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Der Pharma Chemica, 2015, 7(10):556-562
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis, characterization and antioxidant activity of Schiff base ligand and its metal complexes containing thiazole moiety

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ABSTRACT

The main objective of the present study is to synthesize a new Schiff base ligand N-(4-phenylthiazol-2-yl)-2-(thiophen-2-ylmethylene)hydrazinecarboxamide and its Cu(II), Co(II), Ni(II) and Zn(II) complexes and study their antioxidant activity. Newly prepared compounds are characterized by elemental analysis, FT-IR, ^{1}H NMR, mass, UV-visible and ESR spectral techniques. The elemental analysis data and spectral study indicate octahedral geometry for Cu(II), Co(II) and Ni(II) complexes and tetrahedral geometry for Zn(II) complex. All the newly prepared compounds were tested for antioxidant activity, the Schiff base ligand ***(L)****, Cu(II) and Co(II) complexes showed good activity.*

Keywords: Schiff base, thiazole, thiophene-2-carboxaldehyde, antioxidant, ESR

INTRODUCTION

The chemistry of coordination compounds with heterocyclic Schiff base ligands containing oxygen, nitrogen and sulfur as donor atoms has attracted the attention of chemist in recent years [1-3]. The Schiff base ligands containing these hetero atoms coordinate to the metal atom in different ways [4]. The chelating properties of Schiff base ligands display manifold applications in medicine, industry and agriculture [5]. The compounds containing thiazole moiety have a wide ranging biological activity, such as antiviral, antitumor, antimicrobial, anti-tuberculosis and antifungal activities [6-9]. Now a day, interest is focused on the synthesis of macrocyclic ligands and their metal complexes complexes with potential applications, such as cancer diagnosis and treatment of tumor. The biological activities may be related to the redox properties of the metal complexes. The studies on the electrochemical properties of some copper (II) complexes indicate that the complexes having lower reduction potential enhance the biological activity [10]. Metal ions present in complexes were found to accelerate drug action and the efficiency of organic therapeutic agents [11]. The pharmacological efficiencies of metal complexes depend on the nature of the metal ions and the ligands [12, 13].

Thiazoles are an important class of heterocycles and the compounds containing thiazole group have attracted significant attention to the researcher because of their interesting physico-chemical properties and prominent biological activities [14-16]. These classes of compounds are present in many natural and synthetic products with a broad range of biological activities, such as anticancer, antiviral, antimicrobial antioxidant and anticonvulsant activities. Thiazole nucleus also finds application in other fields, such as polymer chemistry, study of liquid crystals and preparation fluorescent dyes. Therefore, it has been found interesting to study the metal complexes containing the thiazole moiety.

Thus, the available literature exhilarated us to prepare the metal (II) complexes with new Schiff base ligand **(L)** derived from the reaction of *N*-(4-phenylthiazol-2-yl)hydrazinecarboxamide with thiophene-2-carboxaldehydeand its Cu(II), Co(II), Ni(II) and Zn(II) complexes. The structures of the complexes are elucidated by various spectral techniques. Also the antioxidant activity Schiff base ligand **(L)** and its metal complexes have been studied

MATERIALS AND METHODS

Materials

All solvents and chemicals were of commercial reagent grade and used as they are received. The precursor *N*-(4-phenylthiazol-2-yl)hydrazinecarboxamidewas prepared as per literature methods [17].

Analysis and physical measurement

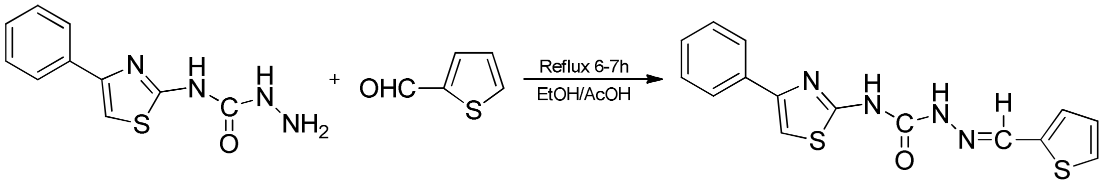
Elemental analysis was performed on a Vario EL III CHNS analyzer. IR spectra were recorded as KBr pellets on a Perkin Elmer-Spectrum RX-I FTIR spectrophotometer. ^{1}H NMR spectra was recorded on the FT-NMR spectrometer model BrukerAvance II, 400 MHz using d_6-DMSO as solvent. ESI-MS was recorded on a mass spectrometer equipped with electrospray ionization (ESI) source having mass range of 4000 amu in quadruple and 20,000 amu in Tof. The electronic spectra were recorded at 25 °C on a ELICO SL-164 double beam UV visible spectrophotometer in the range 200-1100 nm using ca. 10^{-3} M solution in DMF. At room temperature ESR spectrum of the Cu(II) complex in the polycrystalline state was recorded on a BRUKER Bio Spin Gmbh spectrometer at a microwave frequency 8.75-9.65 GHz at room temperature. Molar conductivity measurement was recorded on ELICO (CM-180) conductivity bridge in dry DMF ca. 10^{-3}M solution using a dip-type conductivity cell fitted with a platinum electrode and magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of Schiff base ligand (L)

