Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2013, 5(2):111-117
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis, spectral and biological study of four and five co-ordinate copper (II) complexes derived from 5-chloro-2-hydroxy acetophenone *N*(4)-methyl thiosemicarbazone

J. R. Gujarathi[*] N. S. Pawar and R. S. Bendre[a]

[a]*School of Chemical Science, NMU, Jalgaon*
**Pratap College, Amalner (M.S.)*

ABSTRACT

Heterocyclic base adducts of copper (II) complexes have been synthesized by the reaction of copper (II) chloride with 5-chloro-2-hydroxy acetophenone N(4) methyl thiosemicarbazone in presence of heterocyclic base like pyridine (py), 2,2'-bipyridine (bipy), 1,10-phenanthroline (Phen), α/β-picoline. Thiosemcarbazone has been characterized by ^{13}C, ^{1}H NMR as well as IR, electronic spectra. The magnetic and spectroscopic data indicate a square planner geometry for the four coordinate and a distorted square pyramidal for five coordinate complexes. The thiosemicarbazone and its copper (II) complexes show growth inhibitory activity against Pseudomonas Putida, Escherichia Coli, Aspergillus Niger and Candida Albicans. Thiosemicarbazone and its copper (II) complexes have been found antioxidant.

Keywords: Thiosemicarbazone, Bioactive metal complexes, antimicrobial, antioxidant activity.

INTRODUCTION

The chemistry of thiosemicarbazone complexes has received much attention owing to their significant biological activities [1] and medicinal properties [2]. Spectral and structural investigations of a series of biologically active 2-acetylpyridine *N*(4) substituted thiosemicarbazone [3,4]. Base adducts of Cu(II) complexes of chelating agents formed by condensation of salicylaldehydes with 5-alkyl esters of dithiocarbazoic acid [5] and thiosemicarbazone [6] have been studied extensively. Studies on Cu(II) complexes of 5-bromo salicylaldehyde 2-methyl thiosemicarbazone [7] and 5-nitro salicylaldehyde *N*(3)-substituted thiosemicarbazone [8] have been reported by West et al. ESR and electrochemical studies of four and five coordinate copper (II) complexes containing mixed ligands have been reported [9]. Recently 3-aminopyridine-2-carboxaldehyde thiosemicarbazone has been developed as an anticancer drug and has reached clinical phase II on several cancer types [10,11]. Presently the areas in which thiosemicarbazones are receiving more attention can be broadly classified according to their antitumor, antiaprotozoal, antibacterial or antiviral activities and in all cases their action has been shown to involve interaction with metal ions [12,13]. One of the most promising areas in which thiosemicarbazone compounds are being developed is their use against cancer. The presence of metal ion increases the activity or contributes to migrate the side effects of the organic parent compounds [14]. Synthesis, characterization and biological activity of complexes of Fe(III) and Ga(III) have been reported. 2-Acetylpyridine *N*,*N*-dimethyl thiosemicarbazone, 2-acetylpyridine *N*-pyrolidinyl thiosemicarbazone, acetylpyridine *N*,*N*-dimethyl thiosemicarbazone, acetylpyrazine *N*-pyrrolidinyl thiosemicarbazone and acetylpyrazine *N*-piperidinyl thiosemicarbazone were studied [15]. 3-Amino 2-formylpyridine, 2-acetylpyridine, 2-pyridine formamide thiosemicarbazones as well as their *N*-4 dimethylated analogues were studied [16].

