^{-4} M of the Schiff base was added) was transferred to the measurement cell. The cell was shaken well for few seconds to ensure complexation. The concentration of metal ion was determined spectrophotometrically and the recovery percentage was obtained.

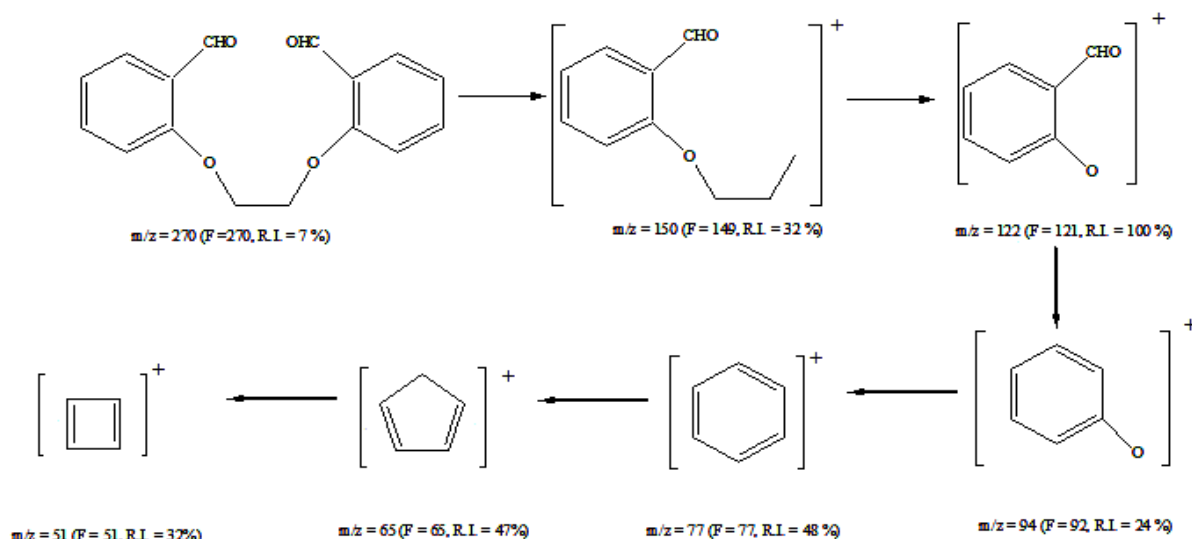
3. Results and Discussion

3.1. Mass spectra

The important peaks and their relative intensities for the molecular ions are shown in Scheme (1). Mass spectrum is characterized by moderate to high relative intensity molecular ion peaks. Scheme (1) shows a well-defined base parent peak fragment at $m/z = 121$ (R.I = 100%, base peak) is attributed to $\text{C}_7\text{H}_5\text{O}_2$ ion.

3.2. Molecular modeling

The molecular modeling of the bisaldehyde ligand shows that all bond lengths in the left and right hand sides are typical due to the similarity of moieties on the two sides. It is considered as symmetrical structure and all bond angles predict sp^3 and sp^2 hybridization confirming the structure. The data were obtained using Chem3D ultra 8.0 software program.



Scheme (1): Mass fragmentation pattern of organic ligand.

3.3. Molar conductance measurements

The molar conductivities of 10^{-3} M solutions of the metal chelates at 25 ± 2 °C are measured and the data obtained are listed in Table (1). It is concluded that the molar conductance values of the Cr(III) and Fe(III) chelates are 107.2 and $118.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, respectively, indicating the ionic nature of these complexes. It also indicates the non-bonding of the chloride anions to the Cr(III) and Fe(III) ions. So, the Cr(III) and Fe(III) chelates are considered as 1:1 electrolytes. On the other hand, the molar conductance values of Co(II), Ni(II), Cu(II) and Zn(II) chelates are found to be 14.34 - $27.06 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. It is obvious from these data that the chelates are non ionic in nature and are non electrolytes.