An equimolar mixture of *N*-(4-phenylthiazol-2-yl)hydrazinecarboxamideand thiophene-2-carboxaldehyde in ethanol (25 mL) was refluxed with a catalytic amount of glacial acetic acid (1-2 drops) for about 6-7 h on a water bath. The pale yellow colored product **(L)** which separated in hot was filtered off, washed with hot ethanol, dried and crystallized from 1, 4-dioxane. The pathway for the synthesis of Schiff base ligand **(L)** is presented in **Scheme 1.**

General procedure for the synthesis of Cu(II), Co(II), Ni(II) and Zn(II) complexes

To the hot solution Schiff base ligand N-(4-phenylthiazol-2-yl)-2-(thiophen-2-ylmethylene)hydrazinecarboxamide (0.001 mol) in ethanol (20 mL) was added a hot ethanolic solution (15 mL) of respective metal chlorides (0.001 mol). The reaction mixture was then refluxed on a water bath for about 5-6 h. The pH of the reaction mixture was adjusted ca.7.0-7.5 by adding an alcoholic solution of sodium acetate (0.5 g) and refluxing continued for about an hour more. The reaction mixture was cooled to room temperature and poured into distilled water. The colored solids separated were collected by filtration, washed with distilled water, then with hot ethanol and finally dried in a vacuum over anhydrous calcium chloride in a desiccator.



Scheme 1: Synthesis of Schiff base ligand (L)

Antioxidant assay (free radical scavenging activity)

The free radical scavenging activity of the Schiff base ligand **(L)** and its Cu(II), Co(II), Ni(II) and Zn(II) test samples was determined using 2,2-diphenyl-1-picrylhydrazyl (DPPH) method[18]. Different concentrations of test compounds (12.5, 25, 50 and 100 μg) and standard butylatedhydroxyanisole (BHA) were taken in different test tubes and the volume of each test tube was adjusted to 100 μL by adding distilled DMF. To the tubes containing sample solutions in DMF, 5 mL methanolic solution of DPPH (0.1 mM) was added to these tubes. The tubes were allowed to stand for 30 min. The control experiment was carried out as above without the test samples. The absorbance of test solutions was measured at 517 nm. The reduction of DPPH was calculated relative to the measured absorbance of the control. Radical Scavenging activity was calculated using the following formula:

$$\% \text{ Scavenging of DPPH} = [(\text{Control OD} - \text{Sample OD}) / \text{Control OD}] \times 100$$

RESULTS AND DISCUSSION

Chemistry

The newly prepared metal complexes are colored solids, stable at room temperature and possess high melting point (> 290 °C). The metal complexes are insoluble in water and common organic solvents, but completely soluble in DMF and DMSO. Elemental analysis and analytical data agree well with the proposed composition of Schiff base ligand **(L)** and its metal complexes **(Table 1)**. These data of metal complexes suggest that the metal to ligand ratio of the complexes is 1:2 stoichiometry of the type $[M(L)_2]$ for Cu(II), Co(II) and Ni(II) complexes and [(M)(L)(Cl)] for Zn(II) complex. The measured molar conductance values of the metal complexes were too low to account for any dissociation of the complexes in DMF (18-30 ohm^{-1} cm^{2} $mole^{-1}$) indicating their non-electrolytic behavior [19].

