

Co(II), Cu(II) and Zn(II) Complexes of N,O-Type Schiff Base Ligand Derived from 4,4'-Methylenedianiline Synthesis, Characterization, Antibacterial and Antifungal Studies

¹Hakan Şahal*, ²Erdal Canpolat, ¹Mehmet Kaya and ³Seher Gür

¹Faculty of Sciences, Department of Chemistry, Firat University, 23119, Elazig, Turkey.

²Faculty of Education, Department of Elementary Science Education, Firat University, 23119, Elazig, Turkey.

¹Faculty of Sciences, Department of Biology, Firat University, 23119, Elazig, Turkey.

hakan.shl@gmail.com*

(Received on 12th April 2016, accepted in revised form 2nd February 2017)

Summary: Three new complexes were prepared reacting Co(II), Cu(II) and Zn(II) salts with 2-[(E)-{4-(4-aminobenzyl)phenyl}imino}methyl]-6-ethoxyphenol (LH) and characterized by analytical and spectrochemical methods. The metal:ligand stoichiometric ratio is 1:1 in the complexes of Co(II) and Zn(II), whereas in the Cu(II) complex, the metal:ligand stoichiometric ratio is 2:1. It was determined that bidentate behavior of the ligand is accomplished via the phenolic oxygen and the azomethine nitrogen atoms. The presence of water is revealed by thermograms and supported by the presence of relevant bonds in their IR spectra. These new complexes showed a reasonable amount antifungal activity.

Keywords: Schiff base, Antimicrobial activity, Antifungal activity, Transition metal complexes.

Introduction

Schiff bases are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C,O) has been replaced by an imine or azomethine group [1].

Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, intermediates in organic synthesis, and as polymer stabilisers [2]. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities [3–5]. However, their metal complexes have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [2, 6]. In addition, because of the ability to be coordinated of oxygen and nitrogen atoms in the complexes are effective and stereospecific catalysts for epoxidation reactions, catalytic hydrogenation of olefins and hydrolysis [7-9]. It is well known that some drugs have greater activity when implemented as metal complexes than as free ligands [7].

In our previous studies we investigated the synthesis and characterization of Co(II), Cu(II) and Zn(II) complexes of novel Schiff base [10-19]. In the present paper, the preparation and characterization

of the Schiff base ligand and its metal complexes are described. All the compounds were characterized by elemental analyses, thermogravimetric analyses (TGA), magnetic susceptibility and spectroscopic methods.

Experimental

Materials

Elemental analyses (C,H,N) were carried out using LECO-932 CHNSO by Technical and Scientific Research Council of Turkey, (TUBITAK). IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets. ¹H and ¹³C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constants.

Synthesis

Preparation of the ligand (LH)

To a solution of (1.66 g, 10 mmol) 3-ethoxysalicylaldehyde in 10 ml absolute EtOH, 4,4-diaminodiphenylmethane (1.98 g, 10 mmol) dissolved in 30 ml absolute EtOH were added

*To whom all correspondence should be addressed.

dropwise at 78 °C with continuous stirring for 24 h. The formation of the (C=N) peak and the disappearance of the C=O and -NH₂ peaks during the reaction was monitored by the IR. The precipitate was filtered off after overnight, washed with hot ethanol and dried at room temperature. Yield: 92%. Color: Orange. F.W. : 346.42 Anal. Calc. for C₂₂H₂₂N₂O₂: C, 76.28; H, 6.40; N, 8.09. Found: 76.24; H, 6.02; N, 8.30. FT-IR: ν_{\max} cm⁻¹ (KBr): 1615 (C=N), 1273 (C-O), 3340-3570 (O-H), UV-Vis: ν_{\max} (nm): 322 (n→π* (azomethine)). ¹H-NMR (DMSO-d₆, 400 MHz): 6.48 (s, 2H, NH₂), 7.32-7.08(m, 11H, Arom-H), 8.90 (s, 1H, CH=N), 13.38(s, 1H, OH). ¹³C-NMR (DMSO-d₆, 400 MHz): 14.63 (-CH₃), 64.36 (O-CH₂), 114.33-150.02 (Arom-C), 151.12 (C-OH), 163.40 (CH=N).