3.4. IR spectral studies

The data of the IR spectra of organic ligand and its complexes are listed in Table (1). The IR spectra of the complexes are compared with the free ligand in order to determine the coordination sites that may involved in chelation. Upon comparison it is found that the $\nu(\text{C-O-C})$ stretching vibration of the ether is found in the free ligand at 1061 cm^{-1} . This band is shifted to higher or lower wavenumbers in the complexes (1070 - 1040 cm^{-1}) indicating the participation of the ether oxygen in coordination (M-O). Also, the IR spectrum of the organic ligand shows the $\nu(\text{HC=O})$ stretching vibration at 1686 cm^{-1} . These stretching vibrations are shifted to higher or lower wavenumbers to 1605 - 1699 cm^{-1} for the metal complexes. In addition, new bands are found in the spectra of the complexes at 467 - 571 cm^{-1} , which have been assigned to $\nu(\text{M-O})$ of the chelation mode.

Therefore, from the IR spectra, it is concluded that the organic ligand behave as neutral tetradentate ligand in all the complexes coordinating to the metal ions via 4O donor sites of aldehyde and ether group.

3.5. ^1H NMR spectra

It is found that the CHO signal is found at 10.302 ppm in the spectrum of the organic ligand which deshielded

at 10.287 ppm in case of Zn(II) complex indicating the participation of the CHO group in chelation. Other signals observed at 7.101 - 7.698 and 4.583 - 4.585 ppm in the spectrum of the organic ligand are found at 7.091 - 7.685 and 4.572 - 4.582 ppm in the spectrum of Zn(II) complex which can be attributed to the aromatic and methylene protons.

3.6. Magnetic susceptibility and electronic spectral studies

From the diffused reflectance spectra it is observed that, the Cr(III) chelate exhibits three bands at $12,690$, $17,412$ and $22,057 \text{ cm}^{-1}$, respectively, which may be assigned to the $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$, $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$ and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$ transition in octahedral geometry of the complex³⁸⁻³⁹. The diffused reflectance spectrum of the Fe(III) complex exhibits a band at $22,355 \text{ cm}^{-1}$, which may be assigned to the $^6\text{A}_{1g} \rightarrow \text{T}_{2g}(\text{G})$ transition in octahedral geometry. The $^6\text{A}_{1g} \rightarrow ^5\text{T}_{1g}$ transition appears to be split into two bands at $15,542$ and $13,024 \text{ cm}^{-1}$. The observed magnetic moments of Cr(III) and Fe(III) complexes are 3.50 and 6.33 B.M., respectively. Thus, the complexes formed have the octahedral geometry⁴⁰⁻⁴¹. The Ni(II) complex has a room temperature magnetic moment value of 3.33 B.M.; which supports the octahedral geometry of the Ni(II) complex^{38,39,41}. Its solid reflectance spectrum displays three bands at ν_1 : $12,480 \text{ cm}^{-1}$: $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$, ν_2 : $13,750 \text{ cm}^{-1}$: $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ and ν_3 : $21,548 \text{ cm}^{-1}$: $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$. The spectrum shows also a band at $23,263 \text{ cm}^{-1}$ which may be attributed to ligand - metal charge transfer.

The solid reflectance spectrum of the Co(II) complex gives three bands at $11,870$, $15,784$ and $20,228 \text{ cm}^{-1}$ which are assigned to the transitions $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ (ν_2) and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})$ (ν_3), respectively. This suggests an octahedral geometry around Co(II) ion³⁸⁻⁴² and the region at 26.885 cm^{-1} refers to the charge transfer band. The measured magnetic moment value 4.62 B.M. is an indicative of octahedral geometry³⁸⁻⁴².

