

Synthesis, Characterization, Thermal and Antimicrobial Properties of 1-((5-Nitrobenzothiazol-2-ylimino)methyl)-2-naphthol and its Complexes with Co(II), Ni(II), Cu(II) and Zn(II)

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Abstract

1-((5-nitrobenzothiazol-2-ylimino)methyl)-2-naphthol (LH), has been synthesized from 2-hydroxynaphthaldehyde and 2-aminobenzothiazole in ethanol. Metal complexes prepared from acetate salts of Co(II), Ni(II), Cu(II) and Zn(II) in 1:1 methanol/dioxan mixture. Characterization of the ligand and its complexes were made by microanalyses, FT-IR, ¹³C, ¹H NMR, and UV-Visible spectroscopy, magnetic susceptibility, thermogravimetric analysis. Antimicrobial properties of the synthesized compounds were tested against the Gram-positive *Bacillus subtilis*, *Staphylococcus aureus*, the Gram-negative *Escherichia coli*, *Salmonella typhimurium* and the yeast *Candida glabrata* and *Candida tropicalis* using a standard broth dilution technique, and compared to ampicillin and fluconazol as standard drugs. All the complexes and the ligand showed some degree of cytotoxic activity.

Keywords: 1-((5-nitrobenzothiazol-2-ylimino)methyl)-2-naphthol, 5-nitro-2-aminobenzo-thiazole, 2-hydroxynaphthaldehyde, thiazole, Co(II), Ni(II), Cu(II), Zn(II), metal complex, antimicrobial activity.

Introduction

Schiff bases represent an important series of widely used organic ligands especially with transition metals to prepare metal complexes. It is well known that metal ions involve in biological processes of life. The modes of action of these metal ions are often complex but are believed to involve bonding to the hetero atoms of the heterocyclic residues of biological molecules, *i.e.* proteins, enzymes, nucleic acids, *etc* [1].

Schiff bases and their metal complexes, played an important role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical [2] and biochemically relevant studies of metal complexes [3-6] and found wide range of applications. Thiazoles represent a very interesting class of compounds because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects, e.g. as antibacterial [7], antifungal [8,9], anti-inflammatory [10,11] antihelmintics, antitubercular [12], anti-HIV [13], Antidegenerative [14] and hypothermic [15] activities, herbicides [16]. In recent years thiazole based chemisensors have been investigated and showed to be successfully applicable in biological systems [17-19].

It is known that 2-aminothiazole is a biologically active compound with a broad range of activity and also it is an intermediate in the synthesis of antibiotics and dyes. Numerous thiazole derivative Schiff bases and their transition metal complexes have been investigated by various techniques [20-27].

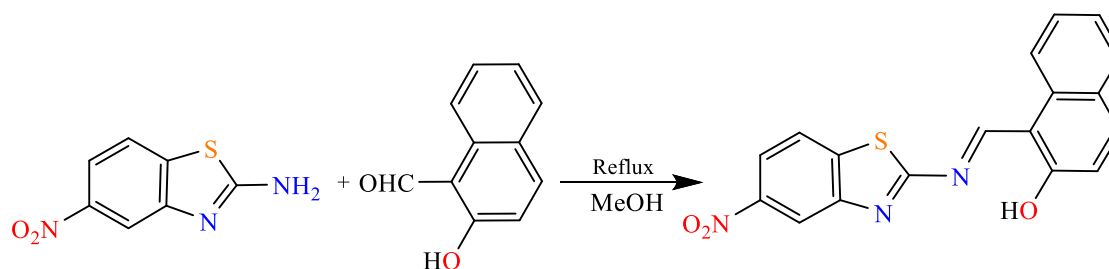
From these points of view, it is interesting to study different types of transition metal complexes of biologically active ligand. In this paper, the synthesis and characterization of the first row transition metal complexes of the type $[ML_2]$ where M is Co(II), Ni(II), Cu(II) and Zn(II) metals, L is a deprotonated ligand (1-((5-nitrobenzothiazol-2-ylimino)methyl)-2-naphthol) have been studied.