Preparation of the Co(II), Cu(II) and Zn(II) complex

Three sample of the ligand (LH) (0.35 g, 1.00 mmol) was dissolved in 20 ml hot absolute ethanol. A solutions of [Co(AcO)₂].4H₂O (0.26 g, 1.00 mmol), [Cu(AcO)₂].H₂O (0.52 g, 2.00 mmol) and [Zn(AcO)₂].2H₂O (0.26 g, 1.00 mmol) in 10 ml of hot absolute ethanol was added dropwise to solution with continuous stirring at 55 °C for 15 h, respectively. The shift of the (C=N) peak and the disappearance of the -OH peak during the reaction was monitored by the IR. The precipitated complexes were filtered off after overnight, washed with water and cold ethanol and dried at room temperature. For Co(II) complex, yield: 64%. Color: Red. F.W.: 499.42 Anal. Calc. for [Co(L)(AcO)(H₂O)₂]: C, 57.72; H, 5.65; N, 5.61. Found: C, 57.48; H, 5.48; N, 5.74. FT-IR: ν_{\max} cm⁻¹ (KBr): 1607 (C=N), 1541 (AcO), 1319 (C-O), 3450-3550 (O-H), UV-Vis: ν_{\max} (nm): 314 (n→π* (azomethine)), 405 (Charge Transfer), 674 (d→d). μ_{eff} (B.M): 4.02. For Cu(II) complex, yield: 65%. Color: Lightbrown. F.W.: 703.68. Anal. Calc. for [Cu₂(L)(AcO)₃(H₂O)₂].H₂O: C, 47.79; H, 5.16; N, 3.98. Found: C, 47.42; H, 5.65; N, 3.68. FT-IR: ν_{\max} cm⁻¹ (KBr): 1611 (C=N), 1543 (AcO), 1383 (C-O), 3430-3550 (H₂O), UV-Vis: ν_{\max} (nm): 308 (n→π* (azomethine)), 414 (Charge Transfer), 537 (d→d). μ_{eff} (B.M): Dia. For Zn(II) complex, Yield: 57%. Color: Yellow. F.W.: 505.90 Anal. Calc. for [Zn(L)(AcO)(H₂O)₂]: C, 56.98; H, 5.58; N, 5.54. Found: 57.32; H, 5.78; N, 5.95. FT-IR: ν_{\max} cm⁻¹ (KBr): 1613 (C=N), 1542 (AcO), 1326 (C-O), 3430-3550 (H₂O), UV-Vis: ν_{\max} (nm): 326 (n→π* (azomethine)), 415 (Charge Transfer). ¹H-NMR (DMSO-d₆, 400 MHz): 6.30 (s, 2H, NH₂), 7.08-6.76(m, 11H, Arom-H), 8.64 (s, 1H, CH=N). ¹³C-NMR (DMSO-d₆, 400 MHz): 15.15 (-CH₃), 63.67 (O-CH₂), 113.89-155.39 (Arom-C), 156.63 (C-O-), 161.25 (C=O)_{AcO}, 169.26 (CH=N). μ_{eff} (B.M): Dia.

Antimicrobial Activity

In order to determine both antibacterial and antifungal activity, the synthesized compounds and the control drugs were dissolved in absolute dimethylsulfoxide (DMSO). Further dilutions were done at the required quantities of 1024, 512, 256, 128, 64, 32, 16, 8, 4, 2, and 1 µg / mL on the microorganisms at the studied concentrations. Stock solutions were prepared in DMSO having no effect on the microorganisms in the studied concentrations. Antimicrobial activities of compounds were determined using the broth dilution method proposed by the National Committee for Clinical Laboratory Standards (CLSI). MIC, which is the lowest concentration of a compound that completely inhibits microbial growth, was determined by a standard broth dilution technique adapted from the CLSI. As quality control strains 1 gram-positive bacterium, 1 gram-negative bacterium, and 2 yeast-like fungi were used. Tested microorganisms were gram-positive *Staphylococcus aureus* ATCC 6538P, *Bacillus subtilis* ATCC 6633, gram-negative *Escherichia coli* ATCC 25922, *Salmonella typhimurium* NRRL B 4420, and the yeast like fungi; *Candida glabrata* ATCC 66032 and *Candida tropicalis* ATCC 13803. Ampicillin (Mustafa Nevzat) and Fluconazole (Pfizer) were used as antibiotic reference for bacteria and yeast, respectively (obtained from Department of Biology, Firat University, Turkey).

Antibacterial and Antifungal Assays

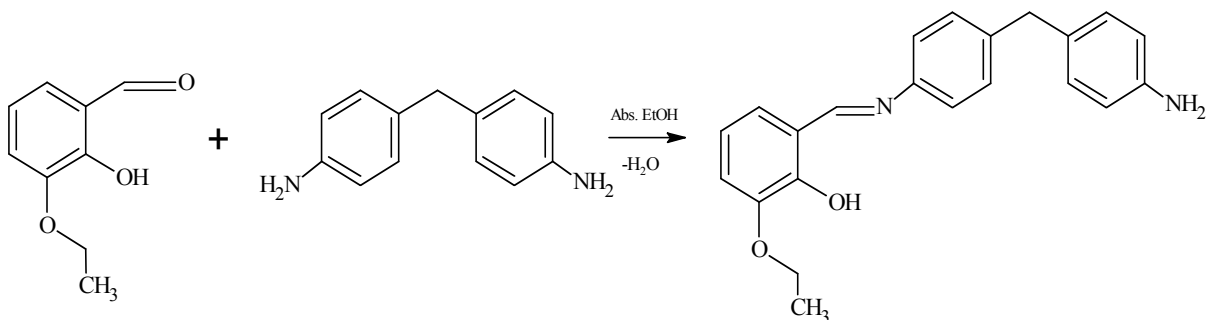
Bacterial cultures were obtained in Mueller-Hinton broth (Difco) for all the bacterial strains after 24 h of incubation at 37 ± 0.1 °C. Yeasts were propagated in Sabouraud dextrose broth (Difco) after incubation for 24 h at 25 ± 0.1 °C. Testing was carried out in Mueller-Hinton broth and Sabouraud dextrose broth at pH 7.4 for bacteria and yeast, respectively. The final inoculum size for bacteria and fungi was 10⁵ CFU mL⁻¹. Test compounds were dissolved in DMSO at an initial concentration of 1024 µg / mL and then serially diluted in culture medium to 1 µg / mL. A set of tubes containing only inoculated broth was kept as control. Antibacterial activity was determined after incubation for 24 h at 37 °C for bacteria and after incubation for 48 h at 25 °C for the yeasts. MIC was defined as the lowest concentration of the compounds that inhibited the visible growth of a microorganism. Every experiment in the antibacterial and antifungal assays was replicated two times to define the MIC values.