The reflectance spectrum of the Cu(II) chelate has a broad bands at 14,225 and 16,550 cm^{-1} which are assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions³⁸⁻⁴². The magnetic moment of 2.05 B.M. supports the octahedral geometry of the Cu(II) complex⁴¹. A moderately intense peak observed at 22,380 cm^{-1} is due to ligand - metal charge transfer transition. The Zn(II) complex is diamagnetic and according to the empirical formula listed in Table (1), an octahedral geometry is proposed for it.

3.7. Thermal analyses studies

Figure (1a-d) and Table (2) show the TG and DTG results of thermal decomposition of the bisaldehyde ligand and its chelates. The TG curve of the bisaldehyde ligand in Figure (1a) exhibits an estimated mass loss of 100.00 % (calcd. 100.00 %) within the temperature range 150-615 $^{\circ}\text{C}$, which may be attributed to complete decomposition of $\text{C}_{16}\text{H}_{14}\text{O}_4$ molecule as gases. The TG curve of the Fe(III) chelate is shown in Figure (1b) and the data are listed in Table (2). It decomposes in four steps, the first step can be attributed to the loss of the HCl and $\frac{1}{2}\text{O}_2$ gases with an estimated mass loss 12.25% (calcd. 12.14%) within the temperature range 30-110 $^{\circ}\text{C}$. The following steps correspond to the removal of variable gas molecules leaving the metal oxide as residue. The overall weight loss amounts to 83.29% (calcd. 83.38%). The thermogram of the Co(II) chelate is shown in Figure (1c). It shows four decomposition steps within the temperature range 25-575 $^{\circ}\text{C}$ (Table 2). The first step of decomposition within the temperature range 25-90 $^{\circ}\text{C}$ corresponds to the loss of HCl and CO gases with an estimated mass loss of 15.59% (calcd. 16.13 %). While the 2nd and 3rd steps occur within the temperature range 90-215 $^{\circ}\text{C}$, correspond to the removal of HCl gas with mass loss of 9.16% (calcd. 9.15%).

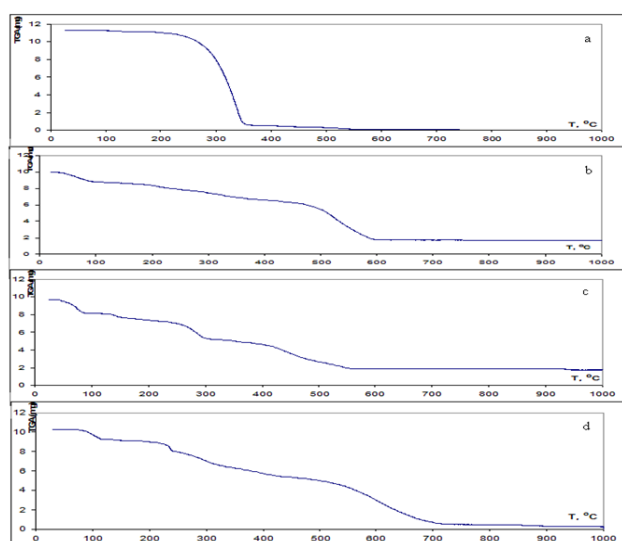


Fig. 1: Thermal analyses of a) organic ligand, b) Fe(III), c) Co(II) and d) Cu(II) complexes.

The removal of $\text{C}_{15}\text{H}_{12}\text{O}_2$ molecule with an estimated mass loss of 56.59% (calcd. 56.01%) is the final stage which occurs within the temperature range from 215-575 $^{\circ}\text{C}$ leaving CoO as a residue. The overall weight loss amounts to 81.34% (calcd. 81.29%).

The thermogram of Cu(II) chelate is shown in Figure (1d). The TG curve of Cu(II) chelate shows four decomposition steps within the temperature range from 50 to 765 $^{\circ}\text{C}$. The 1st, 2nd and 3rd steps of decomposition within the temperature range from 50 to 330 $^{\circ}\text{C}$ corresponds to the loss of 2HCl, CO_2 and $\frac{1}{2}\text{O}_2$ gases. While, the subsequent stage occurs within the temperature range from 330 to 765 $^{\circ}\text{C}$. The overall weight loss amounts to 80.46% (calcd. 80.35%).

