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Synthesis and Characterisation of Transition Metal Complexes with new Schiff base Ligand

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Abstract

A new hexadentate Schiff base ligand derived from condensation of 4-aminoantipyrine with isophthalaldehyde and thiosemicarbazide, and its metal complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility measurement and spectral (IR, Uv-Vis, ¹H NMR, Mass, EPR) studies. It has been originated that the Schiff base ligand with Co (II), Ni (II), Cu (II) and Zn (II) ions from mononuclear complexes on 1 : 1 (metal : ligand) stoichiometry. The conductivity data confirm the electrolytic nature of the complexes. The Co (II), Ni (II), and Zn (II) complexes show an octahedral configuration. Electronic absorption spectra of the Cu (II) complex suggest a square- planar geometry around the central metal ion. The IR spectral data suggest the involvement of sulphur and azomethine nitrogen in coordination to the central metal ion. The synthesized complexes have been subjected to antimicrobial study. The antimicrobial results indicated that the antimicrobial activity of the complexes show the enhanced activity in comparison to free ligand. These findings are giving suitable support for developing new antimicrobial agent and expand our scope for applications.

Key words: 4-aminoantipyrine, Schiff base ligand, isophthalaldehyde, Hexadentate, Thiosemicarbazide.

INTRODUCTION

In recent years, a number of research articles have been published on transition metal complexes derived from 4-amino-antipyrine derivatives with aza or aza-oxo donor atoms. There has been a significant exploitation towards the formulation of new materials containing poly functional units

(ligands) able to coordinate with metallic ions. Schiff base ligands are considered (ligands) able to coordinate with metallic ions. Schiff base ligands are considered “privileged ligands”, because they are easily prepared by the condensation between aromatic amines and aromatic aldehydes or ketones have a wide variety of applications

in many fields. Interest in multidentate acyclic, macro cyclic compounds¹⁻⁴ is continuously increasing because of their unique properties and use in the synthesis of poly nuclear metal complexes⁵⁻⁸. Metal complexes of the Schiff base ligands have a variety applications including clinical⁹, analytical¹⁰, industrial¹¹ and biological¹²⁻¹⁶, in addition to their important roles in catalysis and organic synthesis¹⁷. Some research groups found that the Schiff base metal complexes derived from 4-amino-antipyrine can specially cleave the DNA¹⁸⁻²⁰ and have a variety of application in analytical and biological areas^{21, 22}. The aim of the present study was to synthesize and characterise Co (II), Ni (II), Cu (II) and Zn (II) metal complexes with newly synthesized Schiff base ligand derived from 4-aminoantipyrine, isophthalaldehyde and thiosemicarbazide.

EXPERIMENTAL

Materials and measurements

All chemical are of highest purity and used as supplied. The electro thermal melting point model 9300 was used to measure the melting points of the ligand and its complexes. Elemental analyses of (C.H.N) were estimated by measurement of Micro analytical unit of 1108 C.H.N Elemental

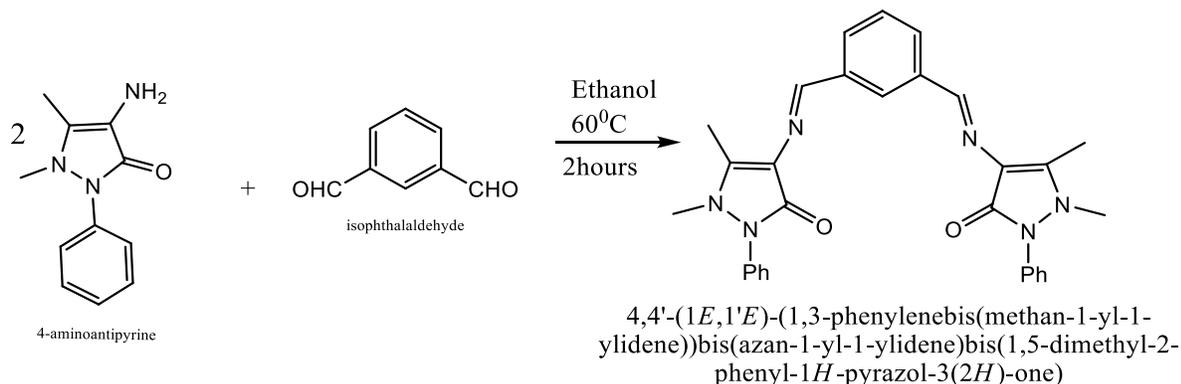
analyzer. FTIR Spectra were recorded using KBr discs in range 4000-400 cm^{-1} of FTIR Shimadzu Spectrophotometer Model 6300- Uv-Vis spectra were recorded in ethanol on Shimadzu spectrophotometer double beam Model 1700-Uv-Vis spectrophotometer. The ¹H NMR spectra were recorded in DMSO-*d*₆ on a Bruker Avance Dry 300 FT-NMR spectrometer, using TMS as the internal reference. Magnetic susceptibility measurement of the complexes was carried out by Gouy balance using copper sulphate pentahydrate as the calibrant²³. Molar conductance measurements were determined in (DMF) by using Alpha Digital conductivity meter Model 800. The physical characterization of the ligand and its metal chelate complexes was listed in Table 1.