Table 1: Physical and analytical data of Schiff base ligand (L)and its metal complexes

Compounds	M.W.	M.P. (°C)	Color (Yield)	Elemental Analysis, found (Calc.) [%]					λ_m	μ_{eff} (BM)
				C	H	N	M	Cl		
$C_{15}H_{12}N_4OS_2$**(L)**	328	246	Yellow (77%)	54.87 (54.91)	3.65 (3.62)	17.07 (17.11)	--	--	--	--
$[Cu(C_{30}H_{24}N_8O_2S_4]$ $[Cu(L)_2]$	719.54	296	Green (61%)	50.03 (50.06)	3.33 (3.37)	15.56 (15.50)	8.83 (8.89)	--	30	1.89
$[Co(C_{30}H_{24}N_8O_2S_4]$ $[Co(L)_2]$	714.93	294	Brown (52%)	50.35 (50.38)	3.35 (3.37)	15.66 (15.60)	8.24 (8.29)	--	19	4.60
$[Ni(C_{30}H_{24}N_8O_2S_4]$ $[Cu(L)_2]$	714.69	295	Brown (53%)	50.37 (50.33)	3.35 (3.37)	15.69 (15.62)	8.21 (8.24)	--	18	2.88
$[Zn(C_{15}H_{12}N_4OS_2)(Cl)]$ $[Zn(L)(Cl)]$	428.40	294	Orange (76%)	42.01 (42.05)	2.80 (2.77)	13.01 (13.05)	15.26 (15.34)	8.16 (8.21)	29	Dia.

IR spectral studies

The characteristic frequencies of the expected functional groups are depicted in **Table 2**. In the IR spectrum of the Schiff base ligand **(L)**, absorption due to amide NH and NH attached to the thiazole moiety have displayed bands at 3344 cm^{-1} and 3260 cm^{-1} respectively. A high intensity bands are observed at 1688 cm^{-1}, 1587 $cm^{-1}$and 854 cm^{-1} are due to carbonyl function ν(C=O), azomethine function ν(C=N) and C-S-C functions respectively.

In the IR spectra of the metal complexes, medium intensity weak bands at 3318 cm^{-1}- 3355 cm^{-1} and 3200 cm^{-1}- 3266 cm^{-1} were due to amide NH and NH attached to thiazole moiety respectively, which appeared almost at the same region as in the case of ligand, thus confirming their non-involvement in coordination with the metal ions. The shift of amide carbonyl ν(C=O) to lower frequency side about 27-73 cm^{-1} which appeared in the region 1661 cm^{-1} - 1615 cm^{-1} in all the metal complexes confirms the coordination of oxygen atom of amide ν (C=O) with the metal ions as such without undergoing enolization [20, 21]. The absorption frequency of azomethine ν(C=N) function shifted to the lower frequency side about 17 cm^{-1} - 40 cm^{-1} and appeared in the region 1570 cm^{-1} - 1547 cm^{-1} suggesting the involvement of nitrogen atom of azomethine function in complexation with the metal ions [22]. The sharp band at 854 cm^{-1} of thiophene moiety in the Schiff base ligand is shifted to the higher frequency side about 5 cm^{-1}- 36 cm^{-1} and appeared in the region 859 cm^{-1}- 890 cm^{-1}.

The complexation of metal ions with ligand was further confirmed by the appearance of new weak intensity, non-ligand bands in the region 560 cm^{-1} - 580 cm^{-1}, 444 cm^{-1}- 496 $cm^{-1}$and 435 cm^{-1} - 467 cm^{-1}in the spectra of all the complexes which are assigned to frequencies of ν(M-O), ν(M-N) and ν(M-S) stretching vibrations respectively. The appearance of new band at 357 cm^{-1} in Zn(II) complex is due to ν(M-Cl) band.

Table 2: IR spectral data of Schiff base ligand (L) and its metal complexes

Compounds	Amide $\nu_{(NH)}$	Thiazole $\nu_{(NH)}$	$\nu_{(C=O)}$	$\nu_{(C=N)}$	Thiophene $\nu_{(C-S-C)}$	$\nu_{(M-O)}$	$\nu_{(M-N)}$	$\nu_{(M-S)}$	$\nu_{(M-Cl)}$
L	3344	3260	1688	1587	854	--	--	--	--
$[Cu(L)_2]$	3355	3252	1655	1570	859	578	468	460	--
$[Co(L)_2]$	3328	3266	1661	1548	871	580	480	435	--
$[Ni(L)_2]$	3318	3200	1654	1547	890	560	444	467	--
$[Zn(L)(Cl)]$	3329	3226	1615	1547	874	566	496	457	357

^{1}H NMR spectral studies

The ^{1}H NMR spectrum **(Fig. 1)** of Schiff base ligand **(L)** was recorded in d_6-DMSO and data is presented in **Table 3**. The ^{1}H NMR spectrum of the Schiff base ligand **(L)** displayed two singlets each at 11.1 and 10.4 ppm are due to the proton of amide NH and NH attached to thiazole moiety respectively. The signal due to azomethine proton resonated at 8.3 ppm (s, 1H, CH=N). The signals due to nine aromatic protons (m, 9H, ArH) have resonated as multiplets in the region 7.1 - 7.9 ppm.

