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Synthesis Epr Study and Biological Evaluation of Four Co-Ordinate Complex and Heterocyclic Base Adducts of Cu (Ii) Derived From N(4) Thiosemicarbazone

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ABSTRACT

3,5 dichloro 2-Hydroxy acetophenone N(4) thioemicarbazone was synthesized by refluxing 3,5 dichloro 2-Hydroxy acetophenone and N (4) methyl thioemicrbazone in the mole ratio 1:1 and characterized by 13C-NMR , 1H NMR as well as IR, electronic spectra and mass spectra. Cu (II) complex and adducts have been synthesized by refluxing the Cu (II) chloride with 3,5-dichloro 2-hydroxy acetophenone N(4) methyl thiosemicarbazone and in presence of heterocyclic bases like pyridine (py),2-chloropyridine, 3-chloropyridine and 4-chloropyridine. The synthesized complex and adducts were characterized by elemental analysis, IR, electronic spectroscopy,EI-MS as well as by TGA, magnetic and conductivity measurement. Square planner geometry for the four coordinate complexes has been predicted from magnetic and spectral data. The thiosemicarbazone and its copper (II) complexes have been found ,antibacterial and show growth inhibitory activity against Staphylococcus aureu,Bacilus subtilis(Gram+ve), Escherichia Coli,Peudomonas aeruginosa (Gram-ve) bacterial species.

KEYWORDS : Thiosemicarbazone,N(4) methyl thiosemicarbazone, EPR, antimicrobial activity.

Introduction

Biologica activity of thiosemicarbazone is related to the substituent at N^4 poition.The sreriochemistry adopted by thiosemicarbazone while interaction with transition metal ions depand on denticity and charge on ligand.Transition metal complexes with thioemicarbazones exhibit potential biological activity.Metal complexes of thioemicarbazones have pharmacological and therapeutic effects.Studies on thiosemicarbazones showed that the thioemicarbazones have antibacterial and antioxidant properties.Transition metal complexes are found to have more activity than uncombined thiosemicarbazones. Scientific research copper(II) complexes possesses activities such as antiulcer [1], antiamoebic [2], antidiabetic [3] anticonvulsant [4], anti-inflamatory [5-7], antimicrobial [8] and antitumor [9].

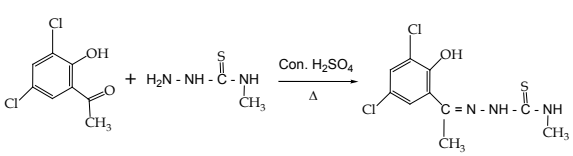
Copper (II) complex of sulfacetamide, (N-[4-(amino-fenil)sulfonil] acetamide),has been used in treatment of ophthalmic and dermatologic infections [10, 11]. Further studies of the copper(II) complexes of sulfacetamide and sulfanilamide [10] and sulfisoxazole [12] have showed good results.Sulfonamide copper(II) complexes showed antimicrobial activity against Gramm(+) *Staphylococcus aureus*, *Bacillus subtilis*) and Gramm(-) *Escherichia coli*, *Pseudomonas euruginosa* [13] a slightly higher activity was obsered in Gram(-) bacteria [14]. The copper(II) complexes of benzimidazoles showed strong activity against fungi [15]. The complexes of thiabendazole with Cu (II) were found active [16]. Moreover, was also found for A copper(II) complex of p-amino acetophenone benzoylhydrazone was found active against *Aspergillus sp*. and *Penicillium* antifungal species. [17].

In this research article We have reported the synthesis, spectral characterisation and biological studies of four coordinate complexes of copper (II) with 3,5-dichloro 2-hydroxy acetophenone *N*(4) methyl thisemicarbazone.

Experimental

Synthesis of ligand:

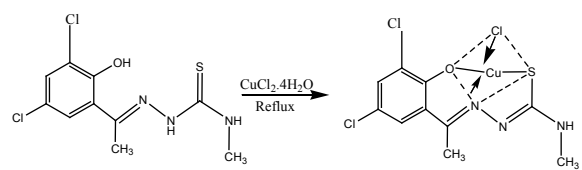
A 0.01 mole soution of 4- methyl-3-thiosemicarbazide in 20 ml ethanol was treated with 0.01 mole ethanolic soution of 3,5 dichloro 2-hydroxy acetophenone and refluxed for 3 hours. The reaction mixture was cooled and faint yellow compound separated out. The solution was filtered, washed well with ethanol and then diethyl ether. The compound was recrystallized from ethanol and dried over P_2O_5 in vacuum (Scheme I).



SCHEME - I

Synthesis of complex:

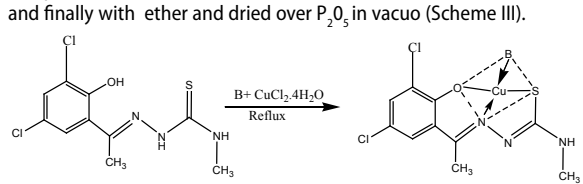
This complex was synthesized by refluxing an ethanolic solution of ligand (0.01 mole) with ethanolic solution of $CuCl_2.4H_20$ (0.01 mole) for 3 hours. The brown complex formed was filtered, washed with hot water,cold ethanol and finally with ether and dried over P_20_5 in vacuo (Scheme II).