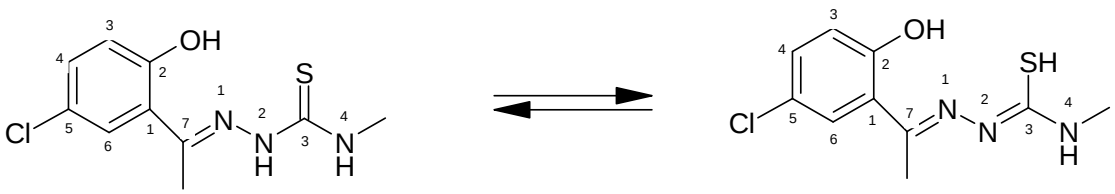
Thiosemicarbazones of aromatic o-hydroxyaldehydes and ketones have recently attracted considerable attention because of their potential biological properties. These aromatic thiosemicarbazones most often coordinate as the dianion to form mononuclear as well as binuclear complexes with the metal ion on deprotonation of the ring hydroxyl group and loss of the *N*(2) hydrogen of the thiosemicarbazone moiety. Such types of tridentate ONS donor thiosemicarbazones and their transition metal complexes have been studied in recent years owing to their pharmacological interest [17,18]. Thiosemicarbazones exist in the thione form in the solid state and in solution they exist as an equilibrium mixture of thione and thiol forms [19]. Due to the presence of C=N, thiosemicarbazones exist as E and Z stereoisomers. Considering the thermodynamic stability isomer will predominate in the mixture [20]. As a part of studies of *N*(4) substituted thiosemicarbazones [21-23], the crystal structure of salicyladehyde *N*(4)-phenyl thiosemicarbazone was reported [24].

We know report the synthesis, spectral characterisation and biological studies of four and five coordinate complexes of copper (II) with 5-chloro 2-hydroxy acetophenone *N*(4) methyl thisemicarbazone.

MATERIALS AND METHODS

Materials and instrumentation

The *N*(4) thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenone and *N*(4) methyl thiosemicarbazide in the mole ratio 1:1 for 3-4 hours, 2-3 drops of conc. H_2SO_4 was added as a dehydrating agent. The product obtained was filtered and washed with cold ethanol and then diethyl ether. It was recrystalised by hot ethanol and dried over P_2O_5 in vacuum [25].



L = 5-Chloro-2-hydroxy acetophenone N(4) methyl thiosemicarbazone and its thiol form

Preparation of complex

The complex Cu.L.Cl (Where, L is 5-Chloro 2-hydroxy acetophenone *N*(4) methyl thiosemicarbazone) was synthesized by refluxing hot ethanolic solutions of $CuCl_2.4H_2O$ and ligand (L) in the mole ratio 1:1 for 7-8 hours. The complex obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum.

Preparation of adducts

The complex Cu.L.B (Where B is heterocyclic base like pyridine, 2-2'-bipyridine, 1,10 phenanthroline, α-picoline, β-picoline) was synthesized by refluxing hot ethanolic solutions of $CuCl_2.4H_2O$ and ligand and heterocyclic base in the mole ratio 1:1:1 for 7-8 hours. The adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum [26].

Physical measurements-

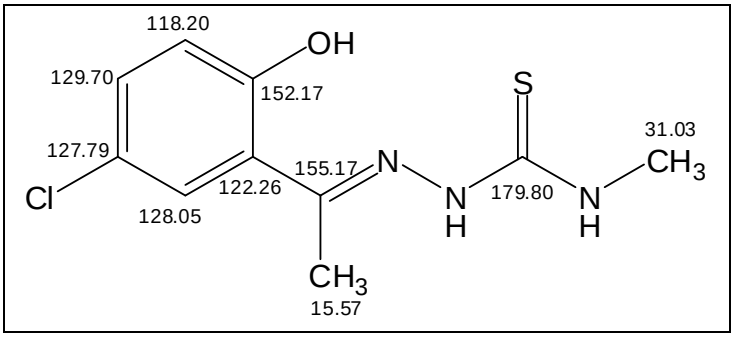
Magnetic measurements were carried out in the polycrystalline state by Faraday method. High purity $[Co(SCN)_4]$ was used as standard. Diamagnetic corrections were made by Pascal's constants. IR spectra were recorded in the range 4000-200 cm^{-1} range using KBr discs. NMR spectra were recorded in the mixture of $CDCl_3$ and DMSO-d_6 (1:1 v/v) with a Bruker AC-300F 300MHz spectrometer. Conductivity measurements were carried out on Conductivity Bridge, Systonics conductivity meter-304. Refluctance spectra were measured on Systonics UV-visible double beam spectrophotometer-2201.