Preparation of new Schiff base ligand

The method of preparation was as follows

Preparation of compound (I)

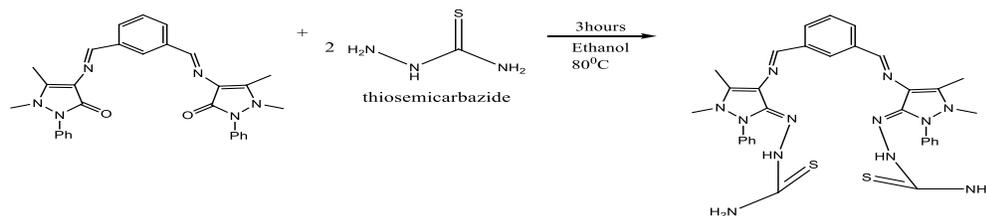
The compound (I) was prepared using the following method by condensation of 4-amino antipyrine (4.06 g, 10 mmol) dissolved in ethanol 30 mL was added to ethanolic solution of isophthalaldehyde (1.34 g, 5 mmol) (2: 1) mole ratio, and few drops of glacial acetic acid were added to reaction mixture with continuous stirring and refluxing at 60°C for (2 hr), the product precipitate was obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous CaCl₂. m.p (143-146°C) Scheme 1.

**Scheme 1****Preparation of Schiff base ligand**

The new Schiff base ligand (L) was prepared by condensation of compound (I) (5.05g, 10 mmol) was dissolved in 50 mL ethanol and refluxed with (1.82 g, 20 mol) of thiosemicarbazide for (15 hr) adding three drops from glacial acetic acid. A clear yellow coloured solution was obtained. The Schiff base ligand was isolated after the volume of mixture was reduced to half by evaporation and recrystallized by hot ethanol and dried over anhydrous CaCl_2 . m.p (118-120°C) Scheme 2.

Preparation of metal complexes

The metal complexes were prepared by the mixing of (30 mL) ethanolic solution of the metal salt (1 mmol) namely ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2) with (0.65g, 1 mmol) of the ligand dissolved in (30 mL) ethanolic solution (1: 1) (metal: ligand) ratio. The resulting mixture was refluxed for (3 hr) with constant stirring. A coloured product appeared on standing and cooling the above solution. The precipitated solid complexes were filtered, washed with (5 mL) of hot ethanol to remove any traces of the unreacted starting materials. Finally, the complexes were dried under vacuum.



Scheme 2: Preparation of the ligand (L)

Table**1: Physical data and analysis of ligand and its complexes**

Compound	Colour	M.P. (°C)	Yield %	Formula	Calc. (Found)%			
					C	H	N	M
L	Yellow	118-120	72	C ₃₂ H ₃₄ N ₁₂ S ₂	62.80 (62.72)	5.23 (5.30)	23.14 (23.26)	-----
[Co(L)]Cl ₂ .H ₂ O	Dark green	138-140	67	[Co(C ₃₂ H ₃₄ N ₁₂ S ₂) Cl ₂ .H ₂ O	52.21 (52.14)	4.58 (4.73)	19.23 (19.37)	6.67 (6.81)
[Ni(L)]Cl ₂ .H ₂ O	Brown	142-144	69	[Ni(C ₃₂ H ₃₄ N ₁₂ S ₂) Cl ₂ .H ₂ O	52.18 (52.44)	4.57 (4.82)	19.22 (19.42)	6.72 (6.48)
[Cu(L)]Cl ₂ .H ₂ O	Red	146-148	80	[Cu(C ₃₂ H ₃₄ N ₁₂ S ₂) Cl ₂ .H ₂ O	51.90 (51.87)	4.55 (4.73)	19.12 (19.33)	7.22 (7.31)
[Zn(L)]Cl ₂ .H ₂ O	Dark yellow	150-152	78	[Zn(C ₃₂ H ₃₄ N ₁₂ S ₂) Cl ₂ .H ₂ O	51.81 (51.67)	4.54 (4.36)	19.09 (19.21)	7.38 (7.19)