EXPERIMENTAL

2-Amino-5-nitrobenzothiazole, and 2-hydroxynaphthaldehyde, were purchased from Aldrich and used without further purification. The elemental analyses were made by using a LECO-CHNS 932 microanalysis. IR spectrums were taken using Mattson 1000 FT-IR spectrophotometer as KBr pellets. ^1H and ^{13}C NMR spectrums were recorded on Jeol FX-90 spectrophotometer. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance model MK1 at room temperature. Thermogravimetric analyses were obtained from a Shimadzu TGA-50 Thermobalance. Melting points were determined with a Gallenkamp apparatus. Electronic spectrums recorded on a Cecil CE 5502 Spectrophotometer in the quartz cell path length of 1.0 cm or as nujoll mull.

Synthesize of the ligand (LH)

10 mmol (1.722 g) of 2-hydroxynaphthaldehyde was dissolved in 25 ml methanol in 250 ml flask and 10 mmol (1.952 g) of 2-amino-5-nitrobenzothiazole dissolved in 25 ml methanol in the hood then added drop wise to flask at room temperature and two drop of concentrated sulfuric acid added as catalyst then the mixture was refluxed for 12 hours, then the temperature brought to room temperature and 10 ml of cold water added and precipitate was filtered and washed with water and ethyl alcohol-water mixture then it was dried at 60 °C temperature, yield 2.95 g (85 %).



Scheme 1. Synthesis of 1-((5-nitrobenzothiazol-2-ylimino)methyl)-2-naphthol (LH).

The characteristic IR bands (KBr pellets, cm^{-1}) are given in Table 1. The ligand found to be soluble in CHCl_3 , THF, methanol, DMSO, DMF, acetone, ethyl acetate and insoluble in diethyl ether, n-hexane, and water, slightly soluble in ethanol. Characteristic ^1H NMR peaks are (CCl_4 TMS, δ ppm), 8.60 (s, $-\text{CH}=\text{N}$), 7.1-8.10 (m, $=\text{CH}-$ in naphthalene ring). Aromatic protons benzothiazole appeared at about 8.3 - 8.5 as multiplets, $-\text{OH}$ signal appeared at 10.3 ppm.

General Procedures for the Synthesize of the complexes

1 mmol of LH dissolved in 15 ml of methanol then 0.5 mmol of acetate salt of metals dissolved in 15 ml of methanol and added drop wise to the ligand solution while it was being stirred and then refluxed for six hours. The reactions were stopped and brought to room temperature; and complexes were filtered off. After that the residue was dissolved in 5 ml of dichloromethane and precipitated in 100 ml of n-hexane then filtered off and dried at 60 °C. The complexes found to be soluble in DMSO, DMF, THF, CHCl_3 , pyridine, dichloro methane, ethanol, ethyl acetate, slightly soluble in 1,4-dioxane, acetone, carbon tetrachloride, and insoluble in water, n-hexane, benzene, diethyl ether, petroleum ether.

The colours yield, melting points, microanalysis results, magnetic moments of the synthesized compounds are given Table 1 and characteristic IR bands as KBr pellets, of the ligand and complexes are given in Table 2.

Table 1 Formulas, colours, melting points, yields, magnetic moments and micro analysis results of ligand its metal complexes.