3.8. X-Ray diffraction

X-ray powder diffraction pattern in the $0^{\circ} < 2\theta < 60^{\circ}$ of the bisaldehyde ligand and its complexes were carried out in order to give an insight about the lattice dynamics of these complexes. It is observed that Fe(III) and Co(II) complexes are found to have amorphous structure, while the remaining complexes are found to have crystalline structures.

3.9. Calculation of activation thermodynamic parameters

The thermodynamic activation parameters of decomposition processes of the complexes are calculated by employing the Coats-Redfern relation⁴³ and the data are summarized in Table (3). 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 lower rates than the normal ones.

3.10. Structural interpretation

On the basis of the above observations, the structures of our complexes are shown in Figure (2).

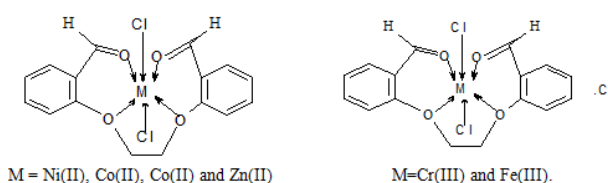


Fig. 2: Structural formulas of metal complexes.

3.11. Biological activity

Testing the biological activity of these complexes and the bisaldehyde ligand against *Aspergillus flavus* and *Candida albicans* (fungi) and, *Staphylococcus aureus* (G^+) and *E. coli* (G^-) bacteria was carried out in order to assess their potential antimicrobial agents. The data are listed in Table (4).

On comparing the biological activity of the bisaldehyde ligand and its metal complexes with specific control of only one biological function and not multiple ones, the following results are obtained:

(a) Using *Escherichia coli* bacteria (G^-)

All the complexes have higher biological activity than that of the free ligand and both of them are lower than Tetracycline (antibacterial agent) standard. Therefore, the biological activity of the complexes follow the order: standard > Zn(II) > Co(II) > Ni(II) = Cu(II) > Cr(III) > Fe(III) > ligand.

(b) Using *Staphylococcus aureus* (G^+)

The biological activity of the organic ligand is lower than that of the standard and the metal complexes. All the complexes have lower activity than the standard except Zn(II) complex. The biological activity of the complexes follow the order: Fe(III) = ligand < Cr(III) < Cu(II) < Co(II) < Ni(II) < Zn(II) = standard.

(c) Using *Aspergillus flavus* fungus

It is clear from Table (4) that there is no antifungal activity for the free organic ligand or its complexes toward this organism.

(d) Using *Candida albicans* fungus

The bisaldehyde ligand has no fungal activity. The fungal activities of our complexes are lower than the Amphotericin B (antifungal) agent standard. The fungal activity of the complexes follow the order: Fe(III) < Cr(III) = Cu(II) = Zn(II) < Co(II) < Ni(II) < standard. Therefore, it is claimed here that the synthesis of these complexes might be recommended and/or established a new line for search to new antitumour particularly when one knows that many workers studied the possible antitumour action of many synthetic and semisynthetic compounds e.g., Hodnett et al.⁴⁴ and Hickman⁴⁵.

4. Application**4.1. Spectrophotometric determination to Fe(III) ions in natural water**

In this work, the bisaldehyde ligand is utilize for the spectrophotometric determination of Fe(III) in different natural water samples. This reaction produces a stable coloured product which can be measured spectrophotometrically at 410 nm. Different analytical parameters were optimized in order to achieve maximum recovery under the recommended conditions. They are found to be: suitable pH is 3.5, temperature 25 °C, time 30 min and 1:1 [Fe(III)]:[ligand] ratio.

