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Binuclear Schiff base ligand and its metal(II) complexes derived from 1,6-diaminohexane and 2,2'- dihydroxysalicylalacetone

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Abstract

A new symmetrical Schiff base ligand was derived from 1,6-diaminohexane and 2,2'-dihydroxy salicylalacetone and then it is allowed to react with metal salts to form binuclear Schiff base metal complexes. All the synthesized complexes were characterized based on elemental analyses, IR, ^{1}H NMR, magnetic moment, molar conductance, UV-visible, fluorescence, cyclic voltammetry and thermal analysis. The molar conductance reveals that the chelates are non-electrolytic in nature. An IR spectrum shows that the Schiff bases are coordinated to phenolic moieties. The formation of ligand was also ascertained by ^{1}H NMR spectra. The electronic absorption spectra and magnetic susceptibility measurements show that Cu(II) complex possess square planar geometry whereas Ni(II), Co(II) and Zn(II) complexes possess tetrahedral geometry. The cyclic voltammetric studies of Cu(II) complex in DMSO indicate the structural changes during the course of redox reaction and irreversible nature of the Schiff base binuclear copper(II) complex. Thermal stability of the ligand and its Ni(II) complexes were also evaluated. The synthesized ligand, in comparison to their metal complexes were screened for their antimicrobial activity against the bacteria such as *Staphylococcus aureus*, *Bacillus subtilis*, *Salmonella typhi* and *Escherichia coli* and the fungus *Candida albicans* and *Aspergillus niger* have been carried out. The activity data show that metal complexes are more potent antimicrobial activity than the free ligand.

***Keywords**: 1,6-diaminohexane, disalicylalacetone, Metal complexes, TG analyses, Biological studies.*

1. Introduction

The Designing and synthesis of a new ligand was perhaps the most important step in development of metal complexes which exhibit unique properties and novel reactivity due to electron donor, electron acceptor properties, structural, functional groups and position of ligand in the coordination sphere.

Transition metal complexes containing a salicylaldehyde are commonly found in biological media and play important roles in processes such as catalysis of drug interaction with biomolecules [1]. Salen metal complexes are the interest of many workers because of their applications in food industry, in the treatment of cancer [2], as antibactericide agents [3,4], as antivirus agents [5], as fungicide agents [6], and for other biological properties [7]. Dibenzalacetone derivatives contain two aromatic rings with an unsaturated chain. Many biological activities have been attributed to this group, such as antitumoral [8], anticancer and antioxidant [9], antifungal [10], antimitotic [11], chemoprotective [12], anti-inflammatory [13,14] antimicrobial [15], anti-nociceptive [16], and antibacterial [17] activities.

Metal complexes of Schiff base derived from the reaction of substituted salicylaldehydes with aliphatic and aromatic amines represent a series of compounds containing nitrogen, sulphur and oxygen ligand donor atoms that has been widely studied [18,19]. Schiff base molecules afford potential sites for bio-chemically active compounds that are related to intermolecular hydrogen bonding and proton transfer equilibria [20]. Metal complexes of Schiff base ligands possess a variety of applications in the biological, analytical, clinical, and industrial areas [21]. In recent times, transition metal complexes of Schiff base ligands have gained considerable attention, not only due to their spectroscopic properties and applications [22] but also due to their remarkable antifungal, antibacterial and antitumor activities [23]. With respect to the biological activity and desirable physicochemical, stereochemical, electrochemical, structural and catalytic properties of Schiff base metal complexes, their values has attracted significant attention and is also relevant for their application as tools for the analysis of pharmacological constituents.

Based on the above facts, we have been intense in studying the role of Schiff base ligand with various transition metal complexes on antimicrobial studies. Hence, our present investigation focuses on the synthesis of metal(II) complexes containing new novel Schiff base ligand obtained from the reaction of 1,6-diaminohexane and 2,2’-dihydroxysalicylalacetone. The structure of the ligand and its metal(II) complexes has been characterized by various spectroscopic techniques. The entire synthesized compound has been subjected to assess their interacting ability with microbial strains.