L = ligand.

RESULTS AND DISCUSSION

The ligand was yellow powder, but the prepared complexes of this ligand vary in colour depending of metal ion. The experimental results of the elemental analyses of the ligand and its metal complexes are good agreement with theoretical expectation. The elemental analyses of the complexes indicate that the (metal: ligand) ratios were (1: 1) in the $[ML]Cl_2$ where M = Co (II), Ni (II), Cu (II) and Zn (II). The complexes were found to be stable in air and moister at room temperature and insoluble in water, but its soluble in common organic solvents. The observed molar conductance value of the complexes in DMF at room temperature is consistent with electrolytic nature of the complexes. Physical and analytical data of the ligand and its complexes are listed in Table 1.

Microanalysis

The elemental analysis data the complexes as shown in Table 1 exhibit the formation 1: 1 [M: L] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base ligand was listed by TLC technique and C, H and N elemental analyses.

Infrared spectral studies of the ligand and its complexes

The data of the IR spectra of Schiff base ligand and its complexes were compared with the IR spectra of the free ligand in order to determine the involvement of coordination sites in chelation and to detect the changes that might have taken place. The obtained data are summarized in Table 2 with some assignments of the important characteristic bands.

Table 2: IR frequencies in (cm^{-1}) of the ligand and its metal complexes

Ligand/complexes	ν (OH)	ν	ν	ν	ν	ν
	water	(C=N)	(NH-C=S)	(C=S)	(M-N)	(M-S)
L=(DEAPH)	----	1645	1180	804	---	---
[Co(L)]Cl ₂ .H ₂ O	3400	1630	1161	765	534	503
[Ni(L)]Cl ₂ .H ₂ O	3405	1625	1164	761	530	495
[Cu(L)]Cl ₂ .H ₂ O	3408	1628	1178	805	537	498
[Zn(L)]Cl ₂ .H ₂ O	3400	1635	1160	760	530	502

In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamido -NH-C=S functional group. The ν (S-H) band at 2560 cm^{-1} is absent in the IR spectrum of ligand but ν (N-H) band at 3261 cm^{-1} and 3170 cm^{-1} are present, indicating that in the solid state, the ligand remains as the thione tautomer^{24,25}. The infrared spectrum of the ligand indicated the presence of primary amine ν (NH_2) group due to appearance of absorption of frequency²⁶ at 3371 cm^{-1} . A strong absorption band at 1645 cm^{-1} due to ν (C=N) present in the free ligand has shifted to lower side by $15\text{-}25\text{ cm}^{-1}$ in all four complexes, this indicates the involvement of (C=N) azomethine group in coordination²⁷. The appearance of broad band around 3400 cm^{-1} in the spectra of complexes may be due to ν (OH) water molecules^{28, 29}. The bands near ($1180, 804$) cm^{-1} in the free Schiff base ligand may be assigned to ν (NH-C=S) and ν (C=S). This has shifted to lower wave number in complexes indicates that sulphur is co-ordinating to the metal ion³⁰ excepted the copper complex appearance do not changes of these groups. The far IR spectra of the

metal chelates show some new bands at $534 \pm 10\text{ cm}^{-1}$ and $503 \pm 10\text{ cm}^{-1}$ have been assigned to ν (M-N) and ν (M-S) modes respectively³¹⁻³³. Representative example for there is given in Fig. 1.