Compounds	FW g/mole	Color	Yield %	Mp (°C)	Found % (Calculated), %				μ_{eff} (B.M.)
					C	H	N	S	
LH C ₁₈ H ₁₁ N ₃ O ₃ S	349.39	Yellow- Orange	86	196	62.25 (61.88)	3.03 (3.17)	12.42 (12.03)	9.45 (9.18)	---
[CoL₂] C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Co	755.66	Dark Red	73	259	57.38 (57.22)	3.09 (2.67)	11.52 (11.12)	8.62 (8.49)	4.23
[NiL₂] C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Ni	755.44	Dark Red	66	253	57.36 (57.24)	2.98 (2.67)	11.50 (11.13)	8.17 (8.49)	2.93
[CuL₂] C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Cu	760.27	Light Brown	60	242	56.93 (56.88)	3.13 (2.65)	11.11 (11.05)	8.32 (8.44)	1.67
[ZnL₂] C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Cu	762.10	Orange	70	305	56.42 (56.74)	2.86 (2.65)	11.36 (11.03)	8.84 (8.41)	Dia.

RESULTS AND DISCUSSION

The synthesis of the ligand was given in Scheme 1. Authentication of the ligand was checked by FT-IR, ¹H NMR and elemental analysis. The coordination compounds of the ligand were synthesized in absolute methanol in good yield (80-95%). The found and calculated element analyses (C, H, N and S) are in good agreement, in addition the thermal analysis results of the complexes confirm the proposed molecular formula of the isolated complexes. All the complexes have 1:2 ratio of metal to ligand and have an octahedral configuration.

IR spectra and mode of bonding

The IR spectra of the free ligand and metal complexes were carried out in the range of 4000 – 400 cm⁻¹ (Table 2). The IR spectra of the ligand show a broad band in between 3200 - 3450 cm⁻¹, which can be attributed to phenolic OH group. This band disappears in all complexes after complexation, which is an indication of involvement of phenolic OH in coordination. The involvement of deprotonated phenolic OH group in complexes are confirmed by the shift of $\nu(\text{C-O})$ stretching band observed at 1208 cm⁻¹ in the free ligand to the lower frequency to the extent of 10 cm⁻¹ [28]. The IR spectrum of the ligand revealed a medium band at 1561 cm⁻¹ $\nu(\text{C=N})$ thiazole ring, which is changed to higher frequencies after complexation indicating that it has been involved in the coordination. The unchanged band after complexation at 780 in the free ligand suggests non-involvement of the coordination to metal which was assigned as $\nu(\text{C-S-C})$ [29]. In the IR spectrum of all the complexes IR band observed between 557-581 cm⁻¹ which is attributed to the $\nu(\text{M-N})$ stretching vibrations and the second band appeared between 498-502 cm⁻¹ which is assigned to the phenolic oxygen to metal atoms stretching vibrations $\nu(\text{M-O})$ [Error! Bookmark not defined.].

Table 2 Characteristic IR bands of the ligand and its complexes as KBr pellets.

Mode of vibration	Ligand (LH)	CoL ₂	NiL ₂	CuL ₂	ZnL ₂
v(O-H)	3430 br	----	----	----	----
v(C=N) _{azomethine}	1621 w	1615 m	1618 m	1617 m	1617 m
v(C=N) _{thiazole}	1561 m	1574 m	1566 m	1570 m	1578 m
v(C=C) _{benzene}	1340 m	1331 w	1330 m	1330 w	1331 w
v(C-O)	1208 m	1215 m	1219 m	1218 m	1214 m
v(C-S-C)	779 w	780 w	780 w	781 w	780 w
v(M-N)	-	566 w	581 w	569 w	557 w
v(M-O)	-	498 w	487 w	498 w	502 w

Key: s (strong), m (medium), br (broad), w (weak).

UV-Vis. spectra and magnetic moments

The electronic spectrum of the Schiff base and its complexes were taken in DMSO and in nujol mull and both spectra showed similar features. Two strong bands at 360 nm and 225 nm were observed in the spectra of the ligand, which is attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the aromatic ring and C=N chromophore [30]. The cobalt complex has three bands at 670, 500 and 310 nm which is assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4T_{1g}(F)$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}(P)$ transitions respectively. Calculated 10 Dq energy of the Co(II) complex is 18590 cm^{-1} and the Racah parameter is 475 cm^{-1} . From the position of the bands and the magnetic moment value of 4.23 B.M. the geometry of the cobalt complex suggested the geometry of the complex as octahedral. The observed d-d transition of the nickel complex at 685, 475 and 325 nm, corresponding to the transition of ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in the octahedral field. Magnetic moment value of 2.93 BM supports the hexa coordinated configuration of the nickel complex. Calculated 10 Dq and the Racah parameters are 14600 and 665 cm^{-1} respectively.