2. Experimental

2.1. Materials and methods

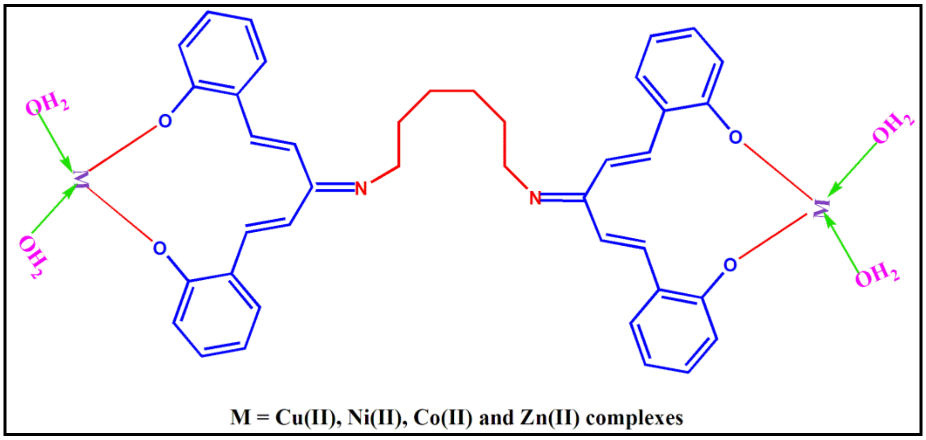
All chemicals were obtained from Aldrich Chemical & Co. and used without purification. The UV-Vis spectra of the ligand and metal complexes were recorded using a JASCO V-530 spectrophotometer. Infrared (IR) spectra in KBr discs were recorded on a SHIMADZU FT-IR 460 plus spectrophotometer at USIC, Madurai Kamaraj University, Madurai. Cyclic voltammetry measurements were carried out at room temperature in DMSO (CH Instruments, USA, voltammograph) using a three electrode cell containing a reference Ag/AgCl electrode, Pt wire auxiliary electrode and glassy carbon working electrode with tetrabutylammonium perchlorate as supporting electrolyte. The metal contents of the complexes were estimated by incinerating them to metal oxides [24]. Elemental analyses were performed at SAIF, CDRI, Lucknow. ^{1}H-NMR spectrum was recorded in $CDCl_3$ using a Bruker DRX-300, 300MHz NMR spectrometer. Magnetic Susceptibility of the complexes was measured on a MSB mark 1 Sherwood, UK at Thiagarajar College, Madurai. Effective magnetic moments were calculated using the formula $\mu_{eff} = (2.828\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. Molar conductances of the complexes (10^{-3} mol L^{-1}) were measured in DMSO at room temperature using a Systronic conductivity bridge.

2.2. Synthesis of 1,6-diimino-bis-(2,2’-tetrahydroxy)salicylalacetone [DIBTHSA] (L)

2, 2’-dihydroxysalicylalacetone [25] (5 g, 2 mmol) was reacted with 1,6-diaminohexane (1.16 g, 1mmol) in 20 ml ethanol. It was allowed to stir for two hours at room temperature. Yellow colour precipitate was separating out [26]. The contents were washed several times with ethanol. It was filtered, dried and recrystallized from ethanol. Yield 76%.

2.3. Synthesis of metal(II) complexes

To a solution of 0.6g (1 mmol) of ligand (DIBTHSA) and 0.34g (2 mmol) of the metal(II) chlorides (Cu(II), Ni(II), Co(II) and Zn(II)) were dissolved in 30ml of ethanol. The reaction mixture was stirred for 3hrs. The obtained colored complexes were reduced to one half of the solution to get the precipitate. The precipitate was filtered and washed with ethanol, dried under vaccum. Yield: 67%



Scheme 1. Proposed structure of metal(II) complexes

3. Biological activity

Antimicrobial activity of the compounds was tested *in vitro* by the well diffusion method [27] against the bacteria *Staphylococcus aureus*, *Escherichia coli*, *Salmonella enterica typhi*, *Bacillus subtilis* using agar nutrient as the medium. Antifungal activity was evaluated against *Aspegillus niger* and *Candida albicans* cultured on potato dextrose agar as medium. All the bacterial strains mentioned above were incubated in Nutrient Broth (NB) at 37 °C for 24 h and fungal isolates were incubated in PDA broth at 28 °C for 2-3 days. The well each of 5 mm in diameter was made in Muller Hinton agar using cork borer. The test solution was prepared in mM^{-1} concentration (DMSO) and then 100 µL of the solution was transferred into each well. The plates were incubated for 24 h at 37° C and examined for clear inhibition zone around the well.

4. Results and discussion

All the complexes are colored, stable in air and non-hygroscopic in nature. They are freely soluble in organic solvents such as DMSO, DMF and acetonitrile. The Cu(II), Ni(II), Co(II) and Zn(II) complexes and $[M_2L(H_2O)_4]$ type were obtained in good yield through the reaction of (DIBTHSA) with the corresponding metal salts scheme 1. The physical property of the ligand (DIBTHSA) and its metal(II) complexes are listed in Table 1. The molar conductance of complex was measured to determine the charge of the metal ion and implied that the complex is non-electrolytes [28]. The analytical data of the metal(II) complexes are in good agreement with the general formula $[M_2L(H_2O)_4]$.