Table-1: Spectroscopic data for ligand and its complexes.

Compound	Selected IR (cm ⁻¹) ν (C=N)	¹ H-NMR δ(ppm)	¹³ C-NMR δ(ppm)	UV-Vis (nm)
LH	1615	13.38(s, 1H, OH) 7.32-7.08 (m, 11H, Ar) 8.90 (s, 1H, CH=N) 6.48 (s, 2H, NH ₂) 4.02 (m, 2H, -OCH ₂ -) 3.75 (s, 2H, -CH ₂ -) 1.28 (t, 3H, J=10 Hz, -CH ₃)	163.40 (CH=N) 151.12 (C-OH) 114.33-150.02 (Arom-C) 64.36 (O-CH ₂) 14.63 (-CH ₃)	322 (n→π*)
a	1613	7.08-6.76 (m, 11H, Ar) 8.64 (s, 1H, CH=N) 6.30 (s, 2H, NH ₂) 3.95 (m, 2H, -OCH ₂ -) 3.75 (s, 2H, -CH ₂ -) 3.42 (s, 6H, AcO) 1.29 (t, 3H, J=7.2 Hz, -CH ₃)	169.26 (CH=N) 161.25 (C=O) _{AcO} 156.63 (C-O) 113.89-155.39 (Arom-C) 63.67 (O-CH ₂) 17.56 (C=O) _{AcO} 15.15 (-CH ₃)	326 (n→π*) 415 (C-T)*
b	1607	paramagnetic	paramagnetic	314 (n→π*) 405 (C-T) 674 (d-d)
c	1611	Paramagnetic (in solvent)	Paramagnetic (in solvent)	308 (n→π*) 414 (C-T) 537 (d-d)

^a[Zn(L)(AcO)(H₂O)₂], ^b[Co(L)(AcO)(H₂O)₂], ^c[Cu₂(L)(AcO)₃(H₂O)₂].H₂O

*Charge Transfer



Scheme-1: Structure of the ligand.

Result and Discussion

The ligand (LH) was prepared by reacting equimolar amounts of 3-ethoxysalicylaldehyde with 4,4'-diaminodiphenylmethane in absolute ethanol (Scheme-1). The formation of the complexes may be represented as follow.



[n:0, x:1 for Co(II) and Zn(II) and n:1, x:3 for Cu(II)]

IR Spectra

Band at around 1615 cm⁻¹ in the IR spectra of the Schiff base ligand has been appointed to the stretching vibrations of the ν (C=N) (Table-1). This band has shifted between 2 cm⁻¹ and 8 cm⁻¹ to lower wave numbers due to coordination in the IR spectra of the complexes. This shifts are indicative of the coordination of the ligand through their azomethine nitrogen atoms.

This band around 3340-3570 cm⁻¹ stretching vibration of ν(OH) in the spectra of the free ligand was absent in the spectra of all the complexes, indicating the deprotonation of Schiff bases prior to coordination through its oxygen atom [7-18]. Also, in the ligand strong band at 1273 cm⁻¹ belonging to C-O (phenolic) was shifted to higher frequency by 46-110 cm⁻¹ due to the coordinated to the metal of oxygen in the complexes [7, 17-19]. All complexes show the broad diffuse band centered at 3550-3430 cm⁻¹ due to the stretching and bending modes of lattice and coordinated water [18, 20].

In addition, weak bands are detectable at 830-836 cm⁻¹ region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion [21]. The shoulder at 1541 cm⁻¹ in the complex may be attributed to the ν_{as}(CO) of the CH₃COO⁻ group (Fig. 1) [22].