Cu(II) complexes take a wide range of geometries, often with a low symmetry and in most geometries the electronic spectra exhibits a very broad band with maximum which contains all the expected transitions [31]. The magnetic moment of Cu(II) complex is 1.67 BM and UV-visible spectra of the Cu(II) complex, has two band the first one being very strong at 450 nm and the second one being broad at 720 nm, assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition with a tailing to higher wavelength which is well known for octahedral copper complex, [32,33].

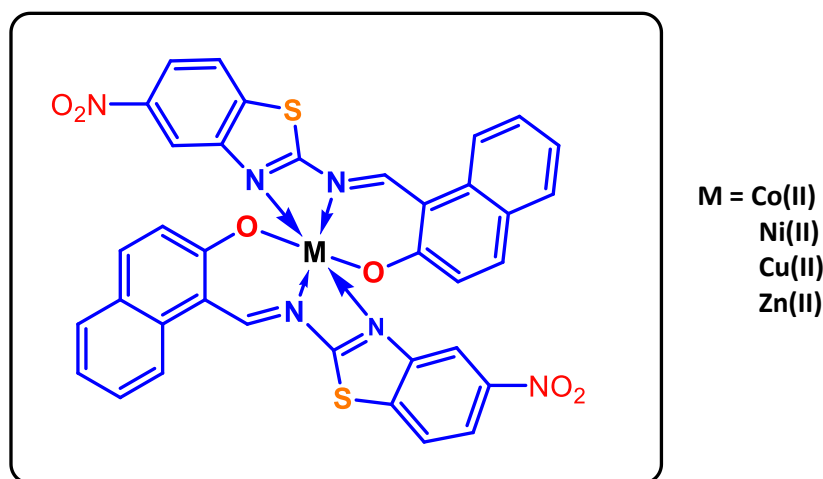


Figure 1 Suggested structure of the Co(II), Ni(II), Cu(II) and Zn(II) complexes

Thermal Analysis

Thermogravimetric analysis of the ligand and complexes carried out up to 900 °C. While Ni(II) and Cu(II) complexes were decomposing in two successive steps, ligand, Co(II) and Zn(II) complexes were decomposed in three steps. Figure 2 shows the thermograms of the ligand and the complexes.

The thermogram of the ligand shows that the weight loss begins at 210 °C and decomposes in three steps which are 210-285 °C, 285-480 °C and 480-700 °C leaving 6 % residue. The first step is 5.0 % weight loss corresponds to hydroxyl group (calculated 4.9 %), activation energy of 111.4 kJmol⁻¹, and the second decomposition step occurred between 285-480 °C with 38.3 % weight loss corresponding to naphthalene group (calculated 39.8 %) with the activation energy of 271.0 kJmol⁻¹, and in the third step between 480-700 °C it further decomposes leaving 6.0 % residue with the activation energy of 144.0 kJmol⁻¹.

The Co(II) complex, is thermally decomposed in three steps with the first step is being very fast, accompanied with weight loss of 49.7 % within the temperature range of 385-420 °C corresponding to loss of two C₇H₃N₂O₂S groups (calculated 47.4) with the activation energy of 399.0 kJmol⁻¹. Second and the third steps occurred within the temperature range of 420-490 and 490-580 °C with the mass loss of 16.7 % and 24.6 % leaving 10.2 % residue as CoO (calculated 9.9 %) with the activation energies of 311.8 and 254.3 kJmol⁻¹ respectively.