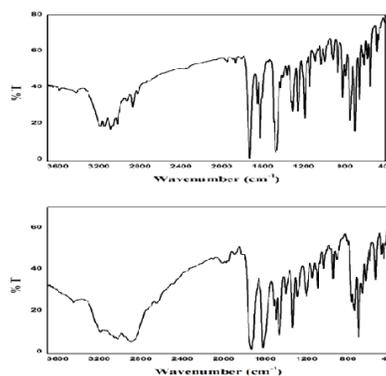


Fig1: spectra of the ligand (L) & [Co(L)]Cl₂.H₂O

Electronic spectral and magnetic moments

The spectral data and the magnetic moment of prepared complexes are listed in Table 3. Fig. 2 Shows the spectra of the ligand and $[\text{CuL}]\text{Cl}_2\cdot\text{H}_2\text{O}$. The electronic spectrum of the Schiff base ligand exhibits intense absorption at 242 nm (41322 cm^{-1}), 285 nm (35087 cm^{-1}) and 309 nm (32362 cm^{-1}), which are attributed to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$, respectively.

Table 3: Electronic spectra, conductivity and magnetic moment of complexes

Complexes	Abs. nm	Transition	Conductivity	μ_{eff}
	(cm^{-1})		$\text{S.mol}^{-1} \cdot \text{cm}^2$	(B.M)
(L)	242 (41322)	$\pi \rightarrow \pi^*$	----	---
	285 (35087)			
	309 (32362)	$n \rightarrow \pi^*$		
		653 (15313)		
[Co(L)]Cl ₂ .H ₂ O	610 (16393)	${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$	145	5.47
[Ni(L)]Cl ₂ .H ₂ O	570 (17543)	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$	138	3.21
	670 (14925)	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$		
	468 (21367)	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$		
	541 (18484)	${}^2B_{1g} \rightarrow {}^2A_{1g}$		
[Cu(L)]Cl ₂ .H ₂ O	350 (28571)	INCT	156	1.75
	301 (3322)	INCT		
[Zn(L)]Cl ₂ .H ₂ O	----	INCT	148	Dia

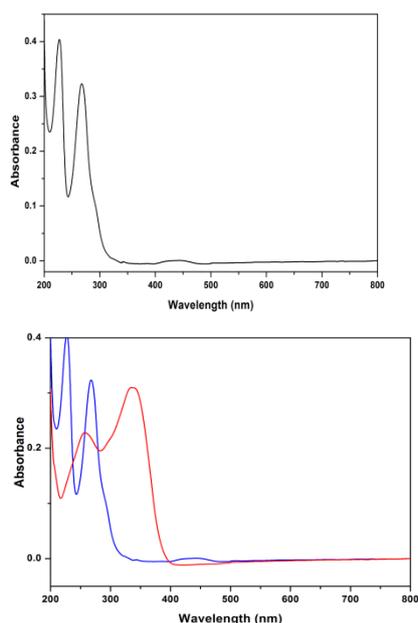


Fig. 2: Electronic spectrum of the ligand (L), [Cu (L)] Cl₂.H₂O

Cobalt complex (II)

The electronic spectrum of Co (II) complex showed three broad peaks at 653 nm (15313 cm⁻¹), 610 nm (16393 cm⁻¹) and 570 nm (17543 cm⁻¹) assigned to $^4T_{1g} \rightarrow ^4T_{2g}$ (F), $^4T_{1g} \rightarrow ^4A_{2g}$ (F) and $^4T_{1g} \rightarrow ^4T_{1g}$ (P), respectively³⁴. The magnetic moment value of the Co (II) (d⁷) complex is (5.47 B.M)³⁵. The spectrum resembles those reported for octahedral complex³⁶.

Nickel (II) complex (II)

The magnetic moment for the complex of Ni (II) (d⁸) was found to be (3.21 B.M), which with the range of octahedral Ni (II) complex³⁷. The electronic spectrum of this complex show

band at 670 nm (14925 cm⁻¹) and 468 nm (21367 cm⁻¹) which can be assigned to $^3A_{2g} \rightarrow ^3T_{1g}$ (F) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P), respectively³⁸.

Copper (II) complex (II)

The magnetic moment value of Cu (II) (d⁹) complex (1.75 B.M), this value indicate within the expected for one electron, and d-d spectrum of this complex show band at 541nm (18484 cm⁻¹), 350 nm (28571 cm⁻¹) and 301 nm (3322 cm⁻¹) which may assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ transition and two intra-ligand charge transfer bands, these data suggest square-planar geometry around Cu (II)^{39, 40}.