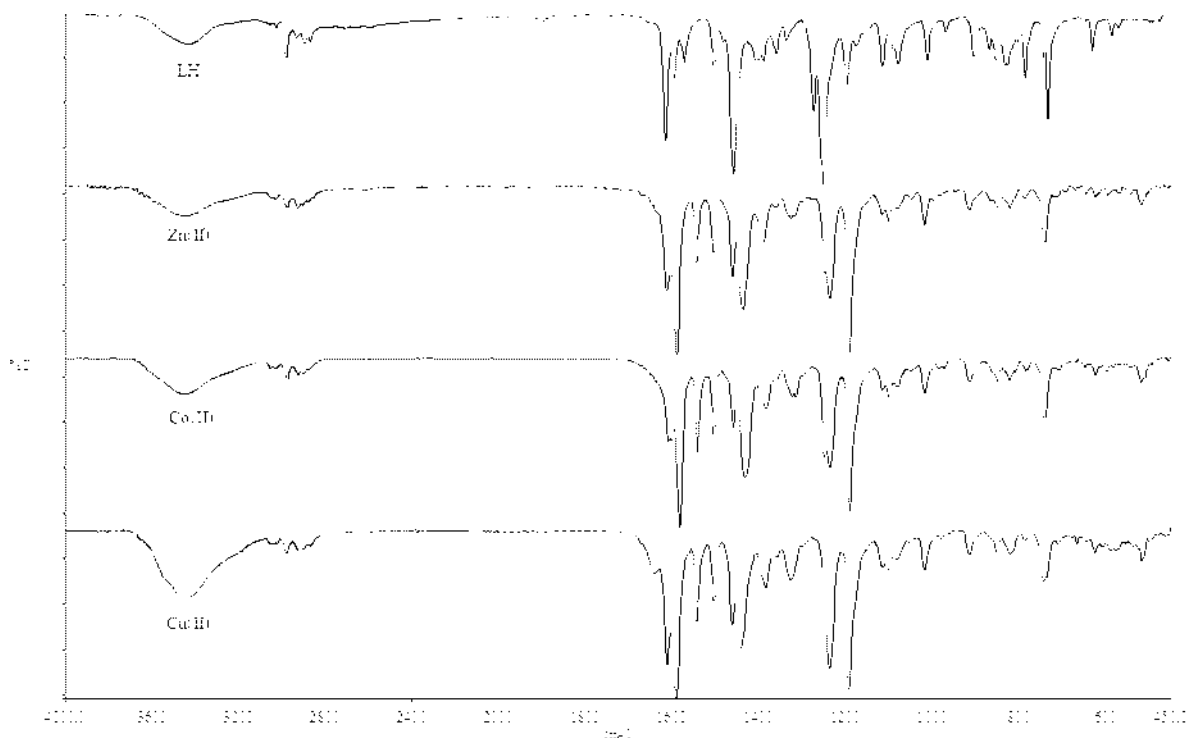


Fig. 1: IR spectrum of ligand and complexes.

UV-Vis Spectra

The UV-Vis spectral results recorded in DMF solution at room temperature of all the compounds are presented in Table-1.

The band around 322 nm is due to $n \rightarrow \pi^*$ transition of the nonbonding electrons present on the nitrogen of the $-C=N$ in the free ligand. The complexes of cobalt(II) and copper(II) show less intense shoulder at ca. 674 and 537 nm, which are appointed as the $d \rightarrow d$ transition of the metal ions, respectively. All the coordination compounds show an intense band at ca. 308-326 nm, which is appointed to the $n \rightarrow \pi^*$ transition related with the azomethine linkage [23] and band at 405-415 nm, which can be appointed to a charge transfer transition [12, 25-27] in experimental section.

1H and ^{13}C NMR spectra

The 1H -NMR and ^{13}C -NMR spectra of the ligand and its diamagnetic Zn(II) complex have been analyzed in DMSO- d_6 and data are given in Table-1. Comparison of the chemical shifts of the ligand with those of the complex shows that the signal due to the phenolic proton (OH) is absent in the complex, suggesting the coordination of the phenolic oxygen to the metal ion after deprotonation

[7, 23]. The azomethine proton ($CH=N$) undergoes a significant shift, indicating coordination of the azomethine nitrogen to the metal ion. More detailed information about the structure of the ligand was provided by ^{13}C -NMR spectral data. C-OH and $CH=N$ carbon atoms are observed at 151.12 and 163.40 ppm, respectively for LH. The detailed ^{13}C -NMR spectral data are given in Table-1. ^{13}C -NMR spectrum of Zn(II) complex C-O and $CH=N$ carbon atoms are observed at 161.25 and 169.26 ppm respectively. These signals are shifted to higher field after complexation, which means that the shifts are due to coordination of the ligand to metal atom by the azomethine nitrogen and phenolic oxygen [7, 23, 24]. The results confirm the proposed structure of Zn(II) complex (Fig. 2).

Magnetic Susceptibility Measurements

The magnetic moment value of 4.02 B.M measured for the cobalt complex lies in the range expected for a d^7 system, which contains three unpaired electron with mononuclear octahedral geometry. [28] The zinc (II) complex is diamagnetic due to its d^{10} configuration. Furthermore, the copper (II) complex is diamagnetic because of the dimeric structure [29]. In order to investigate the presence of magnetic properties in the copper(II) complex, 1H -NMR instrument was employed. It was found that

copper(II) complex is paramagnetic, therefore the NMR spectra of the copper(II) complex could not be obtained. According to results obtained from ^1H -NMR spectra and the magnetic moment, the magnetic properties of the Cu(II) complex are different in solid and solution state. These values are in agreement with similar structures [30, 31].