The Ni(II) complex, decomposed in two successive steps within the temperature range of 360-570 °C. First step occurred in between 360-410 °C with a mass loss of 29.8 % attributed to C₈H₄N₃O₂S groups (calculated mass loss 27.3 %). The calculated activation energy of was 980.0 kJmol⁻¹. Decomposition of the remaining of the complex occurred in between 410-570 °C with the mass loss of 57.8 %, leaving 10.8 % residue as NiO (calculated 9.9 %) with calculated activation energy of 124.9 kJmol⁻¹.

The Cu(II) complex, decomposed in two steps, with the first step is being mass loss of 21.2 % within the temperature range of 285-360 °C may attributed to liberation of C₇H₃N₂O₂S group (calculated 23.6 %). The activation energy of this step was calculated as 311.8 kJmol⁻¹. The second decomposition step of occurred in between 360-500 °C with a mass loss of 69.1 % leaving 9.7 % residue as CuO (calculated 10.4 %). The activation energy of the second step was found to be 98.0 kJmol⁻¹.

The Zn(II) complex, decomposed in three steps within the temperature range of 360-630 °C leaving 11.5 % residue as ZnO (calculated 10.6 %). The first and the second steps occurred in between 360-540 with the total mass loss of 50.8 % corresponding to two C₇H₃N₂O₂S groups (calculated 47.0 %) with the activation energy of 998.9 and 236.7 kJmol⁻¹ respectively. The third step occurred between 540-630 °C with the calculated activation energy of 412.7 kJmol⁻¹, leaving 11.5 % ZnO residue.

Kinetic analysis

Kinetic parameters of the decomposition such as activation energy (ΔE^*) enthalpy (ΔH^*) entropy (ΔS^*) and free energy change (ΔG^*) of the ligand and its complexes evaluated graphically by the Coats-Redfern equations given below [28].