Table 1. Physical characterization, analytical, and molar conductance data of the ligand and metal(II) complexes

Compound	**F.W. (g/mol)**	**Color**	**Calculated (Found) (%)**				**Λ_M (Ohm^{-1} cm^{2}mol^{-1})**
			C	**H**	**N**	**M**	
DIBTHSA (**L**)	612.0	Yellow	78.43 (77.40)	6.53 (5.11)	4.57 (3.66)	-	-
$[Cu_2(DIBTHSA)(H_2O)_4]$(**1**)	806.08	Pale green	59.55 (58.10)	5.46 (4.20)	3.47 (2.60)	15.63 (14.61)	8.2
$[Ni_2(DIBTHSA)(H_2O)_4]$(**2**)	796.38	Light green	60.30 (59.12)	5.53 (4.21)	3.51 (2.81)	14.57 (13.40)	7.4
$[Co_2(DIBTHSA)(H_2O)_4]$(**3**)	796.86	Dark brown	60.12 (59.00)	5.49 (5.70)	3.21 (2.80)	14.50 (13.88)	6.2
$[Zn_2(DIBTHSA)(H_2O)_4]$(**4**)	810.76	Dark green	59.26 (58.00)	5.43 (5.01)	3.46 (2.79)	16.05 (15.18)	9.3

4.1. Electronic spectra and magnetic moment

The absorptions in ultraviolet region are attributed to transitions within the ligand orbital and those in the visible region are probably due to allowed d-d transitions and metal-to-ligand charge transfer transitions. The electronic spectra of ligand and its metal complexes were recorded in DMSO. The absorption spectrum of ligand show strong peak at 31948 cm^{-1} and 40000 cm^{-1} which are attributed to π-π^* and n- π^* transitions respectively. The electronic spectral data of ligand and its complexes are given in the Table 2.

Generally the tetrahedral complexes of cobalt(II) shows bands in the region (15000-16000 cm^{-1}) which corresponding to the transition $^4A_2(F) \rightarrow {}^4T1(P)$. The electronic spectrum of cobalt(II)complex shows peak in the region (15847-16339cm^{-1}), which can be tentatively assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ transition for the tetrahedral geometry [29]. Nickel(II) complex exhibit absorption bands at 15847cm^{-1} due to $^3T_1(F) \rightarrow {}^3T_1(P)$ transition corresponding to tetrahedral geometry [30]. The molar intensity of nickel complex is in range 502 L mol^{-1} cm^{-1}. The magnetic moment of Co(II) and Ni(II) complexes have magnetic moment values 4.25 B.M and 2.91 B.M. respectively, confirms tetrahedral geometry [31,32]. Generally square planar copper complexes show bands in the region 14000-20000 cm^{-1}. The copper (II) complex display bands at 13800 cm^{-1} corresponding to the $^2B_1g \rightarrow {}^2A_1g$ transition of tetrahedrally distorted square planar geometry [33]. The magnetic moment value 1.73 B.M. for copper(II) complex fall within the range normally observed for distorted square planar environment [34].

Table 2. Electronic and magnetic susceptibility data of ligand and their metal(II) complexes

Compound	λ_{max}(cm^{-1})	Transition	Geometry	μ_{eff} (B.M)
DIBTHSA (**L**)	31948 40000	INCT* INCT	-	-
[Cu_2(DIBTHSA)(H_2O)$_4$](**1**)	13800	$^2B_{1g} \rightarrow ^2A_{1g}$	Square planar	1.73
[Ni_2(DIBTHSA)(H_2O)$_4$](**2**)	15847	$^3T_1(F) \rightarrow ^3T_1(P)$	Distorted tetrahedral	2.91
[Co_2(DIBTHSA)(H_2O)$_4$](**3**)	16339 15 847	$^4A_2(F) \rightarrow ^4T_1(P)$ $^4A_2(F) \rightarrow ^4T_1(F)$	Distorted tetrahedral	4.25

*Intra-ligand charge transfer bands

4.2. ^{1}H NMR Spectral data

Nuclear Magnetic Resonance spectroscopy involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field. The ^{1}H NMR spectrum of ligand is recorded in $CHCl_3$. The peaks are assigned as follows: Hydroxyl group proton as singlet at (s, 13.681 δ), aromatic protons as multiplet at (6.887-8.381 δ), CH_2-CH_2-CH_2-CH_2 at (8H, m,1.4352-2.973 δ) and CH_2-CH_2 (4H, t,3.567-3.608δ) values respectively. The ^{1}H NMR spectrum of zinc(II) complex were recorded in DMSO solution. It is observed that the signal of methylene proton are influenced by chelation, but the multiplet due to the aromatic protons is broader and shifts to lower field, indicating that the chelation perturbs the electron density distribution through the phenyl ring to some extent. The hydroxyl signal at 13.681 δ disappeared, thus indicating OH is involved in coordination [35]. ^{1}H NMR spectrum of ligand and its Zn(II) complex depicted in Fig.1a,1b.