Zinc (II) complex

Metal complex is diamagnetic consistent with the (d¹⁰) configuration and the electronic spectra of these complex exhibit high intense charge transfer transition which are assigned to (INCT).

¹H NMR spectrum studies

The newly synthesized ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of ¹H NMR chemical shift. ¹H NMR spectra were determined in solution of DMSO with tetra methyl silane as an internal reference. The ¹H NMR spectrum of the ligand displays a triplet at ca. δ

2.116-2.444 ppm (s, 6H, 2H₃C-C), due to the six protons of two methyl groups attached to the CH₂ groups and two multiplet at ca. δ 5.7–5.9 ppm (m, 12H, 6CH₂) due to the protons of six methylene groups, multiples signals at δ (7.2-7.8) ppm which were assigned to aromatic protons of phenyl ring of isophthalaldehyde and antipyrine respectively. Multiple signals at δ (8.3-8.5) ppm which belong to amine (-NH₂) groups⁴¹. Singlet at δ (3.3) ppm belongs to the proton of methyl groups attached to the pyrazoline rings as shown in Fig. 3.

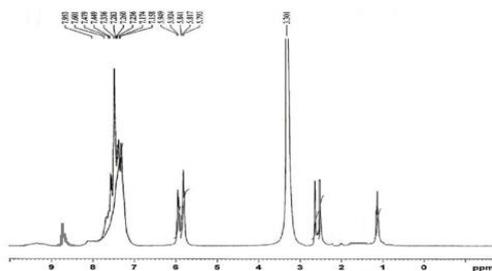


Figure:3 ¹H-NMR spectrum of the ligand **L**.

Mass spectra

Mass spectra provide a vital clue for elucidating the structure of compounds. The ESI-mass spectra of synthesized Schiff base ligand (L) and its copper complex was recorded at room temperature which further confirmed their

proposed stoichiometry. The obtained molecular ion peaks confirmed the suggested formulae for the synthesized compounds. The spectrum of L showed a molecular ion peak [M+1]⁺ at m/z = 650 equivalent to its molecular weight, corresponding to its molecular formula, C₃₂H₃₄N₁₂S₂. In addition to this, the fragmentation peaks observed at m/z 365, 289, 214 and 77 were due to the fragment of [C₁₉H₂₀N₆S]⁺, [C₁₃H₁₆N₆S]⁺, [C₁₂H₁₄N₄]⁺, and [C₆H₅]⁺ respectively. The results confirmed the formation of Schiff base **L** supporting the IR and NMR results and its Cu(II) complex showed a molecular ion [M⁺] at m/z 714, equivalent to its molecular weight having the formula [C₃₂H₃₄N₁₂S₂Cu]⁺. Thus, the mass spectral data results along with the elemental analyses data agree with the formation of [ML]Cl₂ type complexes of 1:2 stoichiometry⁴².

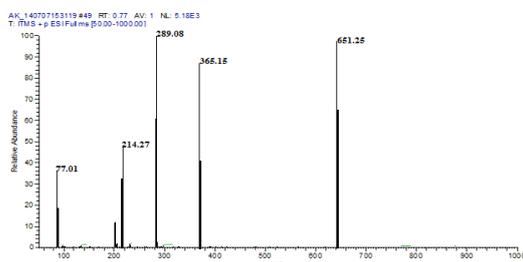


Figure 4. Mass spectrum of the ligand L.

EPR Spectra

The X-band EPR spectrum of the copper(II) complex was recorded in DMSO at liquid nitrogen temperature (LNT) as exposed in (Fig.5). It showed four lines ⁴³ with nuclear hyperfine spin 3/2 due to hyperfine splitting. The spin Hamiltonian parameters of complex were calculated. The observed g_{\parallel} values were less than 2.3 indicating considerable covalent character in the M-L bonds. The trend $A_{\parallel}(158) > A_{\perp}(88)$; $g_{\parallel}(2.28 > g_{\perp}(2.08) > 2.0027$ indicated that the unpaired electron was located in the $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state) to envisage a square planar geometry around Cu(II) ions. The axial symmetry parameter G is defined as

$$G = \frac{g_{\parallel} - 2.0023}{g_{\perp} - 2.0023} \dots\dots\dots (2)$$

According to Hathaway ⁴⁴, if the G value > 4 , the exchange interaction is

negligible, while a value is < 4 gives an indication for considerable exchange interaction in the complex. The axial symmetry parameter (G) of the reported Cu(II) complex was > 4 (4.8) suggesting that the local tetragonal axes were aligned parallel or slightly misaligned and the unpaired electron is present in the $d_{x^2-y^2}$ orbital. This result also indicates that the exchange coupling effects are not operative in the present complex.