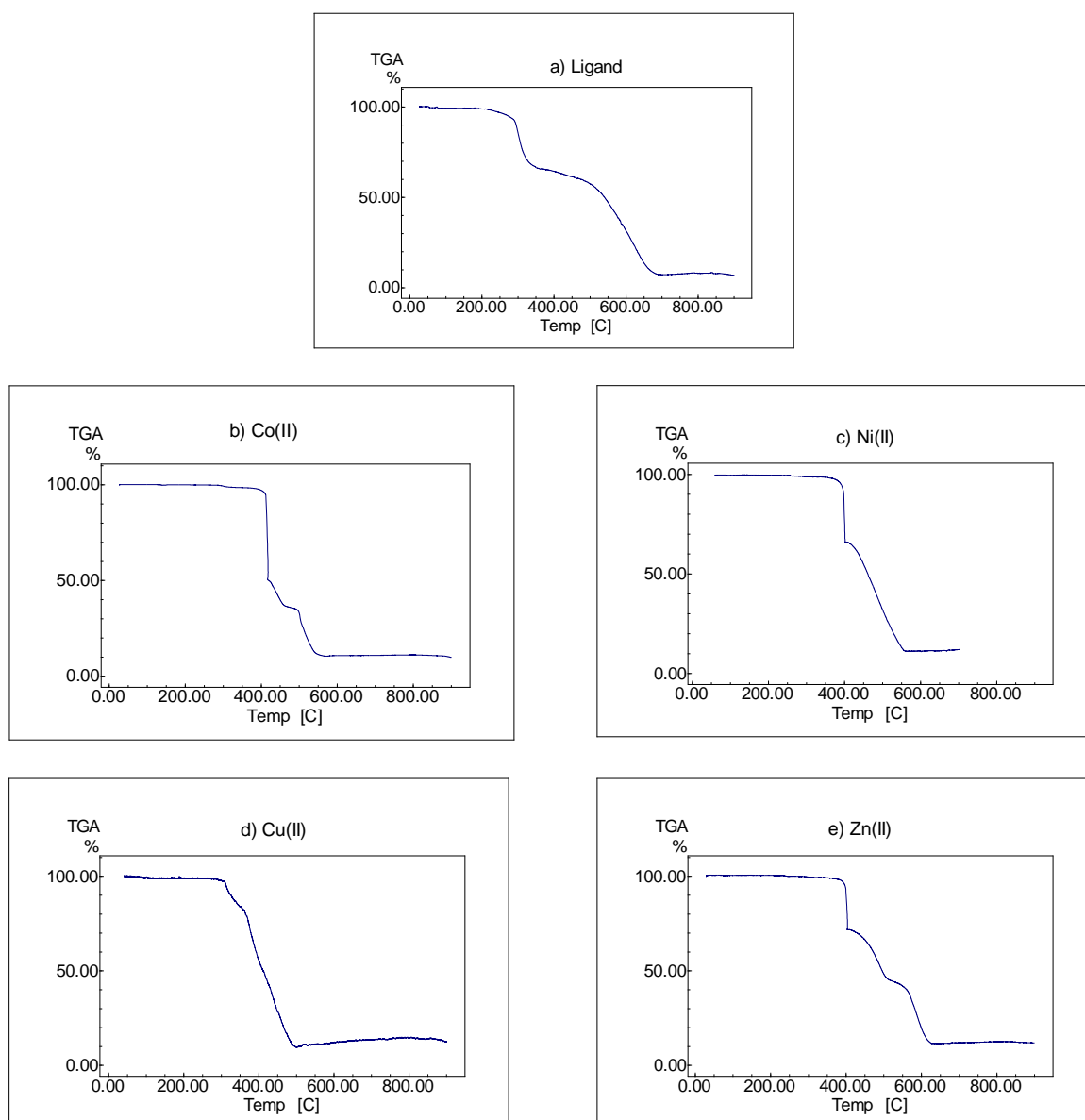


Figure 2 Thermograms of the ligand and metal complexes

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

$$\Delta S^* = 2.303R \left[\log \left(\frac{Ah}{kT} \right) \right] \quad [2]$$

$$\Delta H^* = E^* - RT \quad [3]$$

$$\Delta G^* = H^* - TS^* \quad [4]$$

Where W_f is the mass loss at the completion of the reactions, W is the mass loss up to the temperature T , R , k and h are the gas Boltzman and Planck constants respectively, E^* is the activation energy in kJmol^{-1} ,

θ is the heating rate, and $(1-2RT/E^*) \cong 1$. Activation energy (E^*) and Arrhenius constants (A) of the decomposition steps were calculated from Eq. (1), a plot of the left-hand side of the Eq. (1) against $1/T$ gives a straight line from which the activation energy were calculated from the slope of the line, and Arrhenius constants were determined from the intercept. The entropy, enthalpy and free energy change of the activation were calculated using the Eq. 2,3 and 4. The correlation coefficient of the Arrhenius plots of the thermal decomposition steps were found to lie in the range of 0.970-0.999, showing a good fit with the linear function. The calculated thermodynamic properties of the ligand its metal complexes are given it Table 3.

Table 3 Thermodynamic data of the thermal decomposition of the ligand and its complexes