RESULTS AND DISCUSSION

The colours, elemental analysis, stoichiometries of ligand and its complexes are presented in Table 1.1. Elemental analysis data are consistent with 1:1 ratio of metal ion, thiosemicarbazone for complex and 1:1:1 ratio for metal thiosemicarbazone and heterocyclic base for all adducts. The complex and all adducts are insoluble in most of the

common polar and non polar solvents. They are soluble in DMF in which conductivity measurements were made (27^0C), showing all complexes to be non electrolyte [27].

The magnetic susceptibility of complex and adducts carried out at room temperature (27^0C) in polycrystalline state fall in the range of 1.80-2.00 B.M (Table 1.1). These are very close to the spin-only value of 1.73 B.M. for d^9. The ^{1}HNMR signals at 10.45 and 3.40 ppm are assigned to –OH and $–CH_3$ protons respectively. The signals at 2.19 and 2.91 corresponds to $–^4$NH and H^4N-CH_3 respectively. Absence of ^{2}NH protons signal suggests enolization of ^{2}NH-C=S group to ^{2}N=C-SH. The aromatic protons show multiplet at 6.9, 7325, 7.45 ppm range.^{13}C-NMR (DMSO-D_6): δppm 118.20 (C=C); 129.70 (C=C); 127.79 (C=C-Cl); 128.05 (C=C); 122.26 (C=C); 152.17 (C=C-OH), 155.39(C=N); 179.80 (C=S); 31.03 (NH-CH_3)



ESI-MS m/z ligand (L) 243.80, ESI-MS m/z Cu.L.Cl 354.70, ESI-MS m/z Cu.L.py 398.42, ESI-MS m/z Cu.L.bipy 475.42, ESI-MS m/z Cu.L.phen 499.52, ESI-MS Cu.L.α-pico 412.37, ESI-MS Cu.L.β-pico 412.37. Mass spectra data confirm the structure of ligand as indicated by molecular ion peak (M+1) corresponding to their molecular weight.

Table 1.1 : Physicochemical analysis of synthesized compounds

Compounds	Colour	Empirical Formula	Molar conductance $Ohm^{-1}cm^2mole^{-1}$	Magnetic Moment B.M.	Elemental Analysis Found (Calculated) %				
					Metal%	%C	%H	%N	%S
L	Faint yellow	$C_9H_{10}N_3SClO$			-	44.03 (44.35)	4.36 (4.14)	17.62 17.24)	13.33 (13.16)
Cu-L.Cl	Brown	$C_9H_9N_3SClOCu$	62.4	1.83	15.95 (15.09)	33.51 (33.87)	2.09 (2.84)	11.18 (11.84)	8.69 (9.04)
Cu-L.Py	Brown	$C_{14}H_{13}N_4SClOCu$	93.6	1.87	17.91 (17.61)	45.62 (45.22)	3.44 (3.80)	14.43 (14.06)	8.44 (8.05)
Cu-L.Bipy	Brown	$C_{19}H_{16}N_5SClOCu$	62.4	1.96	13.36 (13.83)	50.11 (50.52)	3.48 (3.82)	14.42 (14.73)	6.60 (6.74)
Cu-L.Phen	Brown	$C_{21}H_{16}N_5SClOCu$	72.4	2.05	12.72 (13.20)	52.11 (52.90)	3.72 (3.63)	14.72 (14.02)	6.12 (6.42)
Cu.L.α-Pico	Brown	$C_{15}H_{15}N_4SClOCu$	31.2	1.86	15.41 (15.09)	46.27 (46.60)	4.51 (4.16)	13.51 (13.59)	7.24 (7.77)
Cu-L.β-Pico	Brown	$C_{15}H_{15}N_4SClOCu$	41.6	1.82	15.41 (15.09)	46.27 (46.60)	4.62 (4.16)	13.21 (13.59)	7.24 (7.77)