Thermal Analysis

The thermal behavior of the ligand and all the complexes has been investigated using thermogravimetric techniques in the temperature range from ambient to 800 °C at heating rate of 10 °C/min. The decomposition temperature and the weight losses of the ligand and the complexes were calculated from TGA data. The ligand is stable up to 175 °C and its decomposition starts at 175 °C and is completed at 690 °C. Thermogravimetric studies of the Zn(II) and Co(II) complexes showed no weight

loss up to 125 and 133 °C respectively, indicating absence of the lattice water molecules in the complexes [32]. In the Zn(II) and Co(II) complexes, the first weight loss stage has a decomposition temperature range of 125-360 and 133-375 °C, with a weight loss of 6.63% and 7.85%, which corresponds to the loss of two coordinated water molecules (calc. 7.20% and 7.12%) respectively [33]. On the other hand in the copper(II) complex, the first 2.55% (calc. 2.55%) weight loss occurred in the 25-115 °C range and second, 5.65% (calc. 5.11%) in the 115-375 °C range. The result indicates the loss of one lattice water molecule in the former step and two coordinated water molecules in the latter [34]. In the complexes obtained, the lattice coordinated water molecules are also confirmed by the results of IR spectra [21]. When the complexes are heated to higher temperature, they decompose to give oxides at the MO type (Table-2) [35, 36]

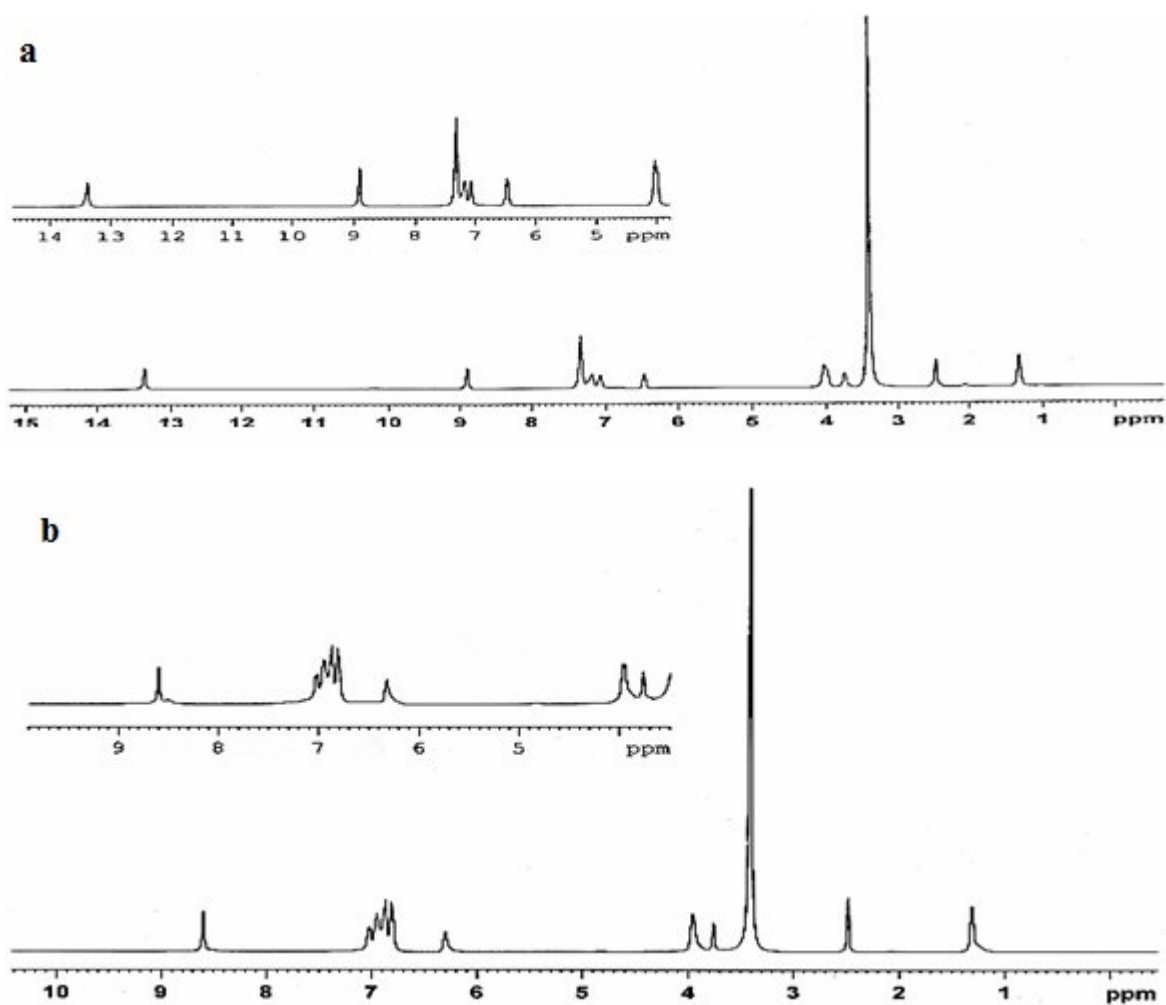


Fig. 2: ^1H -NMR spectrum ligand and Zn(II) complex (a) Ligand (b) Zn(II) complex.

Table-2: TGA data of the complexes.