Compound	Decomposition Temperature (K)	E^* (kJ mol ⁻¹)	A (s ⁻¹)	ΔS^* (J mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)
LH	210-285	111.4	$7.58 \cdot 10^{10}$	-41	107.0	128.5
C ₁₈ H ₁₁ N ₃ O ₃ S	285-480	271.1	$1.80 \cdot 10^{24}$	213	266.3	142.2
	480-700	144.0	$8.57 \cdot 10^{13}$	12	136.8	125.5
[CoL ₂]	290-420	399.0	$1.90 \cdot 10^{99}$	3889	393.6	-2134.3
	420-490	311.8	$5.10 \cdot 10^{23}$	202	306.1	166.7
C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Co	490-580	254.3	$1.86 \cdot 10^{17}$	78	240.0	188.4
	360-410	988.0	$2.60 \cdot 10^{80}$	1288	982.8	158.3
[NiL ₂]	410-570	124.9	$5.63 \cdot 10^8$	-84.5	118.8	181.6
	285-360	311.8	$2.92 \cdot 10^{17}$	83	306.9	257.9
C ₃₆ H ₂₀ N ₆ O ₆ S ₂ Ni	360-500	98.0	$2.40 \cdot 10^7$	-110	92.4	167.5
	360-410	998.9	$8.79 \cdot 10^{80}$	1298	993.5	149.7
[ZnL ₂]	410-540	236.7	$5.79 \cdot 10^{16}$	69	230.7	181.3
	540-630	417.2	$3.96 \cdot 10^{25}$	236	410.1	210.3

Antimicrobial Properties

The antimicrobial activity of the ligand and complexes were tested by using agar dilution procedure outlined by the National Committee for Clinical Laboratory standards [34, 35] against four bacteria and two fungi. Minimum inhibitory concentration (MIC) of the synthesized compounds were investigated against the Gram-positive *Bacillus subtilis*, *Staphylococcus aureus*, the Gram-negative *Escherichia coli*, *Salmonella typhimurium* and the yeasts *Candida glabrata* and *Candida tropicalis*. The stock solutions were prepared in dimethyl sulfoxide (DMSO) which have no effect on the microorganisms in the concentrations studied. All the dilutions were done with distilled water or DMSO. Ampicillin and fluconazol were used as the reference compounds for the experimental conditions. All the MIC results are presented in Table 4. The obtained data shows that all the compounds are able to inhibit the growth of the selected microorganism in vitro showing MIC values between 256 and 128 $\mu\text{g ml}^{-1}$.

Table 4 Antimicrobial activity results (MIC values $\mu\text{g ml}^{-1}$) of ligand its complexes against standard drugs.

Sample	B. Sub	E. Coli	S. Aureu	S. Typh	C. Glob	C. Trop
Ligand	256	256	256	256	128	128
NiL ₂	256	256	256	256	256	128
CuL ₂	256	256	256	256	128	128
CoL ₂	256	256	256	256	128	128
ZnL ₂	128	128	128	256	128	128
Ampicilin	2	2	2	2	-	-
Fluconazol	-	-	-	-	8	8

CONCLUSION

Analysis of all synthesized complexes shows that the divalent metal ions surrounded by two ligand molecule which have an octahedral geometry. The structure of the complexes also supported by UV-Vis spectra and magnetic moment measurements together with microanalysis and TGA analysis. The ligand and complexes showed some degree of cytotoxic activity against tested microorganisms.