Table 1.2: Electronic spectral assignments (cm^{-1})

Compound	Mode	d-d	L→M	n→π*	π→π*
L	DMF	-	-	25974(4.05) 28571(3.85)	40860(3.35)
Cu-L.Ci	DMF	17301(2.71)	24096(4.40) 25641(4.32)	29412(4.66) 35088(4.21)	35587(4.15) 37037(4.04)
Cu-L-Py	DMF	16949(2.73)	23810(4.25) 25641(4.32)	30960(4.61) 34130(4.42)	35088(4.31) 37736(4.15)
Cu-L-Bipy	DMF	18018(2.37)	24390(4.15) 25445(4.27)	29326(4.37) 33898(4.58)	37037,41322, 34483(4.50)38462(4.15)
Cu-L-Phen	DMF	13680(2.15) 17331(2.45)	24390(4.38) 25510(4.31)	30769(4.61) 29240(4.40)	35461(4.61) 40000(4.17)
Cu-L-α Pico	DMF	18181(2.34)	34390(4.35) 25641(4.38)	29762(4.50) 36364(4.35)	34483(4.35) 37736(3.90)
Cu-L-β Pico	DMF	18018(2.38)	24390(4.37) 25773(4.35)	29586(4.55) 35971(4.40)	34483(4.40) 37313(3.95)

(absorbance)

UV Studies:

UV-visible spectra of metal complexes in DMF solution and solid state indicate that all complexes have same structure both in solid state and solution state (Table 1.2). The thiosemicarbazone and Cu (II) complexes have band n- π* at 32000 cm^{-1} and π- π*band at 40,000 cm^{-1}. The n- π* band located below 30,000 cm^{-1} in uncomplexed thiosemicarbazone is observed at about 30,000 cm^{-1} in Cu (II) complexes. There are two L-M charge transfer bands are observed at 26,000 and 21000-25000 cm^{-1}. The higher energy band is due to S-Cu (II) transitions [28]. The band 21000-25000 cm^{-1} is due to phenoxy O-Cu (II) transitions [29]. The d-d bands of Cu (II) complexes are observed in the range 16,000-20,000 cm^{-1}. This shows square planer structure [30,31]. The solid electronic spectra of Cu.Lbipy and Cu.LPhen show d-d bands at about 12600 cm^{-1} and 18400 cm^{-1}. These bands show square pyramidal structure [32].

IR Studies:

The absence of any band in 2600-2800 cm^{-1} region of the IR spectrum of L shows the absence of thiol tautomer in the solid state [33]. Coordination of the azomethine nitrogen $^{7}C=N^{1}$ shift the frequency to the lower side by 20-40 cm^{-1} [34] as the band shifts from 1638 cm^{-1} in uncomplexed thiosemicarbazone to 1555 cm^{-1} in the spectra of complexes. A new band at 414-468 cm^{-1} confirms the coordination of azomethine nitrogen [35-38]. The increase in frequency of ^{1}N-^{2}N is due to the increase in double bond character off-setting the loss of electron density via donation to the metal. This confirms the coordination of the ligand through the azomethine nitrogen atom. The band ^{2}N-H of thiosemicarbazone disappears in the complexes indicating the deprotonation of the ^{2}N-H proton. A thioamide band which is partly due to C=S found at 1368 and 795cm^{-1} shifted to lower side in complexes indicating coordination through thiolate sulfur [39]. A new band in 306-318 range due to Cu-S is another indication of the involvement of sulfur coordination. The phenolic oxygen occupies the third coordination on loss of OH protons. These causes of shifting of ν(CO) 1288 cm^{-1} in uncomplexed thiosemicarbazone to lower side in the complexes by 50-61 cm^{-1}. The new bands due to Cu-O in complexes in the range 500-525 cm^{-1} confirm coordination through oxygen. The heterocyclic base nitrogen atom(s) occupies fourth (and fifth) coordination site. The band is assigned for ν (Cu-N) due to heterocyclic base in 272-285 cm^{-1} range in the spectra of all complexes [40-42]. The characteristics bands of coordinated heterocyclic bases are also observed in IR spectra of all complexes[43-45] (Table 1.3).