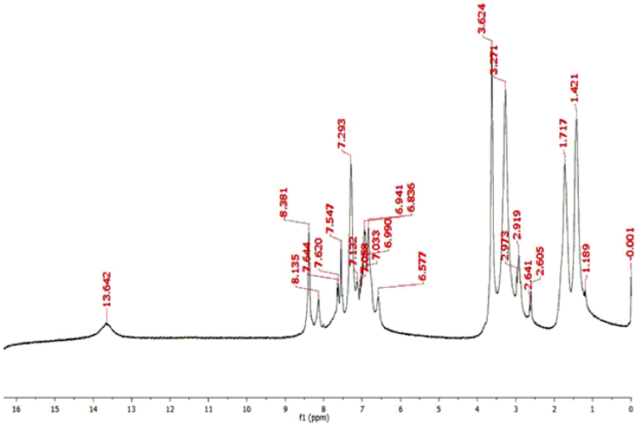


Figure 1a. 1H NMR spectrum of the ligand

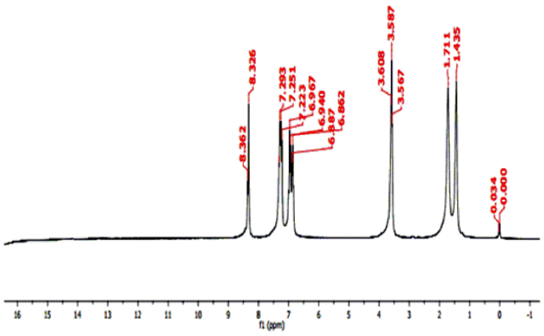


Figure 1b. 1H NMR spectrum of Zn(II) complex

4.3. IR spectra

IR spectral technique is the most suitable one to arrive information related to nature of bonding of the ligand to metal ion. The IR spectra of both free ligand and metal complexes were carried out in the range 4000-400 cm^{-1} and the values are presented in Table 3. In the infrared spectra of ligand, the formation of condensation product was noted by the absence of band at 1720 cm^{-1} ν(C=O). The spectrum of the ligand shows a peak at 3383 cm^{-1} which may be due to ν(OH) [36,37] stretching vibration. The phenyl group shows ν(CH) at 3047 cm^{-1} and ν(C=C) at 1558 cm^{-1}. The bands at 1680 and 1275 cm^{-1} are assigned to ν(C=N) azomethine [38] and phenolic ν(C-O) [37] respectively. The ligand as well as its coordinating complexes shows peaks at 2880 and 2940 cm^{-1} due to C-H stretching in CH_2 group of 1,6-diamino hexane molecule. The *ν*(C=N) (azomethine) in the spectra of all metal(II) complexes remains unchanged. It indicates azomethine nitrogen does not involve in coordination. The involvement of deprotonated phenolic moiety in complexes is confirmed by the shift of *ν*(C-O) stretching band observed at 1275 cm^{-1} in the free ligand to a lower frequency [39]. The shift of *ν*(C-O) band at 1275 cm^{-1} to a lower frequency suggests the weakening of *ν*(C-O) and formation of strong M-O bond. The broad band at 3418-3448 cm^{-1} complex is due to O-H stretching in the coordinated water [40]. In addition, the IR spectra of complexes show new band at 508-522 cm^{-1} assigned to *ν*(M-O) mode respectively [41,42].

Table 3. IR spectral data of ligand (DIBTHSA) and its metal(II)complex (cm^{-1}).

Compounds	**ν(C=O)**	**ν(C=N)**	**ν(C-O)**	**ν(H_2O)**	**ν(M-O)**
DIBTHSA (**L**)	1720	1680	1275	-	-
[Cu_2(DIBTHSA)$(H_2O)_4$](**1**)	-	1678	1254	3420	522
[Ni_2(DIBTHSA)$(H_2O)_4$](**2**)	-	1680	1248	3424	512
[Co_2(DIBTHSA)$(H_2O)_4$](**3**)	-	1680	1232	3418	508
[Zn_2(DIBTHSA)$(H_2O)_4$](**4**)	-	1681	1250	3448	516

4.4. Electrochemical studies

The free ligand does not show oxidation or reduction peak values. The Cyclic voltammogrm of copper(II) complex shows one reduction peak at -0.378 V in cathodic side and oxidation peak at 0.346 V in anodic side. The peak separation, ΔE_p = 0.724 V which is greater than required for reversible process (59mV) indicates that the redox couple is irreversible [43] and the ratio of cathodic to anodic peak current corresponding to a simple one electron process. The cyclic voltammogram of copper(II) complex is shown in Fig 2.