Compounds	Temperature range (°C)	Dehydration stage	
		Weight loss (%) found	(calculated)
[Co(L ¹)(AcO)(H ₂ O) ₂]	25-133	---	---
	133-375	7.85	(7.12)
[Cu ₂ (L ¹)(AcO) ₃ (H ₂ O) ₂].H ₂ O	25-115	2.55	(2.55)
	115-375	5.65	(5.11)
[Zn(L ¹)(AcO)(H ₂ O) ₂]	25-125	---	---
	125-360	6.63	(7.20)

*Coord. = Coordinated

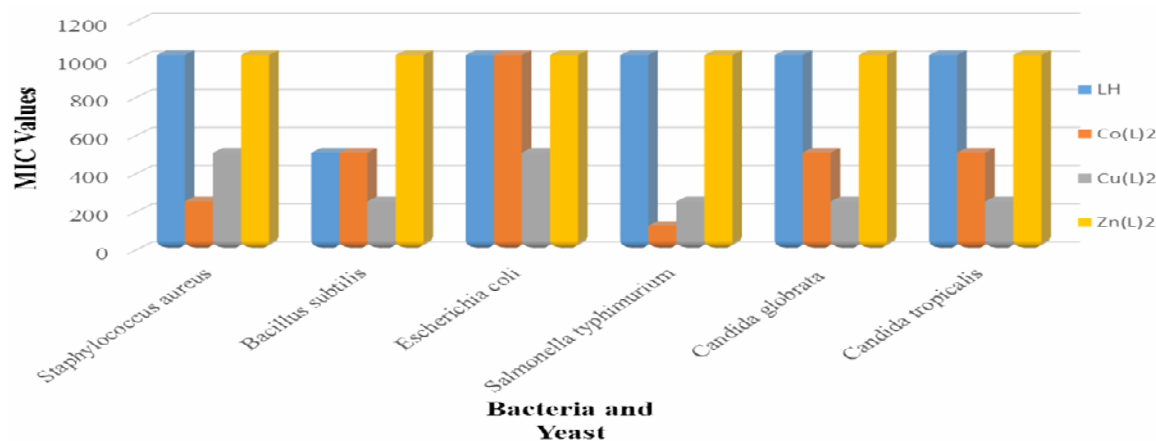


Fig. 3: Comparison of the MIC values (in µg /mL) of the complexes and the standard drugs against different bacteria.

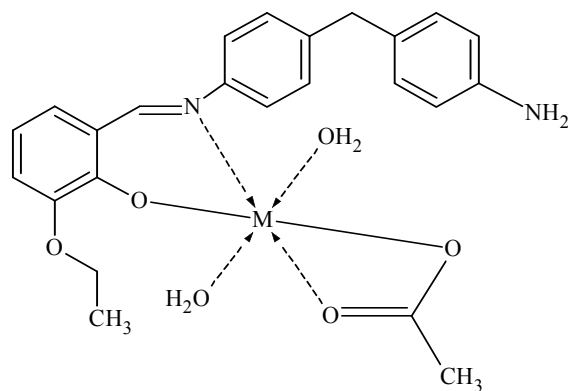
Antimicrobial Activity Study

We have designed and synthesized novel Schiff base ligand and its novel [Co(L)(AcO)(H₂O)₂], [Cu₂(L)(AcO)₃(H₂O)₂].H₂O and [Zn(L)(AcO)(H₂O)₂] complexes in order to Fig out their antimicrobial activities. Minimum inhibitory concentration (MIC) of the synthesized compounds was determined against gram-positive *Staphylococcus aureus* ATCC 6538P, *Bacillus subtilis* ATCC 6633, gram-negative *Escherichia coli* ATCC 25922, *Salmonella typhimurium* NRRL B 4420, and yeast-like fungi *Candida glabrata* ATCC 66032 and *Candida tropicalis* ATCC 13803 using a standard broth dilution technique. Their antimicrobial activities were compared to ampicillin and fluconazole as standard drugs. The synthesized Schiff base compounds have comparable and similar inhibitory effects (low to moderate MIC values 256 and 1024 µg/mL) on the growth of tested strains (Fig. 3).

Conclusions

The satisfactory analytical data and all of the physico-chemical studies presented above suggest that these complexes may be formulated as [Zn(L)(AcO)(H₂O)₂], [Co(L)(AcO)(H₂O)₂] and [Cu₂(L)(AcO)₃(H₂O)₂].H₂O. Suitable monomeric and dimeric structures have been proposed for these

complexes Fig. 4 and 5. The Schiff base ligand and its cobalt(II), zinc(II) and copper(II) complexes were synthesized and characterized by elemental analyses, IR, UV-Vis, ¹H and ¹³C-NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses(TGA). According to the results obtained, the zinc(II) and cobalt(II) complexes are mononuclear and octahedral, whereas the copper(II) complex is dimeric structure. All the metal complexes were found to have showed weak antimicrobial activity against some bacterial strains.



M = Co(II) and Zn(II)

Fig. 4: Suggested structure of the Co(II) and Zn(II) complexes.

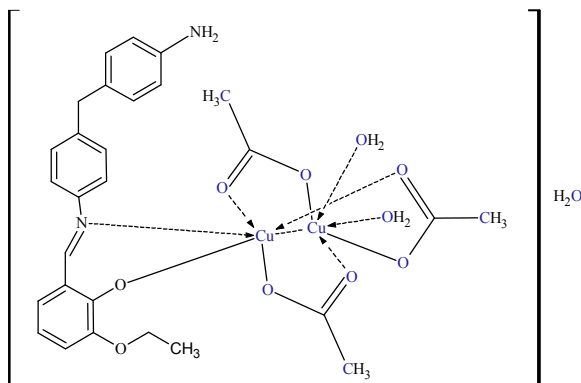


Fig. 5: Suggested structure of the dimeric Cu(II) complex.