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REFERENCES

- [1] Erwin B. and Omoshile C., *J. Chem. Soc. Perkin Trans. 2*, 1333 (1995).
- [2] Luo X.F., Hu X., Zhao X.Y., Goh S.H. and Li X.D., *Polymer*, 44, 5285 (2003).
- [3] Razakantoanina V., Phung N.K.P. and Jaureguiberry G., *Parasitol. Res.*, 86, 665 (2000).
- [4] Royer R.E., Deck L.M., Vanderjagt T.J., Martinez F.J., Mills R.G., Young S.A. and Vanderjagt D.L., *J. Med. Chem.*, 38, 2427 (1995).
- [5] Baumgrass R., Weiwad M. and Edmann F., *J. Biol. Chem.*, 276, 47914 (2001).
- [6] Quintana P. J. E., Peyster de A., Klatzke S. and Park H.J., *Toxicol. Lett.*, 117, 85 (2000).
- [7] Agarwal N., Kumar S., Srivastava A. K., Sarkar K.P.C., *Ind. J. Het. Chem.*, 6, 291-294 (1997).
- [8] Sup R. C., Sukp R.Y., Bang C. W., *Korean J. Med. Chem.*, 5, 72 (1995).
- [9] Buristrov S. I., and Bobashko Z. A., *USSR. Pat. No: 154861*, (1964). (Chem Abstr. 60, 5508c, (1964))
- [10] Hadjipavlou L. D., Geronikaki A., Sotiropoulou E., *Res. Commun. Chem. Path.*, 79, 355 (1993).
- [11] Geronikaki A., Hadjipavlou-Litina D., Amourgianou M., *Il Farmaco*, 58, 489 (2003).
- [12] Tsuruoka M. and Seikutsugaka I., *Med. Biol.*, 10, 296 (1947).
- [13] Maass G., Immendoerfer U., Koenig B., Leser U., Mueller B., Goody R., Pfatt B., *Antimicrob. Agents. Chemotter.*, 37, 2612 (1993).
- [14] Anna M. P., Athina G., Remi M., Venera C., Barbara G. and Irini D., *Bioorganic & Medicinal Chemistry*, 11, 2983 (2003).
- [15] Kapoor R. P., Rastogi M. K., Khanna R. and Garg C. P., *Indian J. Chem.*, 23B, 390 (1984)
- [16] Metzger J. V., Katritzky A. R., Rees W., Potts K. T., (Eds.). *Comprehensive Heterocyclic Chemistry*, (Pergamon Oxford, 1984; Vol. 6)
- [17] Bhattacharya S. and Thomas M., *Tetrahedron Letters*, 41, 10313 (2000).
- [18] Parker D., *Chem. Commun.*, 47 (2000).
- [19] Thompson R. B., Ge Z., Patchan M., Muang C. C., Fierke C. A., *Bioelectron.*, 11, 557 (1996).
- [20] Eynde Vanden J. J. and Fromont D., *Bull. Soc. Chim. Belg.*, 106, 393 (1997).
- [21] Castro R., Garcia-Vazquez J. A., Romero J. and Sousa A., *Polyhedron*, 12, 2241 (1993).
- [22] Saydam S. *Synth. Reac. Inorg. Met.-Org. Chem.*, 32, 437 (2002).
- [23] Ieda H., Fujiwara H., Fuchita Y., *Inorganica Chimica Acta*, 319, 203 (2001).
- [24] Borrás E., Alzuet G., Borrás J., Server-Carrió J., Castineiras A., Liu-Gonzalez M., Sanz-Ruiz F., *Polyhedron*, 19, 1859 (2000).

- [25] Saydam S., Alkan C., Polish Journal of Chemistry, 75, 29 (2001).
- [26] James M., Kawaguchi H. and Tatsumi K., Polyhedron, 16, 1873 (1996).
- [27] Mohamed G. G., Spectrochimica Acta, Part A, 57, 411 (2001).
- [28.] Omar M. M. Mohamed G. G., Spectrochimica Acta Part A, 61, 929-936 (2005)
- [29.] Castro R., Garcia-Vazquez J.A., Romero J. and Sousa A., Polyhedron, 12, 47 (1993).
- [30] Williams D. H. and Fleming I., Spectroscopic Methods in Organic Chemistry, 4th Edition, (McGraw-Hill, London, 1989).
- [31] Drago R. S., Physical Methods for Chemists, (Sounders College Publishing, New York, 1992).
- [32] Gul A. and Bekaroglu O. J. Chem. Soc. Dalton Trans., 2537 (1983).
- [33] Greenwood N. N. and Earnshaw A., Chemistry of the Elements, (Pergamon Press, Oxford, 1984).
- [34.] National Committee for Clinical Laboratory standards (NCCLS), Methods for dilution antimicrobial susceptibility tests for bacteria that grow aerobically, Approved Standard M7-A2, NCCLS, Villanova, PA, 1997.
- [35.] National Committee for Clinical Laboratory standards (NCCLS), Reference Methods for broth dilution antifungal susceptibility testing of yeasts. Proposed Standard Document M27-P, NCCLS, Villanova, PA, 1992.