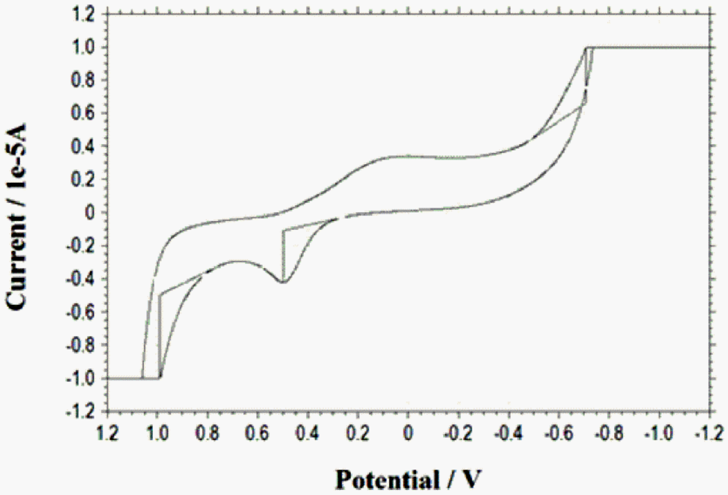


Figure 2. Cyclic voltammogram of $[Cu_2(DIBTHSA)(H_2O)_4]$

4.5. Fluorescence studies

The ligand (DIBTHSA) shows fluorescence excitation maximum at 375,447,488 nm and emission maximum at 492 nm in DMSO solvent. The Cu(II), Ni(II), and Co(II) complexes exhibit emission bands at 413-445 nm upon photo excitation gives bands around 371-438 nm. Significant differences in the positions of emission maximum of ligand and its complexes establish the coordination of metal ion to the ligand. Enhancement of fluorescence through complexation is much interesting as it opens up the opportunity for photochemical applications of these complexes. The emission is readily observed for complexes with the naked eyes under UV light, whereas the ligand exhibits quite weak fluorescence. The fluorescence spectra of ligand and its copper(II)complex are shown in fig 3a and 3b Table 4. The fluorescence quantum yields of the ligand and its metal(II) complexes were obtained using the following relation.

$$\Phi_S = A_S / A_R \ x \ (AbS)_R / (AbS)_S \ x \ \Phi_R$$

Table 4. Excitation and emission values of ligand and its metal(II) complexes

Compounds	Excitation Maximum (nm)	Emission Maximum (nm)	Quantum Yield

DIBTHSA (L)	375,447,488	492	1.205
$[Cu_2(DIBTHSA)(H_2O)_4](1)$	422	425	0.891
$[Ni_2(DIBTHSA)(H_2O)_4](2)$	438	445	0.931
$[Co_2(DIBTHSA)(H_2O)_4](3)$	371	413	0.250