4.2. 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 organic ligand were subjected to the described spectrophotometric procedure. The tolerance limit is taken as the amount that caused $\pm 2\%$, are summarized in Table (5). As can be seen, all the investigated foreign

ions with a relatively high concentration have no adverse effect on the Fe(III) ions to be determined. Therefore, the recommended procedure may be finding its applications to the natural water samples without interfere up to 2000 fold excess as in fluoride ion.

4.3. 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 is done in a way to provide a wide variety of sample matrices characterized by different types of interferences. Solutions of pre-filtered water samples (10 ml, each) containing Fe(III) with a concentration of 3.47 or 7.95 mg/l were recovered under the recommended conditions. 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. The data listed in Table (6) show a satisfactory recovery of Fe(III).

5. Conclusion

The synthesis and characterization of new metal (II)/(III) complexes have been realized with physicochemical and spectroscopic methods. The study of the interaction of complexes with the bisaldehyde ligand has been performed with UV spectroscopy. The geometry can be described as octahedral geometry and the thermal study indicates the coordination with metal ion. Electronic spectra, magnetic moment and conductance study evidence the fact of the geometry of complexes. All these studies give good evidence of proposed structure. The nuclear magnetic resonance studies are in good agreement with those obtained from IR studies. XRD analysis suggests the crystalline and morphological structural studies of the complexes. We have evaluated in vitro activities for the synthesized bisaldehyde ligand and its new metal complexes. The results obtained from this research demonstrated that the newly synthesized complexes have well to moderate antibacterial and antifungal activity against the bacterial and fungal strains.

In the analytical application, a new method was developed to determine Fe(III) in aqueous solution, based on the reaction of Fe(III) with bisaldehyde organic ligand. The main features and advantages of this method are the method is sensitive, where the method does not vary with Fe(III) concentration, low reagent consumption or with the chemical composition of the water. The procedure is simple and does not require any difficult or time-consuming operations. It can be performed by using standard laboratory instruments. The organic ligand solution is stable and can be stored for a month as a stock solution. The Fe(III) complex is also stable in natural waters, which allows one to perform spectrophotometric measurements several hours after Fe(III) has reacted with the organic ligand.

Table (1): Analytical and physical data of the organic ligand and its complexes

Compound	Colour (%yield)	M.P. (°C)	% Found (Calc.)				$\mu_{\text{eff.}}$ (B.M.)	(Λ_m) $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$	IR * (cm^{-1})
			C	H	M	Cl			
L = $\text{C}_{16}\text{H}_{14}\text{O}_4$	Pale Green (82)	92	70.84 (71.11)	6.00 (5.19)	-----	-----	-----	-----	$\nu(\text{HC}=\text{O})$ 1686sh $\nu(\text{C}-\text{O}-\text{C})$ 1061sh
$[\text{Cr}(\text{L})\text{Cl}_2]\text{Cl}$	Black (99)	100	44.97 (44.81)	3.53 (3.27)	12.01 (12.13)	24.90 (24.85)	3.50	107.2	$\nu(\text{HC}=\text{O})$ 1659sh $\nu(\text{C}-\text{O}-\text{C})$ 1069sh $\nu(\text{M}-\text{O})$ 571s
$[\text{Fe}(\text{L})\text{Cl}_2]\text{Cl}$	Yellowish Brown (70)	93	44.66 (44.41)	3.50 (3.24)	12.11 (12.91)	24.50 (24.64)	6.33	118.8	$\nu(\text{HC}=\text{O})$ 1651sh $\nu(\text{C}-\text{O}-\text{C})$ 1053 sh $\nu(\text{M}-\text{O})$ 477w
$[\text{Co}(\text{L})\text{Cl}_2]$	Brown (76)	108	48.01 (48.01)	3.48 (3.50)	13.54 (14.74)	17.07 (17.75)	4.62	27.06	$\nu(\text{HC}=\text{O})$ 1682sh $\nu(\text{C}-\text{O}-\text{C})$ 1070m $\nu(\text{M}-\text{O})$ 467w
$[\text{Ni}(\text{L})\text{Cl}_2]$	Yellowish Green (69)	120	48.47 (48.03)	3.38 (3.50)	14.50 (14.70)	17.09 (17.76)	3.33	24.74	$\nu(\text{HC}=\text{O})$ 1605br $\nu(\text{C}-\text{O}-\text{C})$ 1049sh $\nu(\text{M}-\text{O})$ 486m
$[\text{Cu}(\text{L})\text{Cl}_2]$	Yellow (77)	216	47.91 (47.47)	3.02 (3.46)	15.68 (15.70)	17.23 (17.55)	2.05	20.55	$\nu(\text{HC}=\text{O})$ 1699sh $\nu(\text{C}-\text{O}-\text{C})$ 1040sh $\nu(\text{M}-\text{O})$ 471s
$[\text{Zn}(\text{L})\text{Cl}_2]$	Brown (72)	90	47.68 (47.26)	3.93 (3.45)	15.99 (16.07)	17.71 (17.47)	Diam.	14.34	$\nu(\text{HC}=\text{O})$ 1655sh $\nu(\text{C}-\text{O}-\text{C})$ 1052sh $\nu(\text{M}-\text{O})$ 469w