Table 1.3: Infrared Spectroscopic Assignment (cm^{-1})

Compounds	νOH	ν^{2}NH	νCO	νCN	νCS	ν(C=N-N=C)	νNN	νMO	νMN.H.B	νMS	$\nu M^{1}N$	Bands due to heterocyclic bases
L	3225	2925	1288	1638	795,1368	-	1049	-		-	-	-
Cu.LCl	-	-	1227	1616	677,1288	1534	1118	500	-	309	414	-
Cu.LPy	-	-	1227	1614	679,1288	1534	1083	515	285	318	420	1288,679,463
Cu.LBi	-	-	1227	1633	679,1288	1529	1059	512	277	316	444	1404,1177,679
Cu.L.Phen	-	-	1219	1570	720,1322	1566	1123	509	281	316	465	1404,728.671
Cu.L.α-Pi	-	-	1227	1623	679,1288	1545	1118	525	283	309	419	1404,679,463
Cu.L.β-Pi	-	-	1227	1555	671,1288	1539	1111	512	272	306	468	1404,617,463

TGA Analysis

The TGA curves of the copper (II) complex and adducts were carried out within a temperature range from room temperature up to 800^{0}C. The data from gravimetric analysis clearly indicated that the decomposition of complex proceed in several steps. Hydrations of water molecules were lost in between 30-110^{0}C. There is no change up to ~ 200^{0}C after that there is break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 600^{0}C. Finally the metal oxides were formed above 600^{0}C. The decomposition was complete at ~ 780^{0}C.

It has been found that Cu (II) complex was stable up to 200^{0}C and decomposition started at this temperature was completed at 336.36^{0}C (Table 1.4). The second step temperatures are in the range of 317-407^{0}C. The solid residue was CuO [46].

Table 1.4: TGA analysis data

Complex	First step	Mass loss %	Second step	Mass loss %	Residue	Temperature	% (Cal) found
Cu.L.Cl	200	3.04	320.83	37.05	CuO	779	38.43(37.68)
Cu.L.Py	226	1.56	317.39	42.70	CuO	781.51	35.59(34.00)
Cu.L.Bipy	214.81	2.64	407.40	47.90	CuO	781	30.93(29.00)
Cu.L.Phen	210.34	0.55	322.22	56.62	CuO	780.76	27.47(26.12)
Cu.Lα.Pico	200	2.95	336.36	54.12	CuO	778.26	25.25(24.70)
Cu.L.β-Pico	200	2.90	336.36	54.10	CuO	778	25.20(24.70)

The complexes prepared with different metals decompose in two steps. It is evaluated that the coordination of metal ion to ligand is responsible for the thermal stabilities of metal complexes [47].

Biological activity (Agar well diffusion method)

The antibacterial activity was determined using the agar well diffusion method. The well was dug in the media with a sterile borer and eight-hour bacterial inoculums containing ca. 104 - 106 colony-forming units (CFU)/ml was spread on the surface of the nutrient agar using a sterile cotton swab. The recommended concentration of the best sample (2 mg/ml in DMSO) was introduced into respective wells. Other wells containing DMSO and the reference antibacterial drug served as negative and positive controls, respectively. The plates were incubated immediately at 37°C for 20 h. The activity was determined by measuring the diameter of the inhibition zone (in mm) showing by the hanging drop method. Biological activity was measured in two different molar concentrations (10^{-3}M, 10^{-4} M). The chelate Cu.L.phen showed maximum activity against bacterial and fungal species than free ligand. The results of antibacterial and antifungal studies are given in Table 1.5. Out of these seven compounds tested, Cu.L.phen was found more active against four cultures. The N(4) substituted 5-chloro 2-hydroxy acetophenone methyl thiosemicarbazone was found less active than its copper complex and adducts. Thus increase in coordination number from four to five in copper complexes increases microbial activity [49].