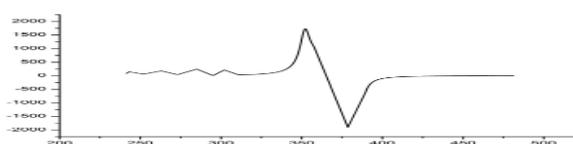


Figure: 5 EPR spectrum of the [Cu (L)] Cl₂.H₂O complex.

On the basis of above discussion, the structures of complexes are given in Figure

Antimicrobial activities

The data of the antifungal and antibacterial activities of ligand and complexes are given in Tables 4 and 5. The data reveal that the complexes have higher activities than the free ligand (Figure 7). This enhancement of the activity of ligand on complexation can be explained by Overtone's Concept and Chelation Theory ⁴⁵. The theory states that

chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π -electron delocalization over the whole ring. This results with increasing of the lipophilic character of the complex and favour the permeation of the complex through the lipid layer of cell membrane. The complex blocks the metal binding sites in the enzymes of microorganisms.

Consequently, the complex disturbs the metabolism pathways in cell and as a result microorganisms die.

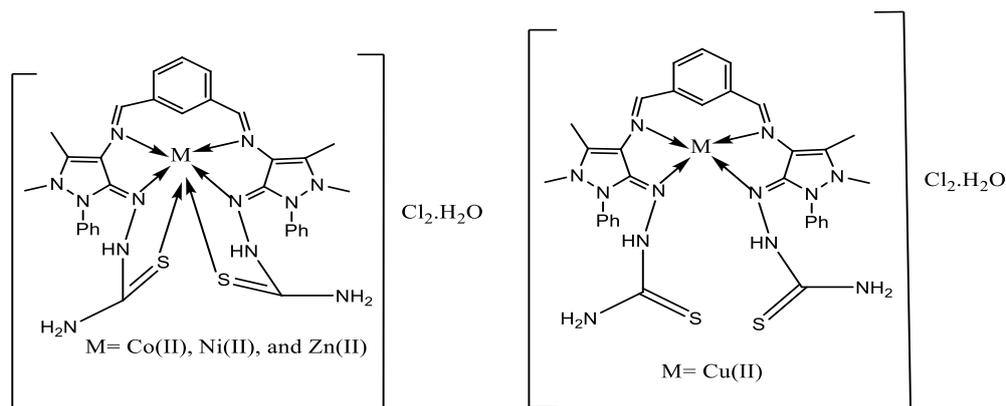


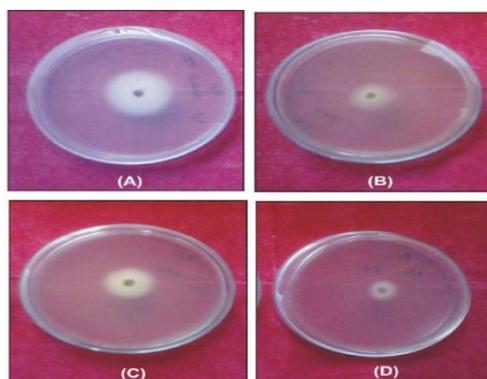
Fig. 6: The proposed structural formula of the metal chelate complexes

Table 4. Antifungal activity data of the compounds.

Compound		Fungal inhibition (%) (conc. in $\mu\text{g}\cdot\text{mL}^{-1}$)								
		<i>A. brassicae</i>			<i>A. niger</i>			<i>F. oxysporum</i>		
	100	200	300	100	200	300	100	200	300	
Ligand (L)	40	52	62	35	50	58	42	60	66	
[Co(L)]Cl ₂ .H ₂ O	50	60	68	48	61	65	50	68	76	
[Ni (L)]Cl ₂ .H ₂ O	58	68	75	62	75	82	58	75	86	
[Cu(L)]Cl ₂ .H ₂ O	58	70	81	65	71	85	59	74	88	
Standard (Captan)	70	80	100	75	90	100	65	75	100	

Table 5. Antibacterial activity data of compounds.