* sh = sharp, m = medium, br = broad, s = small, w = weak

Table (2): Thermoanalytical results of the organic ligand and its metal complexes

compound	TG range (°C)	DTG _{max} (°C)	n*	Mass Loss Calcd (Estim) %	Total mass Loss %	Assignment	Metallic residue
L	150-615	318	1	100 (100)	100 (100)	-Loss of $\text{C}_{16}\text{H}_{14}\text{O}_4$.	-----
$[\text{Fe}(\text{L})\text{Cl}_2]\text{Cl}$	30-110	64	1	12.14 (12.25)		-Loss of HCl and $\frac{1}{2}\text{O}_2$	FeO 16.61 (16.54)
	110-265	205	1	6.01 (6.07)		-Loss of C_2H_2 .	
	265-440	306	1	16.42 (16.50)		-Loss of Cl_2 .	
	440-650	530	1	48.81 (48.64)	83.38 (83.46)	-Loss of $\text{C}_{14}\text{H}_{11}\text{O}_2$.	
$[\text{Co}(\text{L})\text{Cl}_2]$	25-90	70	1	16.13 (15.59)		-Loss of HCl and CO.	CoO 18.73 (18.66)
	90-215	140,183	2	9.13 (9.16)		-Loss of HCl.	
	215-575	276	1	56.01 (56.59)	81.27(81.34)	-Loss of $\text{C}_{15}\text{H}_{12}\text{O}_2$.	
$[\text{Cu}(\text{L})\text{Cl}_2]$	50-250	100,235	2	18.05 (18.04)		-Loss of 2HCl.	CuO 19.65 (19.71)
	250-330	289	1	14.83 (14.44)		-Loss of CO_2 and $\frac{1}{2}\text{O}_2$.	
	330-765	372,602	2	47.47 (47.81)	80.35 (80.29)	-Loss of $\text{C}_{15}\text{H}_{12}$.	

n* = number of decomposition steps.

Table (3): Thermodynamic data of the thermal decomposition of metal complexes of the organic ligand