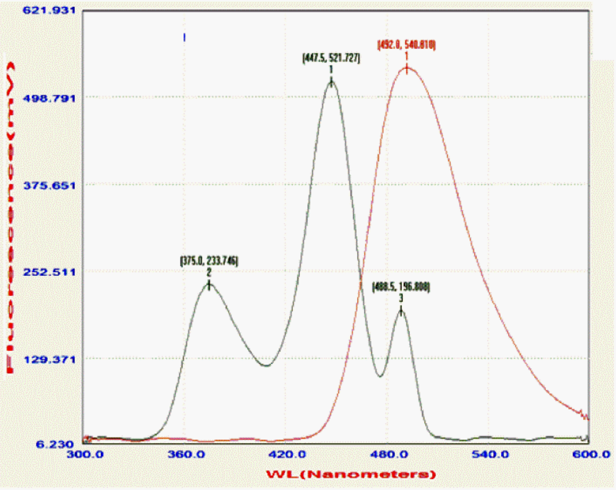


Figure 3a. Fluorescence spectrum of the ligand

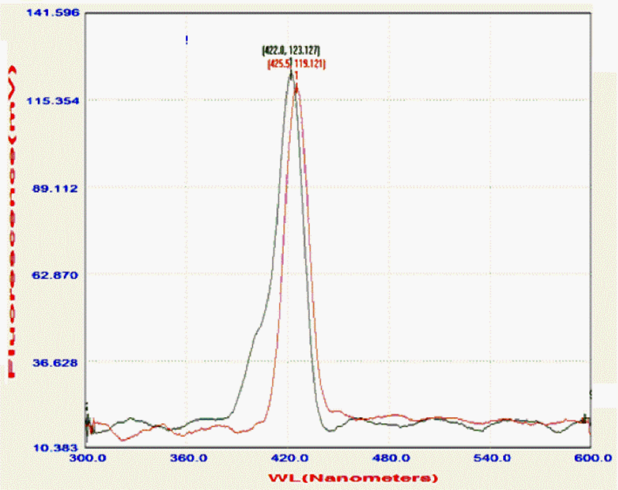


Figure 3b. Fluorescence spectrum of the Cu(II) complex

4.6. Thermo gravimetric studies

The thermoanalytical data of ligand and its Ni(II) complex were carried out in the temperature range 31 to 800°C. The thermal decomposition of ligand takes place in two steps and Ni(II) complexes takes place in three steps. The stages of decomposition, temperature range, decomposition products as well as the observed and calculated mass loss percentages of ligand and Ni(II) complex are good agreement with the theoretical formula as suggested from analytical data. The TG graphs of ligand and Ni(II) complex are given in figures 4(a) and 4(b). The data reveal the following findings: $[C_{40}H_{40}N_2O_4$ (L)] was thermally decomposed in two steps. The first decomposition step with estimated mass loss 17.70% (calculated mass loss 18.95%) within the temperature range of 28-175°C, may be attributed to the loss of 1,6-diaminohexane molecule. The second and third steps were found within the temperature range of 176-253°C with an estimated mass loss of 80.32%, (calculated mass loss 82.35%) which corresponds to the loss of disalicylalacetone moieties. In the case of $[Ni_2(DIBTHSA)(H_2O)_4]$ complex the first step at 28-114°C range by estimated mass loss of 8.16%, (calculated mass loss 9.05%) may be attributed to the loss of four water molecules. The second step within the temperature range 116-323°C mass loss of 13.10%, (calculated mass loss 14.57%) which corresponds to 1,6-diaminohexane molecule and third steps are within temperature range 324-411°C, with an estimated mass loss of 62.18%, (calculated, mass loss 63.31%) accounting for the expulsion of the disalicylalacetone molecules. The remaining mass loss 13.80%, (calculated mass loss 14.59%) is regarded as NiO residue within the temperature range 412-585°C.

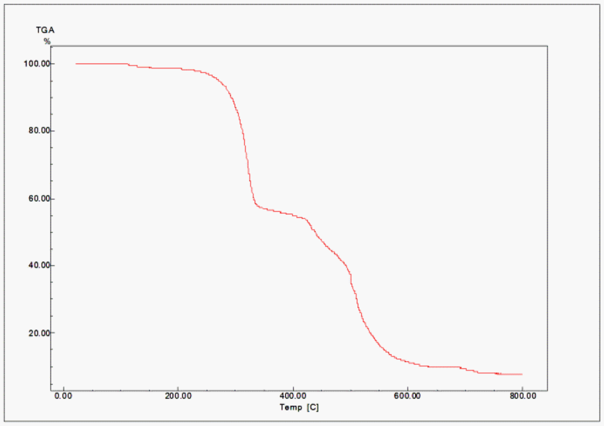


Figure 4a. TG graph of the ligand

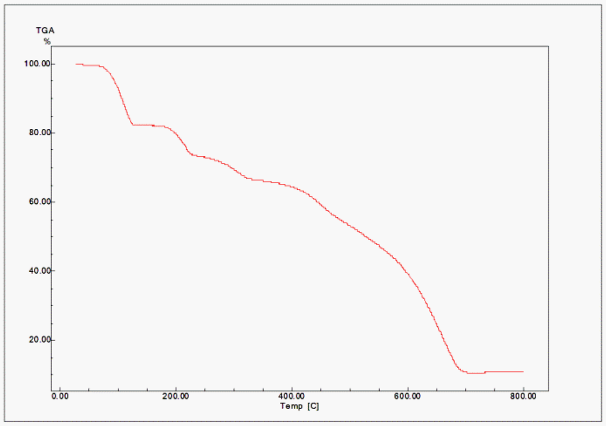


Figure 4b. TG graph of Ni(II) complex

4.7. Antimicrobial study

The ligand and its metal complexes were evaluated by well-diffusion method. The ligand and their metal complexes were tested for antimicrobial activity against the bacteria *Staphylococcus aureus* and *Bacillus subtilis* as gram-positive bacteria, *Salmonella typhi* and *Escherichia coli* as gram-negative bacteria and antifungal activity against the fungi *Candida albicans* and *Aspergillus niger*. *Amikacin* and *ketokonazole* were used as reference for antibacterial and antifungal studies Table 5 and Figure 5.

Antimicrobial activity studies were performed in triplicate and the average was taken as the final reading. All the tested compounds showed a remarkable biological activity against different types of bacteria and fungi species. *In vitro* antifungal activity data of the ligand and its metal(II) complexes against tested organisms displayed significant activity with wide range of variation. It is found that all the derived compounds exhibited higher activity against all the organisms but still lower than standard. *In vitro* antibacterial activity data reveals that all the synthesized compounds displayed moderate to significant activity in comparison to standards. Ligand is inactive towards *A.niger* but the metal complexes show higher activity against the same organism compared to standard. In general, the increased activity of metal(II) complexes over ligand can be explained on the basis of Overton's concept and the Chelation theory.