The [Cu (L)(Phen)] chelate exhibited high activity against all the bacteria and fungi. Thus it is evaluated that the coordination of metal ion to ligand is responsible for high biological activity.

Table 1.5: Antimicrobial activity of synthesized compounds

Compounds	*Pseudomonas Putida*		*Escherichia Coli*		*Aspergillus Niger*		*Candida Albicans*	
	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M	10^{-3}M	10^{-4}M
L	12	10	9	8	12	10	10	9
Cu-L.Cl	13	12	12	11	14	11	13	12
Cu-L-Py	13	12	13	12	14	13	14	13
Cu-L-Bipy	15	12	14	13	16	15	15	14
Cu-L- Phen	16	15	15	14	17	16	16	15
Cu-L α-Pico	12	11	12	11	17	16	12	11
Cu-L. β-Pico	12	11	12	11	14	13	11	10

Zone in mm

Antioxidant activity:

The antioxidant activity of ligand and complexes was assessed on the basis of the radical scavenging effect of the stable DPPH free radical (Table 1.6). About 100 _l of each extract or standard (from 21 mg/ml to 21_g/ml) was added to 2 ml of DPPH in methanol solution (100_M) in a test tube. After incubation at 37 ^{0}C for 30 min, the absorbance of each solution was determined at 517 nm using spectrophotometer. The corresponding blank readings were also taken and the remaining DPPH was calculated. IC_{50} value is the concentration of the sample required to scavenge 50% DPPH free radical. Lower the absorbance of the reaction mixture indicated higher free radical scavenging activity [48].

Table 1.6: Antioxidant activity data

µg/ml	Cu-L.Cl	Cu-L-Py	Cu-L-Bipy	Cu-L. Phen	Cu-L.α-Pico	Cu-L. β-Pico	Vit C Std
20	0.035	0.088	0.087	0.085	0.087	0.088	0.026
40	0.035	0.075	0.078	0.082	0.072	0.079	0.023
60	0.032	0.067	0.73	0.069	0.070	0.082	0.018
80	0.028	0.065	0.073	0.067	0.065	0.036	0.017
100	0.025	0.055	0.071	0.056	0.059	0.029	0.015
IC_{50}	133.33	128.60	236.85	132.38	145.18	66.66	51.00