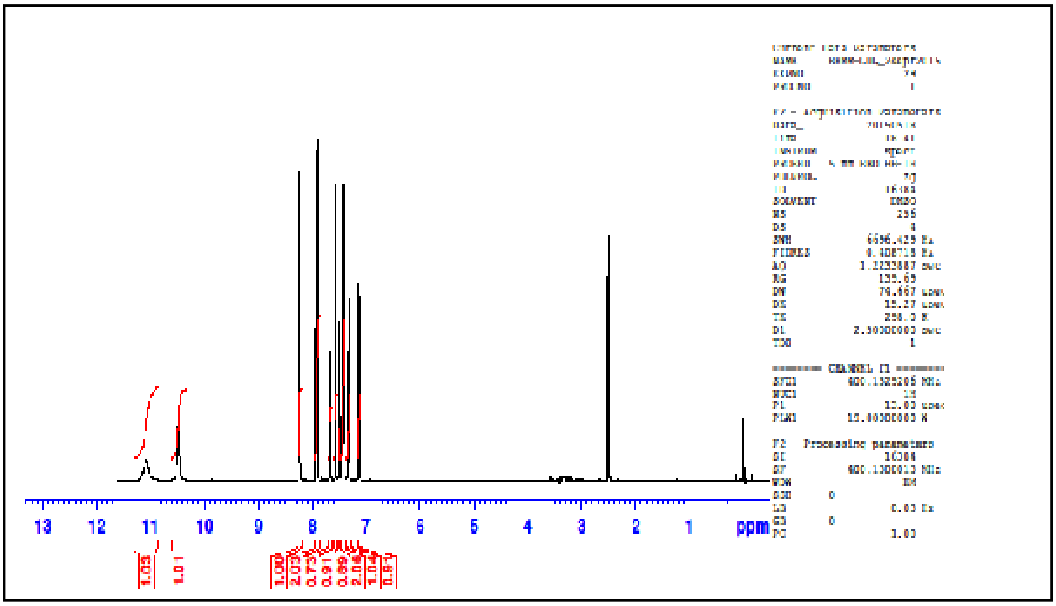


Fig. 1: ^{1}H NMR spectrum of Schiff base ligand (L)

Table 3: ^{1}H NMR data of Schiff base ligand (L)

Ligand**(L)**	^{1}H NMR data (ppm)
$C_{15}H_{12}N_4OS_2$	11.1 (s, 1H, CONH), 10.4 (s, 1H, NH attached to thiazole), 8.3 (s, 1H, HC=N), 7.1 - 7.9 (m, 9H, ArH)

ESI-mass spectral studies

The ESI mass spectrum of the Schiff base ligand **(L)** showed a molecular ion peak recorded at m/z 328 (30%) corresponds to its molecular weight. Similarly, the ESI mass spectra of Cu(II) complex showed a molecular ion peak recorded at m/z 719 (12%) which is equivalent to its molecular weight, thus confirming the structure of the Schiff base ligand **(L)** and its Cu(II) complex respectively.

Electronic spectral studies

The green coloured Cu(II) complex displayed low intensity single broad asymmetric band in the region 15672 - 17692 cm^{-1}. The broadness of the band indicates the three transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and $^2B_{1g} \rightarrow {}^2E_g$($\nu_3$), which are similar in energy and give rise to only one broad absorption band and the broadness of the band may be due to dynamic Jahn-Teller distortion. All these data suggested a distorted octahedral geometry around the Cu(II) ion [23].The electronic spectra of brown coloured Co(II) complex displayed two absorption bands at 16781 and 19889 cm^{-1}. These bands are assigned to be $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) →$^4T_{2g}$ (P) (ν_3) transitions respectively. These data are in good agreement with the reported values [24]. The lowest band, ν_1 could not be observed due to the limited range of the instrument used, but it could be calculated using the band fitting procedure suggested by Underhill and Billing [25]. The above transitions suggest the octahedral geometry of the Co(II) complex.The brown colored Ni(II) complex under present investigation exhibited two absorption bands in the region 15179 cm^{-1} and 25273 cm^{-1} which are assigned to $^3A_{2g}$→ $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) transitions respectively in an octahedral environment. The band ν_1,was calculated by using a band fitting procedure [25].