Compound	Bacterial inhibition zone (mm) (conc. in $\mu\text{g}\cdot\text{mL}^{-1}$)					
	<i>Xanthomonas compestris</i>			<i>Pseudomonas aeruginosa</i>		
	250	500	1000	250	500	1000
Ligand (L)	10	12	15	8	12	14
[Co(L)]Cl ₂ .H ₂ O	14	16	20	14	18	20
[Ni(L)]Cl ₂ .H ₂ O	15	21	24	16	20	25
[Cu(L)]Cl ₂ .H ₂ O	16	22	25	18	23	27

**Figure 7.** Antifungal activity against *Fusarium oxysporum* of: (A) ligand; (B) [Ni(L)]Cl₂.H₂O; (C) [Co(L)]Cl₂.H₂O and (D) [Cu(L)]Cl₂.H₂O.**Conclusions**

A novel 4-aminophenazone analogue ligand and its four transition metal complexes had been synthesized and their *in vitro* antibacterial and antifungal potential was evaluated and characterized on the basis of elemental analysis, IR, UV-Vis, Mass, ¹H-NMR spectral studies, the ligand coordinates to Co(II), Ni(II) and Zn(II) metal ions in a hexadentate manner and Cu(II) metal ion in a tetradentate manner. The screening of biological activities of ligand and its complexes against the fungi *Alternaria brassicae*, *Aspergillus niger* and *Fusarium*

oxysporum and the pathogenic bacteria *Xanthomonas compestris* and *Pseudomonas aeruginosa* indicates that the complexes show enhanced activity in comparison to free ligand.

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REFERENCES

1. H. Keyaur, H. A. Rudbari, R. Azadbakht et al., *J. Chem. Res.*, 361-365 (2009).
2. S. Gopalakrishnan and J. Joseph, *The Korean Society of Mycology*, **37(2)**, 141-146 (2009).
3. R. Amit, Kr. Ashish and R. Sirohi, *VSRD Technical of Non-Technical J.*, **2(8)**, 352-357 (2011).
4. S. Sarkar and K. L. Dey, *Synthesis, Spectrochimica Acta, Part A*, **62**, 383-393 (2005).
5. N. Mahalakshmi and R. Rajavel, *Asian J. Biochem. Pharmaceut. Res.*, **2(1)**, 525-543 (2011).
6. S. Annapoorani and C. N. Krishnan, *Int. J. Chem. Tech. Res.*, **(3)4**, 1962-1968 (2011).
7. F. Ciolan, L. Patron et al., *Rev. Chim. (Bucharest)*, **1(63)**, 34-39 (2012).
8. E. Abd M. Abd Orabi, *J. Chem. Soc. Pak.*, **32(6)**, 704-710 (2010).
9. H. Sharghi and M. A. Nasser, *Bull. Chem. Soc. (Jpn)*, **76**, 137 (2003).
10. T. Mahmud, R. Rehman, A. Abbas et al., *J. Chem. Soc. Pak*, **34(1)**, 67-71 (2012).
11. N. Raman, Y. P. Raja and A. Kulandaismy, *Proc. Ind. Acad. Sci. (Chem. Sc.)*, 183 (2001).
12. M. Usharani, E. Alila and R. Rajavel, *J. Chem. Pharmaceut. Res.*, **4(1)**, 726-731 (2012).
13. A. Nagajothi, A. Kiruthika, S. Chitra and K. Parameswari, *Int. J. Res. Pharmaceut. Biomed. Sci.*, **3(4)**, 1768-1778 (2012).
14. N. Padma Priya, *Int. J. Appl. Biol. Pharmaceut. Technol.*, **2**, 538-547 (2011).
15. K. J. B. Victory, K. U. Sherin and M. K. M. Nair, *Res. J. Pharmaceut. Biolog. Chem. Sci.*, **2**, 324-328 (2010).
16. A. Al-Amiery, A. A. H. Kadhum and A. B. Mohamad, *Bioinorganic Chemistry and Applications*, 1-6 (2012).
17. B. Anupama and C. G. Kumari, *Res. J. Pharmaceut. Biolog. Chem.*, **2**, 140-159 (2011).
18. N. Raman, S. S. A. Fathima and J. D. Raja, *J. Serb. Chem. Soc.*, **73(11)**, 1063-1071 (2008).
19. N. Raman A. Sakthivel, J. Dh. Raja and K. R. Karam, *YPHAJI HEOPTA*, **53**, 254-260 (2008).