Table 5. Antimicrobial activity data of the ligand and their metal(II) complexes

	Zone of inhibition (mm)*					
Compounds	B.subtillis	S.aureus	E.coli	S. typhi	C.albicans	A.niger
DIBTHSA (**L**)	04	03	06	03	09	R
$[Cu_2(DIBTHSA)(H_2O)_4]$(**1**)	09	10	12	07	14	06
$[Ni_2(DIBTHSA)(H_2O)_4]$(**2**)	13	07	10	08	12	9
$[Co_2(DIBTHSA)(H_2O)_4]$(**3**)	09	09	13	09	13	8
$[Zn_2(DIBTHSA)(H_2O)_4]$(**4**)	11	10	15	05	10	07
Amikacin	18	16	20	14	-	-
Ketokonazole	-	-	-	-	20	12

*The test was done using 10^{-3} M concentration of synthesized compounds by well diffusion technique. The values are mean of three replications.

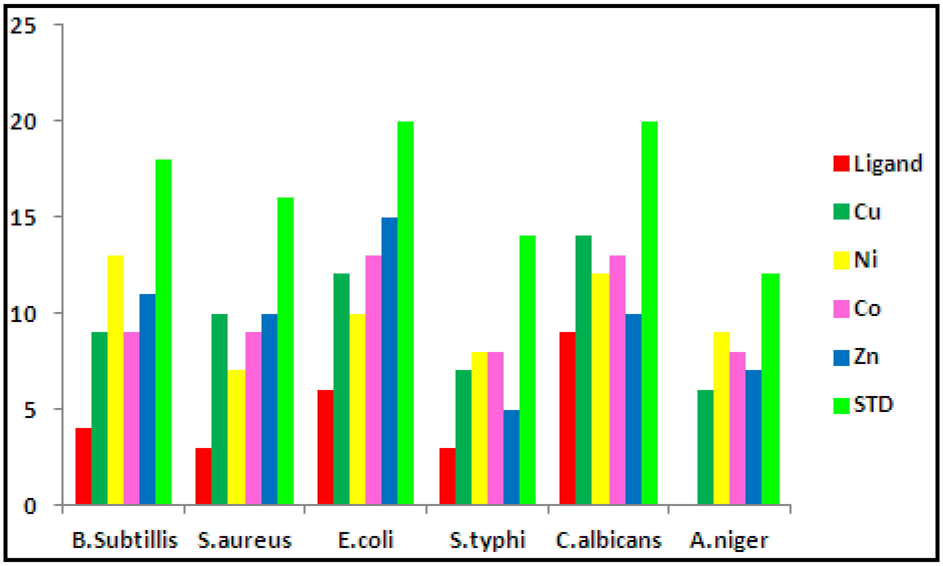


Figure 5: Biospectrum of the ligand and its metal(II) complexes (antibacterial and antifungal)

Conclusion

The metal complexes of Cu(II), Ni(II), Co(II) and Zn(II) complexes (DIBTHSA) were synthesized and characterized by spectral and analytical methods. The spectral and analytical data confirm the bonding of ligand to metal(II) ions and it confirms Cu(II) complex possess square planar geometry whereas Ni(II), Co(II) and Zn(II) complexes possess tetrahedral geometry. The ligand and its metal complexes are fluorescent in nature and potentially active towards all microbial strains. The antimicrobial studies of all the metal complexes show promising results. Such increased activity of the metal complex is of tremendous importance in pharmaceutical field.