The octahedral geometry of Cu(II), Co(II) and Ni(II) complexes was further supported by the calculated values of ligand field parameters, such as Racahinter electronic repulsion parameter (B'), nephelauxetic parameter (β), ligand field splitting energy (10 Dq) and ligand field stabilization energy (LFSE) [26]. The calculated B' values for the Co(II) and Ni(II) complexes are lower than the free ion values, which is due to the orbital overlap. The β values are important in determining the covalency for the metal-ligand bond and they were found to be less than unity suggesting a considerable amount of covalency for the metal-ligand bonds. The β value for the Ni(II) complexes was less than that of the Co(II) complex, indicating the greater covalency of the M-L bond.The band position of absorption band maxima assignments is presented in **Table 4.**

Table 4: Electronic spectral data and ligand field parameters of the Cu(II), Co(II) and Ni(II) complexes

Complexes	Transitions in cm^{-1}			Dq (cm^{-1})	B' (cm^{-1})	β	β%	ν_2/ν_1	LFSE (k cal.)
	ν_1^*	ν_2	ν_3						
$[Cu(L)_2]$	15672 – 17692			_	_	_	_	_	28.59
$[Co(L)_2]$	7831	16781	19889	895	878	0.904	9.577	2.14	15.342
$[Ni(L)_2]$	9350	15179	25273	935	825	0.793	20.67	1.62	32.057

Magnetic susceptibility studies

The magnetic susceptibility measurements of Cu(II), Co(II) and Ni(II) complexes were obtained at room temperature and the data were presented in Table 1 and they were found to be paramagnetic in nature. The observed magnetic moment value for Cu(II) complex is 1.89 BM. The observed value is slightly higher than the spin-only value due to one unpaired electron 1.73 BM, suggesting the octahedral geometry [27]. Thus, in the present Cu(II) complex is devoid of any spin interaction with distorted octahedral geometry. In octahedral Co(II) complex the ground state is ^4T_1g. A large orbital contribution to the singlet state lowers the magnetic moment values for the various Co(II) complexes which are in the range 4.12-4.70 and 4.70-5.20 BM for tetrahedral and octahedral geometry of the complexes, respectively [28]. In the present study the observed magnetic moment value for Co(II) complex is 4.60 BM which suggests the octahedral geometry of the Co(II) complex. The observed magnetic moment value for Ni(II) complex is 2.88 BM, which is well within the expected range of 2.83-3.50 BM, suggesting the consistency with its octahedral environment [29].

ESR spectral studies

The ESR spectrum of Cu(II) complex provides information about the environment of the metal ion within the complex, i.e., the geometry and nature of the ligating sites of the Schiff base and metal.

The X-band ESR spectrum of Cu(II) complex has been recorded in polycrystalline state at room temperature at a frequency of 9.1 GHz with a field set of 3000 G. The spin Hamiltonian parameters for the Cu(II) complex is used to derive the ground state. In octahedral geometry with the g-tensor parameter $g_\perp > g_\parallel > 2.0023$, the unpaired electron lies in the d_{z^2} orbital and $g_\parallel > g_\perp > 2.0023$, the unpaired electron lies in the $d_{x^2-y^2}$ orbital in the ground state [29].

In the present case the observed measurements of Cu(II) complex is $g_\parallel$ (2.132) > $g_\perp$(2.033) > 2.0023 indicate that the complex is axially symmetric and copper site has a $d_{x^2-y^2}$ ground state characteristic of octahedral geometry [30]. The $g_\parallel$ value is an important function for indicating the metal-ligand bond character, for covalent character $g_\parallel < 2.3$ and for ionic character $g_\parallel > 2.3$ respectively [31]. In the present study the $g_\parallel$ value of Cu(II) complex is less than 2.3, indicating an appreciable covalent character of the metal–ligand bond. The geometric parameter (G) is the measure of extent of exchange interactions and is calculated by using g-tensor values of the expression $G = g_\parallel - 2.0023/g_\perp - 2.0023$.

According to Hathaway and Billing, [32] if the G value is greater than 4, the exchange interaction between the copper centers is negligible, whereas if its value is less than 4, the exchange interaction is noticed. The calculated G value for the Cu(II) complex is 4.59, indicate the exchange coupling effects are not operative in the present complex [33, 34].