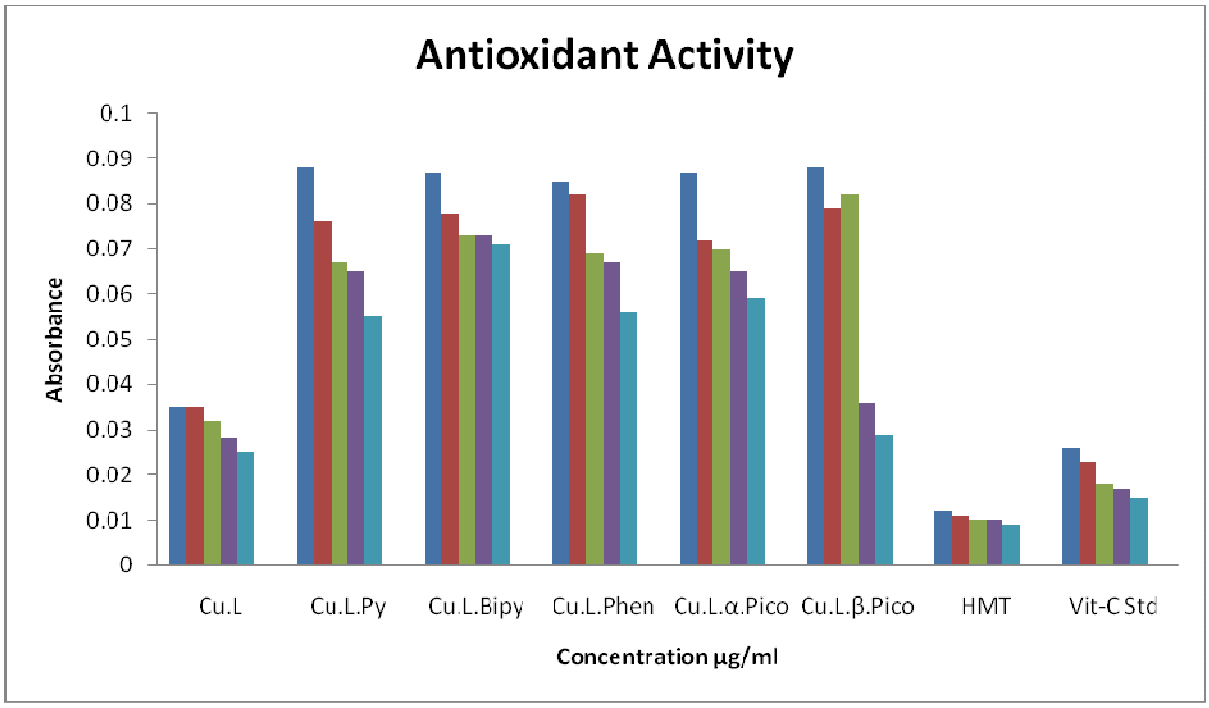


Figure 1.1: Effect of synthesized compounds on DPPH assay

Expected structure

B = pyridine, 2-methyl pyridine, 3-methyl pyridine

REFERENCES

[1] West D X, Padhye S B and Sonawane P S, *Structure bonding*, **1991**, **76**, 1.
[2] Scovill J P, Klayman D L and Franchino C F, *J.Med.Chem.*, **1982**, **25**,1261.
[3] Garg B S, Kurup M R P, Jain S K and Bhoon Y K, *Transition Met Chem.*, **1988**, **13,** 309.
[4] West D X, Bain D A, Butcher R J, Jasinski J P, Pozdniakiv R Y, Tosacano R A and Ortega S H, *Polyhedron*, **1996**, **15,** 665.
[5] Ali M A, Chowdhary D A and Nazimuddin M, *Polyhedron*, **1984**, **3**, 595.
[6] Ali M A, Kabir M H, Nazimuddin M and Majumder S M M H, *Ind J Chem*, **1988**, **27A,** 1064.
[7] Vaidas-Martinez J, Toscano R A, Zentalla-Dehesa A, Salberg M M, Bain G A and West D X, *Polyhedron*, **1995**, **15,** 477.
[8] West D X, Salberg M M, Bain G A, Liberta A E, Valdes-Martinez J and Hernandez-ortega S, *Transition Met.Met.Chem.*, **1996**, **21,** 206.
[9] Bindu P and Maliyeckal R, Kurup P, *Transition Met.Chem.*, **1997**, **22,** 578.
[10] Nutting C M, Van Herpen C M L, Miah A B, *Ann Oncol*, **2009**, **20**,1275.
[11] 11.Ma B, Goh B C, Tan E H, *Invest New Drugs*, **2008**, **26**,169.
[12] Finch R A, Liu M C, Copy A H, Cory J G, Sarlorelli A C, *Adv.Enzyme Regul*, **1999**, **39**, 3.
[13] Antholine W, Knight J, Whelan H, Petering D H, *Mol.Pharmacol*, **1977**, **13**, 89.
[14] French F A, Blanz E J J, *Cancer Res*, **1965**, **25**,1454.
[15] Kowol C R, Berger R, Eichinger R, *J Med Chem*, **2007**, **50**,1254.
[16] Kowol C R, Trondi R, Heffeter P, *J Med. Chem.*, **2009**, **52**,5032.
[17] Campbell M J M, *Co-ordination Chem. Rev.*, **1975**, **15,** 279.