Acknowledgements

The support of the Management Unit of Scientific Research Projects of Firat University FUBAP under research project No: FF.11.06 is gratefully acknowledged.

References

1. C. M. Da Silva, D. L. da Silva, L. V. Modolo, R. B. Alves, M. A. de Resende, C. V. B. Martins and A. de Fatima, Schiff bases: A Short Review of their Antimicrobial Activities, *J. Advanced Search*, **2**, 1 (2011).
2. D. N. Dhar, C. L., Taploo, Schiff Bases and their Applications, *J Sci Ind Res*, **41**, 501 (1982).
3. A. O. de Souza, F. C. S. Galetti, C. L. Silva, B. Bicalho, M. M. Parma and S. F. Fonseca, Antimycobacterial and Cytotoxicity Activity of Synthetic and Natural Compounds, *Quim Nova*, **30**, 1563 (2007).
4. Z. Guo, R. Xing, S. Liu, Z. Zhong, X. Ji and L. Wang, Antifungal Properties of Schiff Bases of Chitosan, N-Substituted Chitosan and Quaternized Chitosan, *Carbohydr Res*, **342**, 1329 (2007).
5. P. Przybylski, A. Huczynski, K. Pyta, B. Brzezinski, F. Bartl, Biological Properties of Schiff Bases and Azo Derivatives of Phenols, *Curr Org Chem*, **13**, 124 (2009).
6. G. Bringmann, M. Dreyer, J. H. Faber, P. W. Dalsgaard, D. Staerk, J.W. Jaroszewski, Ancistrotanazine C and related 5,10- and 7,30-coupled naphthylisoquinoline alkaloids from *Ancistrocladus tanzaniensis*, *J Nat Prod*, **67**, 743 (2004).
7. R. Ramesh and M. Sivagamasundari, Synthesis, Spectral, and Antifungal Activity of Ru(II) Mixed-Ligand Complexes, *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 899 (2003).
8. R. C. Maurya, R. Verma and T. Singh, Synthesis, Magnetic, and Spectral Studies of Some Mono- and Binuclear Dioxomolybdenum(VI) Complexes with Chelating Hydrazones Derived from Acid Hydrazides and Furfural or Thiophene-2-Aldehyde, *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 309 (2003).
9. O. A. M. Ali, M. M. H. Khalil, G. M. Attia and R. M. Ramadan, Group VI Dinuclear Oxo Metal Complexes of Salicylideneimine-2-Anisole Schiff Base, *Spectrosc. Lett.*, **36**, 71 (2003).
10. E. Canpolat, A. Yazıcı and M. Kaya, Synthesis and Characterization of vic-Dioximes Derivatives and Investigation of Its Complexes with Ni(II), Co(II), Cu(II) and UO₂(VI) Metals, *J. Coord. Chem.*, **55**, 961 (2002).
11. E. Canpolat and M. Kaya, Synthesis and Formation of a New vic-Dioxime Complexes, *J. Coord. Chem.* **58**, 1217 (2005).
12. E. Canpolat, M. Kaya and O. F., Ozturk, Studies on Mononuclear Chelates Derived from Substituted Schiff-Base Ligands (part 6): Synthesis and Characterization of a New 3-Ethoxysalicylidene-p-Aminoacetophenone Oxime and Its Complexes with Co(II) Ni(II), Cu(II) and Zn(II), *Journal Of Coordination Chemistry, J. Coord. Chem.*, **60**, 2621 (2007).
13. E. Canpolat, M. Kaya and A. Yazıcı, Mononuclear Chelates Derived from Substituted Schiff Bases Ligands: Synthesis and Characterization of a New 3-Methoxysalicylidene-p-aminoacetophenoneoxime and Its Complexes with Co(II), Ni(II), Cu(II) and Zn(II), *Spectrosc. Lett.*, **38**, 35 (2005).
14. O. Güngör, E. Canpolat and M. Kaya., A New Substitued Bis(vic-dioxime) of Its Mono and Dinuclear Complexes, *Pol. J. Chem.*, **77**, 403 (2003).
15. E. Canpolat, M. Kaya and S. Gür, Synthesis, Characterization of Some Co(III) Complexes with vic-Dioxime Ligands and Their Antimicrobial Properties, *Turk. J. Chem.*, **28**, 235 (2004).
16. E. Canpolat, M. Kaya and A. Yazıcı, Synthesis and Characterization of Co(II), Ni(II), Cu(II), and Zn(II) Complexes with a New vic-Dioxime (E,E)-N'-hydroxy-2-(hydroxyimino)-N-(4-[(2-phenyl-1,3-dioxolan-4yl)methyl]amino}butyl)ethanimidamide, *Russian J. Chem.*, **30**, 87 (2004).
17. E. Canpolat and M. Kaya, Synthesis and Characterization of Two vic-Dioximes Containing the 1,3-Dioxolane Ring and 1,4-Diaminobutane and Their Cobalt(II), Nickel(II),