Complex	Decomp. Temp. °C	A s ⁻¹	E* KJmol ⁻¹	ΔS* JK ⁻¹ mol ⁻¹	ΔH* kJmol ⁻¹	ΔG* kJmol ⁻¹
L	150-615	6.65x10 ³	146.0	-302.0	860.0	105.0
[Fe(L)Cl ₂]Cl	30-110	3.41x10 ³	91.00	-59.00	7.000	85.00
	110-265	7.51x10 ⁵	104.0	-89.00	16.00	129.0
	265-440	1.54x10 ⁷	219.0	-148.0	169.0	182.0
	440-650	3.98x10 ⁶	368.0	-163.0	182.0	209.7
[Co(L)Cl ₂]	25-90	5.01x10 ⁵	71.70	-24.00	35.00	598.0
	90-150	5.86x10 ⁹	164.0	-48.00	69.00	90.00
	150-215	1.27x10 ¹⁰	205.0	-82.00	99.00	117.0
	215-575	8.39x10 ⁵	370.0	-131.0	165.0	19.00
[Cu(L)Cl ₂]	50-130	2.34x10 ¹⁴	117.0	-39.00	59.00	78.00
	130-250	1.09x10 ⁸	250.0	-89.00	112.0	315.0
	250-330	6.78x10 ¹⁰	153.0	-137.0	172.0	205.0
	330-765	1.59x10 ⁵	296.0	-187.0	212.0	246.0

Table (4): Biological activity of the organic ligand and its metal complexes.

Sample		Inhibition zone diameter (mm/mg sample)			
		<i>Escherichia coli</i> (G ⁻)	<i>Staphylococcus aureus</i> (G ⁺)	<i>Aspergillus flavus</i> (Fungus)	<i>Candida albicans</i> (Fungus)
Control: DMSO		0.0	0.0	0.0	0.0
Standard	Tetracycline Antibacterial agent	33	30	----	----
	Amphotericin B Antifungal agent	----	----	18	19
L		11	13	0.0	0.0
[Cr(L)Cl ₂]Cl		14	14	0.0	13
[Fe(L)Cl ₂]Cl		13	13	0.0	11
[Co(L)Cl ₂]		19	19	0.0	15
[Ni(L)Cl ₂]		15	20	0.0	17
[Cu(L)Cl ₂]		15	17	0.0	13
[Zn(L)Cl ₂]		23	30	0.0	13

Table (5): Effect of some foreign ions on the recovery of 5x10⁻⁴ mol/l Fe(III) using 5x10⁻⁴ mol/l of the organic ligand at pH = 3.5, T = 25 °C, t = 30 min and λ_{max} = 410 nm.

Foreign ion added	NH(IV)	Al(III)	Cr(III)	Cd(II)	Ca(II)	Cu(II)	Co(II)	Ni(II)	Zn(II)	Mn(II)	K(I)	Na(I)	Cl ⁻	F ⁻
Tolerance Limit [ion]/[Fe(III)]	200.0	20.00	20.0	20.0	200.0	20.00	20.0	20.00	20.00	20.00	200.0	200.0	200.0	2000
Percent recovery (%)	99.47	99.74	99.77	99.60	99.65	99.41	99.71	99.11	98.13	97.99	99.43	99.64	99.10	99.83

Table (6): Recovery percent (%) of Fe(III) in spiked natural water samples using 5×10^{-4} mol/l organic ligand at pH = 3.5, T = 25 °C, t = 30 min and $\lambda_{\max} = 410$ nm.

Water samples (location)	Fe(III) _{spiked} (mg/L)	Fe(III) _{recovered} (mg/L)	Recovery percent (%)	SD*	RSD* (%)
Distilled water	3.47	3.45	99.42	0.033	0.96
	7.95	7.93	99.75	0.052	0.66
Tap water	3.47	3.41	98.27	0.044	1.29
	7.95	7.90	99.37	0.071	0.90
Nile water (Egypt)	3.47	3.42	98.56	0.065	1.90
	7.95	7.91	99.5	0.042	0.53
Sea water (Gamasah)	3.47	3.45	99.42	0.070	2.03
	7.95	7.93	99.75	0.032	0.40
Underground water (Belqas)	3.47	3.41	98.27	0.081	2.38
	7.95	7.88	99.12	0.092	1.17
Well water (6 th October City)	3.47	3.43	98.85	0.064	1.87
	7.95	7.91	99.50	0.051	0.64

* RSD = relative standard deviation and * SD = standard deviation.

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