References

1. P.O. Lumme and H. Knuuttila, *Polyhedron*, 14(12), 1995, 1553.
2. M. Wang, L.-F. Wang, Y.-Z. Li, Q.-X. Li, Z.-D. Xu, and D.-M. Qu, *Trans. Met.Chem.*, 26(3), 2001, 307.
3. M. A. Musa, M. O. F. Khan, A. Aspedon, and J. S. Cooperwood, *Letters in Drug Design and Discovery*, 7 (3), 2010, 165.
4. M. S. Nair, S. S. Kumari, and M. A. Neelakantan, *J. Coord. Chem.*, 60 (12), 2007,1291.
5. P. Tarasconi, S. Capacchi, G. Pelosi., *Bioorg. Med. Chem.*, 8(1), 2000,157.
6. J. Charo, J. A. Lindencrona, L.-M. Carlson, J. Hinkula, R. Kiessling, *J. Virology*, 78 (20), 2004, 1132.
7. J. G. Muller, S. J. Paikoff, S. E. Rokita, and C. J. Burrows, *J. Inorg. Biochem.*, 54 (3), 1994, 199.
8. M. Cabrera, M. Simoens, G. Falchi*l*., *Bioorg. Med. Chem*., 15, 2007, 3356
9. R.J. Anto, K. Sukumaran, G. Kuttan., *J. Cancer. Lett*,, 97, 1995, 33.
10. K.L. Lahtchev, D.I. Batovska, St.P. Parushev., *Eur. J. Med. Chem*., 43, 2008, 2220.
11. S. Ducki, R. Forrest, J.A. Hadfield., *Bioorg. Med. Chem. Lett*., 8, 1998, 1051.
12. H. Forejtnikova, K. Lunerova, R. Kubinova ., *J. Toxicology*, 208, 2005, 81.
13. J.R. Dimmock, D.W. Elias, M A. Beazely., *J. Curr. Med.Chem*., 6, 1999, 1125.
14. A. Araico, M.C. Terencio, M.J. Alcaraz., *J. Life Sci*., 80, 2007, 2108 .
15. M.L. Go, X. Wu and X.L. Liu, *J. Curr. Med. Chem.*, 12, 2005, 483.
16. L. Santos, L.A. Lima, V. Cechinel-Filho., *Bioorg. Med. Chem*., 16, 2008, 8526
17. D. Batovska, S. Parushev, B. Stamboliyska., *Eur. J. Med. Chem*., 44, 2009, 2211.
18. Ramesh, R.; Suganthy, P.K.; Natarajan, K., *Synth. React. Inorg. Met. Org. Chem.*, *26*, 1996, 47.
19. M.A. Neelakantan, S.S. Marriappan, J. Dharmaraja, T. Jeyakumar, K. Muthukumaran, *Spectrochim. Acta A*, *71*, 2008, 628.
20. E. Akila, M. Usharani and R. Rajavel, *Inter. J. Inorg. Bioinorg .Chem.*, 2 (2), 2012, 15.
21. S. S. Chavan and P. P. Hankare, *J. Indian Chem. Soc.*, 82 (6), 2005, 494.
22. Spange, S.; Vilsmeier, E.; Adolph, S.; Fährmann, A. *J. Phys. Org. Chem.c*, *12*, 1999, 547.
23. J. Anandakumaran, M. L. Sundararajan, T. Jeyakumar, Mohammad Nasir Uddin., *American Chem. Sci. J., 11(3), 2016, 1.*
24. R.J. Angellici, W.B. Saunders., *Syn.Tech.Inorg. Chem.*, 1969.
25. Sri Handayani, Indyah Sulistyo Arty., *J. Phy.Sci.,*19 (2), 2008, 61.
26. Juan Anacona, Yaricruz Pineda, Alina Bravo, Juan Camus., *Med.Chem (Los Angeles).*, 6, 2016, 467.
27. N. Ramana, L. Mitub, A. Sakthivela, M.S.S. Pandia., *J. Iran. Chem. Soc.*, 6, 2009, 738.

28. A. Halve, A. Goyal, *Orient. J. Chem.*, 12, 1996, 87.
29. C.J. Dhanaraja, M. S. Nair, *J. Coord. Chem.*, 62, 2009, 4018.
30. D.X. West, A.A. Nassar, F.A. El-Saied, M.I. Agad, *Trans. Met. Chem*., 23, 1998, 321.
31. D. Arish, M.S. Nair, *J. Coord. Chem.,* 63, 2010, 1619.
32. K. Nakamoto, *Infra-red and Raman Spectra of Inorganic and Coordination Compounds,* 3rd Edn., John Wiley, New York (1978).
33. A.B.P. Lever, *Inorganic Electronic Spectroscopy,* 2nd Edn., Elsevier, New York 1968.
34. P. Tharmaraj, D. Kodimunthiri, C.D. Sheela, C.S. Shanmuga priya. *J. Coord. Chem.,* 62, 2009, 2220.
35. H.A. Bayoumi., *Inter. J. inorg. Chem.*, 2013, 2013, 1.
36. R.M. Silverstein, G.C. Bassler, T.C. Morrill, *Spectrometric Identification of Organic Compounds,* 5th Edn., Wiley, New York, 1991.
37. R.N. Jadeja, J.R. Shah, E. Suresh, P. Paul, *Polyhedron,* 23, 2004, 2465.
38. J.U. Yuhong, R.S. Varma, *J. Org. Chem.,* 71**,** 2006, 135.
39. G. G. Mohamed, Z.M.Zaki, *Synth. React. Inorg. Met.Org.Chem.*, 34, 2004, 1497.
40. M.M. Omar, G.G. Mohammed, A.A. Ibrahim, *Spectrochim. Acta A,* 73, 2009, 358.
41. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds,*Ist Edn., Plenum Press, New York, 1971.
42. G.G. Mohamed, S.M. Khalil, *J. Coord. Chem*., 62, 2009, 645.
43. R. Kannappan, R. Mahalakshmy, T.M. Rajendran, P. Venkatesan, R. Sambasiva, *Proc.Indian Acad.(Chem. Soc.).,* 115, 2003, 1.