20. E. E. Elemike, A. P. Oviawe and I. E. Dtuokere, *Res. J. Chem. Sci.*, **1(8)**, 6-11 (2011).
21. M. S. Suresh and V. Prakash, *Int. J. Phys. Sci.*, **5(14)**, 2203-2211 (2010).
22. A. Earnshaw, *The Introduction to Magneto Chemistry,* Academic Press, London (1980).
23. S. Chandra, S. Raizada, M. Tyagi et al., *Bioinorganic Chemistry and Applications*, 1-7 (2007).
24. A. H. Al-Amiery, K. Al-Majedy, H. A. Razzaq, J. Al-Nahrain University, **14(1)**, 7-14 (2011).
25. B. P. Singh, *Int. Pharmaceut. Res. Development*, **4(3)**, 51-57 (2012).
26. N. Raman, R. Jeyamurugan, B. Rajkapoor et al., *J. Iran Chem. Soc.*, **7(4)**, 917-933 (2010).
27. A. P. Mishra, R. Mishra, Rajendra Jain et al., *The Korean Society of Mycology*, **40(1)**, 20-26 (2012).
28. A. P. Mishra and D. K. Mishra, *Int. J. Pharma. Bio. Sci.*, **2**, B-430-439 (2011).
29. M. H. Moustafa, A. A. Elnaeem and O. A. Abbas, *Ass. Univ. Bull. Environ. Res.*, **14(2)**, 27-40 (2011).
30. K. Krishnankutty, M. B. Ummathur and D. K. Babu, *J. Serb. Chem. Soc.*, **75(5)**, 639-648 (2010).
31. K. Krishnankutty, P. Sayudevi and M. B. Ummathur, *J. Serb. Chem. Soc.*, **72(11)**, 1075-1084 (2007).
32. A. M. Ali, M. A. Hadi and M. S. Mohamad, *National J. Chem.*, **37**, 128-134 (2010).
33. B. N. Figgis and J. Lewis, *Modern Coordination Chemistr.*, Interscience, New York (1960).
34. D. Nicholas, *Pergamon Texts in Inorganic Chemistr.*, Pergamon Press, Oxford 1st Ed. (1973).
35. D. C. Meher, F. M. Monhanty et al., *Indian J. Chem.*, **26(A)**, 698 (1987).
36. A. P. Mishra, A. Tiwari and K. J. Rajendra, *Advanced Materials Letters*, **3(3)**, 213-219 (2012).
37. A. A. S. Al-Hamdani and S. A. Shaker, *Oriental J. Chem.*, **27(3)**, 835-845 (2011).
38. A. S. Munde, A. N. Jagdale, S. M. Jadhav et al., *J. Serb. Chem. Soc.*, **75(3)**, 349-359 (2010).
39. N. Raman, J. Joseph and A. S. K. Velan, *Mycobiology*, **34(4)**, 214-218 (2006).

40. S. Chandra, R. K. Qanugo and S. K. Sharma, *Spectrochimica Acta Part A*, **94**, 312-317 (2012).
41. Silverstein, R.M.; Webster, F.X. *Spectrometric Identification of Organic Compounds*; Wiley: New Delhi, India, 2007
42. Hamming, M.; Foster, N. *Interpretation of Mass Spectra of Organic Compounds*; Academic Press:New York, USA, **1972**.
43. A.Boettcher, H.Elias, E.G. Jaeger, H. Langfelderova, M.Mazur, L. Mueller, H.Paulus, P. Pelikan, M. Rudolph, M. Valko *Inorg. Chem.*, 32 (19), (1993), 4131–4138.
44. B. J. Hathaway, A new look at the stereochemistry and electronic properties of complexes of the copper (II) ion, *Struct. Bond.* 57 (1984), 55-118.
45. Belaid, S.; Landreau, A.; Djebbar, S.; Benali-Baitich, O.; Bouet, G.; Bouchara, J.-P. *J.Inorg. Biochem.* **2008**, 102, 63-69.