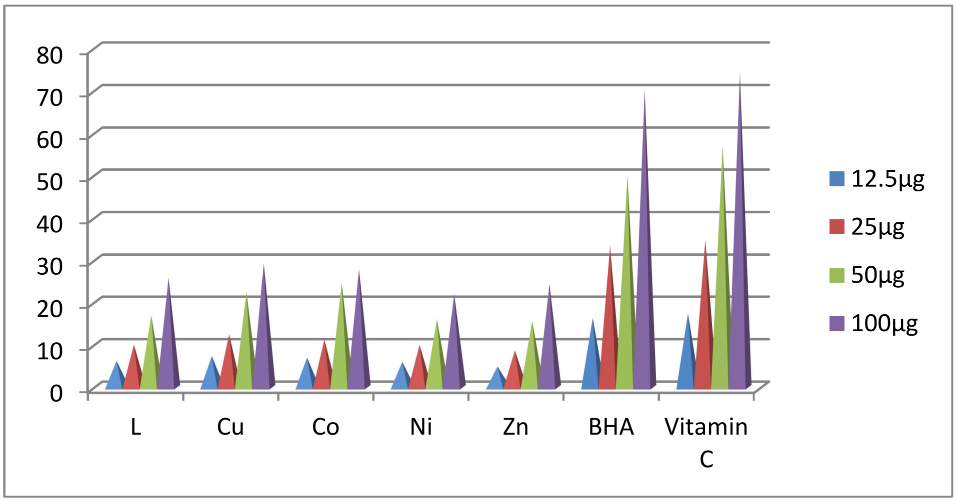


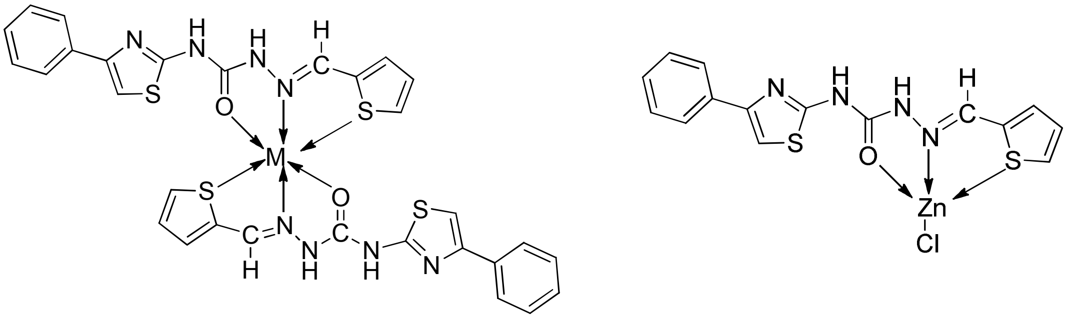
Fig. 2: Antioxidant activity results

Antioxidant assay (DPPH free radical scavenging activity)

The Schiff base ligand **(L)** and its metal complexes were screened for free radical scavenging activity by the DPPH method [18]. The results of free radical scavenger activity of compounds at different concentrations are presented in **Fig. 2**. Among the examined compounds Schiff base ligand **(L)** and its Cu(II), Co(II) complexes have exhibited a good free radical scavenging activity, whereas Ni(II) and Zn(II) complexes have shown moderate activity. Further, the synthesized compounds scavenged the DPPH radical in a concentration dependent manner.

CONCLUSION

A series of Cu(II), Co(II), Ni(II) and Zn(II) complexes were prepared with tridentate ONS donor novel Schiff base ligand (L)derived from N-(4-phenylthiazol-2-yl)hydrazinecarboxamide and thiophene-2-carboxaldehyde and characterized by various physicochemical techniques. The physico-chemical results demonstrate that Cu(II), Co(II) and Ni(II) complexes have octahedral geometry and Zn(II) complex has a tetrahedral geometry. Based on physicochemical evidence, the following structures were proposed for the complexes **(Fig. 3).** The non-electrolytic nature of the complexes was confirmed on the basis of their molar conductance values. Also, the Schiff base ligand **(L)** and its Cu(II) and Co(II) complexes showed good antioxidant activity.



M = Cu(II), Co(II) and Ni(II)

Fig.3: Proposed structures of metal (II) complexes

Acknowledgments

Authors are thankful to Professor and Chairman for providing laboratory facilities. One of the authors (G.Y. Nagesh) is grateful to DST New Delhi for the award of DST-INSPIRE SRF [DST/AORC-IF/UPGRD/2014-15/IF120091]. The authors extend their thanks to IIT Bombay, SAIF Punjab University, for providing spectral data.

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