[18] Jayasree S and Arvindakshan K K, *Transition Met. Chem.*, **1993**, **18**, 85.
[19] Kurup M R P, Joseph M, *Synth React Inorg. Met. Org. Chem.*, **2003**, **33**,1275.
[20] West D X, Liberla A E, Pandhye S B, Chikate R C, Sonawane P B, Kumbhar A S, Yerande R G, *Coord Chem. Rev*, **1993**, **123,** 49.
[21] Bindu P, Kurup M R P, Satyakeerty T R, *Polyhedron*, **1999**, **18**, 321.
[22] Joseph M, Suni V, Kurup M R P, Nethaji M, Kishore A, Bhat S G, *Polyhedron*, **2004**, **23**, 3069.
[23] John R P, Shreekanth A, Rajakannan V, Ajith T A, Kurup M P R, *Polyhedron*, **2004**, **23**, 2549.
[24] Seena E B, Kurup M R P, Suresh E, *J.Chem. Crystalogr*, **2008**, **38,** 93.
[25] Klayman D L, Bartosevich J F, Griffin T S, Mason C J and Scovill J P, *J. Med. Chem.*, **1979**, **22**, 855.
[26] Bindu P, Maliyeckal R, Kurup P, Satyakeerty T R, *Polyhedron*, **1999**, **18**, 321.
[27] Geary W J, *Coord Chem Rev*, **1971**, **7,** 81.
[28] Mikuria M, Okawa H and Kida S, *Inorg.Chem.Acta.*, **1963**, **34**, 13); Ainscough E. Bordie A M and Larsen N G, *Inorg.Chem Acta*, **1982**, **60**, 259.
[29] Mikuria M, Okawa H and Kida S, *Bull Chem.Soc. Jpa*, **1980**, **53,** 3717.
[30] Mahapatra B B and Panda D, *Transition Met.Chem.*, **1979**, **41,** 809.
[31] Ali M A and Teoh S G, *J.Inorg.Nucl.Chem*, **1979**, **41,** 809.
[32] Sacconi L and Speroni G, *J. Am. Chem. Soc.*, **1965**, **87,** 3102.
[33] Jain S K, Garg B S, Bhoon Y K, Klayman D L and Scovill J P, *Spectrochim Acta*, **1985**, **41(A)**, 407.
[34] West D X, Carison C S, Bouck K J and Liberta A E, *Transition Met. Chem.*, **1991**, **16**, 27.
[35] Butcher R J and West D X, *Transition Met. Chem.*, **1993**, **18**, 449.
[36] West D X, Gebremedhin H, Butcher R J and Jasinki J P, *Transition Met. Chem.*, **1995**, **20**, 84.
[37] Akinchan N T, West D X, Yang Y H, Salberg M M and Klein T A, *Transition Met. Chem.*, **1995**, **20**, 481.
[38] 38. West D X, Kozub N and Bain G A, *Transition Met. Chem.*, **1996**, **21**, 52.
[39] 39. Gerg B S, Kurup M R P, Jain S K and Bhoon Y K, *Transition Met. Chem.*, **1988**, **13**, 309.
[40] 40. Inskeep R G, *J. Inorg. Nucl. Chem.*, **1962**, **24**,763.
[41] 41. Schilt A A and Taylor R C, *J. Inorg. Nucl. Chem.*, **1959**, **9**, 217.
[42] 42. Manoyama M, *Inorg. Chim. Acta,*, **1975**, **13**, 5.
[43] 43. Inskeep R G, *J.Inorg.Nucl.*, **1962**, **24**, 763.
[44] 44. Schilt A A and Taylor R C, *J.Inorg.Nucl Chem.*, **1959**, **9**, 217.
[45] 45. Monoyama M, *Inorg.Chem.Acto.*, **1975**, **13**, 5.
[46] 46. Sekerci M and Yakuphanoglu F, *J.Therm.Anal.Cal,*, **2004**, **75**, 189.
[47] 47. Mohamed G G, Nour-EI Dien F A and El-Gamel E A, *J.Therm.Anal.Cal,* **2002**, **67**.135.
[48] 48. Rai S, Wahile A, Mukherjee K, Saha B P, Mukherjee P K, *J. Ethnopharma*., **2006**, **104**, 322.
[49] 49. Albert A, Rees C W, Tomilson A J H, *Rec Trav Chim*, **1956**, **75**, 819.