- Copper(II) and Zinc(II) Metal Complexes, *Transition Met. Chem.*, **29**, 550 (2004).
18. E. Canpolat, Studies on Mononuclear Chelates Derived from Substituted Schiff Bases Ligands (Part 8): Synthesis and Characterization of a New 5-Chlorosalicylidene-p-aminoacetophenoneoxime and Its Complexes with Co(II), Ni(II), Cu(II) and Zn(II), *Pol. J. Chem.*, **79**, 619 (2005).
 19. A. Saxena and J. P. Tandon, Structural Features of Some Organotin(IV) Complexes of Semi-Semicarbazone and Thio-Semicarbazones, *Polyhedron*, **3**, 681 (1984).
 20. H. Temel, Ü. Çakır, B. Otludil and H. İ. Uğraş, Synthesis, Spectral and Biological Studies of Mn(II), Ni(II), Cu(II), and Zn(II) Complexes with A Tetradentate Schiff Base Ligand. Complexation Studies and the Determination of Stability Constants (Ke), *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1323 (2001).
 21. W. Radecka- Paryzek and H. Litkowska, Rare Earth Macrocyclic Complexes Derived from Spermine, *J. Alloys Compd.*, **300**, 435 (2000).
 22. M. Fondo, A. M. Garcia-Deibe, N. Ocampo, J. Sanmartin and M. R. Bermejo, Dinuclear Neutral Complexes of A Symmetric N-2+N-2-Donor Diimine Ligand, *Polyhedron*, **25**, 1714 (2006).
 23. E. Canpolat, A. Yazıcı and M. Kaya, Studies on Mononuclear Chelates Derived from Substituted Schiff-Base Ligands (part 10): Synthesis and Characterization of a New 4-Hydroxysalicylidene-p-Aminoacetophenoneoxime and Its Complexes with Co(II) Ni(II), Cu(II) and Zn(II), *J. Coord. Chem.*, **60**, 473 (2007).
 24. R. C. Maurya, P. Patel and S. Rajput, Synthesis and Characterization of N-(o-Vanillinidene)-p-Anisidine And N,N'-Bis(o-Vanillinidene)Ethylendiamine and Their Metal Complexes, *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 817 (2003).
 25. S. Yamada and A. Takeuchi, The Conformation and Interconversion of Schiff-Base Complexes of Nickel(II) and Copper(II), *Coord. Chem. Rev.*, **43**, 187 (1982).
 26. S. Samal, S. Acharya, R. K. Dey and A. R. Ray, Synthesis and Metal Ion Uptake Studies of Chelating Resins Derived from Formaldehyde-Furfuraldehyde Condensed Phenolic Schiff Bases of 4,4'-Diaminodiphenylether and O-Hydroxyacetophenone, *Talanta*, **57**, 1075 (2002).
 27. M. R. Wagner and F. A. Walker, Spectroscopic Study of 1-1 Copper(II) Complexes with Schiff-Base Ligands Derived from Salicylaldehyde and L-Histidine and Its Analogs, *Inorg. Chem.*, **22**, 3021 (1983).
 28. A. P. Mishra, M. Khare and S. K. Gautam, Synthesis, Physico-Chemical Characterization, and Antibacterial Studies of Some Bioactive Schiff Bases and Their Metal Chelates, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1485 (2002).
 29. V. T. Yılmaz, S. Hamamci and O. Andac, Mono- and Binuclear Copper(II) Complexes of Saccharin with 2-Pyridinepropanol Synthesis, Spectral, Thermal and Structural Characterization, *Transition Met. Chem.*, **28**, 676 (2003).
 30. A. K. Majundar and B. C. Bhattacharya, Anomalous Magnetic Behaviour of Bis(N-Methylsalicylaldimine) Nickel(II) Complex, *J. Inorg. Nucl. Chem.*, **27**, 143 (1965).
 31. C. J. Ballhausen and A. Liehr, Some Comments on the Anomalous Magnetic Behavior of Certain Ni(II) Complexes, *J. Am. Chem. Soc.*, **81**, 538 (1959).
 32. A. L. El-Ansary, A. A. Soliman, O. E. Sherif and J. A. Ezzat, Preparation and Thermal Study of New Complexes of Salicylidene-2-aminothiophenol Schiff Bases, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1301 (2002).
 33. P. K. Sharma, A. K. Sen, K. Singh, and S. N. Dubey, Divalent Cobalt, Copper and Zinc Complexes of N-salicylideneamino Acids, *J. Indian Chem. Soc.*, **74**, 446 (1997).
 34. S. A. Patil, S. N. Unki, A. D. Kulkarni, V. H. Naik, U. Kamble and P. S. Badami, Spectroscopic, In Vitro Antibacterial, and Antifungal Studies of Co(II), Ni(II), and Cu(II) Complexes with 4-Chloro-3-Coumarinaldehyde Schiff Bases, *J. Coord. Chem.*, **64**, 323 (2011).
 35. C. Bi, Y. Fan, G. Sun and J. Chang, Synthesis and Characterization of Th(IV) and U(VI) Complexes with o-Vanillin-p-Phenylenediamine, *J. Radioanal. Nucl. Chem.*, **246**, 221 (2000).
 36. S. Yasodhai, T. Sivakumar and S. Govindarajan, Preparation, Characterisation and Thermal Reactivity of Transition Metal Complexes of Hydrazine with Citric Acid, *Thermochim. Acta*, **338**, 57 (1999).