Scheme II

Synthesis of adducts

The adducts were synthesized by refluxing an ethanolic solution of ligand (0.01 mole) with ethanolic solution of $CuCl_2.4H_20$ (0.01 mole) and ethnolic ligand solution containing heterocyclic base (~10 ml pyridine, , 2-chloro pyridine,3-chloro pyridine, 4-chloro pyridine) in slight excess over the metal: ligand ratio 1:1 for 7 hours. The brown compound formed was filtered, washed with hot water,cold ethanol and finally with ether and dried over P_20_5 in vacuo (Scheme III).



Scheme III

(B = pyridine, 2-chloro pyridine,3-chloro pyridine, 4-chloro pyridine)

Materials and methods

The starting materials and solvents (A.R. grade) were commercially available and used without further purification.Elemental analysis was recorded on a Perkin elmer elemental analyzer.The infrared spectra of the solid samples were recorded in Jasco spectrometer in the range of 4000-200 cm^{-1} .Electronic pectra were recorded uing Jasco UV-visible double beam spectrophotometer using DMF solvent in the range of 200-800 nm.The molar conductivity measurements of the metal complexes were carried out in ~10^{-3}M DMF solutions using digital conductivity meter.Magnetic measurements were carried out by Faraday method. 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.Metal in the complex and adducts was estimated by E.D.T.A using muroxide as an indicator. Chloride in the complex was determined by Mohr's method.

Physical measurements-

Table 1

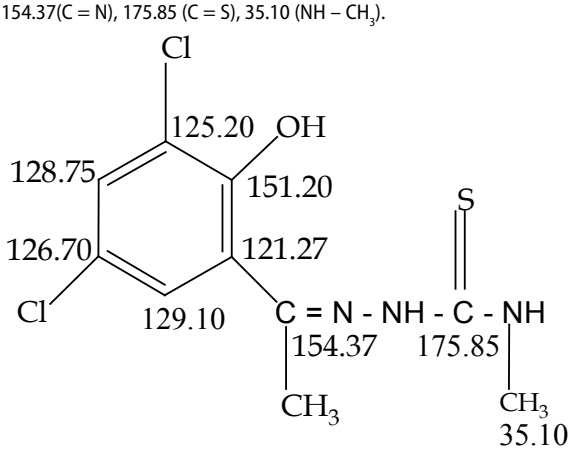
Compounds	Colour	Empirical Formula	Molar conductance $Ohm^{-1}cm^{-2}mole^{-1}$	Magnetic Moment B.M.
L	FaintYellow	$C_{10}H_{11}N_3OSCl_2$	-	-
Cu-L.Cl	Brown	$C_{10}H_9N_3OSCl_3Cu$	50.7	1.80
Cu-L.Py	Brown	$C_{15}H_{14}N_4OSCl_2Cu$	80.6	1.83
Cu-L.2-Cl py	Brown	$C_{15}H_{13}N_4OSCl_3Cu$	70.4	1.85
Cu-L. 3-Cl py	Brown	$C_{15}H_{13}N_4OSCl_3Cu$	60.6	1.87
Cu.L.4-Cl py	Brown	$C_{15}H_{13}N_4OSCl_3Cu$	50.5	1.89

^{1}H-NMR

Signals at 11.6, 3.30 ppm are assigned to – OH, - CH_3 protons respectively.

^{1}H-NMR signals at 12.00 and 2.4 ppm are assigned to – OH and – CH_3 protons respectively. The signals at 2.30, 3.01 correspond to ^{4}NH and H^{4}N-CH_3 respectively. Signal at 10.5 ppm corresponds to ^{2}NH. Aromatic protons show multiplets at 7.0, 7.20, 7.35, ppm.

^{13}C-NMR (DMSO-D_6): δppm 125.20 (C = C-Cl), 128.75 (C = C), 127.79 (C = C – Cl), 126.70 (C = C), 129.10 (C = C), 151.20 (C = C – OH), 154.37(C = N), 175.85 (C = S), 35.10 (NH – CH_3).



(Calcd) found ESI-MS m/z, ion M$^+$: $C_{10}H_{11}N_3OSCl_2$ (292.17) 292.89, $C_{10}H_9N_3OSCl_3Cu$ (389.14) 389.92, $C_{15}H_{14}N_4OSCl_2Cu$ (432.79) 432.09, $C_{15}H_{13}N_4OSCl_3Cu$ (467.23) 467.89, $C_{15}H_{13}N_4OSCl_3Cu$ (467.23) 467.82, $C_{15}H_{13}N_4OSCl_3Cu$ (467.23) 467.78.

Table.2 Analytical data

Compounds	Elemental Analysis Found (Calculated) %				
	Metal%	%C	%H	%N	%S
L	-	41.74 (41.11)	3.13 (3.79)	14.88 (14.38)	10.21 (10.97)
Cu-L.Cl	16.63 (16.33)	30.11 (30.86)	2.74 (2.33)	10.13 (10.80)	8.73 (8.24)
Cu-L.Py	14.23 (14.68)	41.21 (41.63)	3.91 (3.26)	12.37 (12.95)	7.71 (7.41)
Cu-L.2-Cl py	13.20 (13.60)	38.11 (38.56)	2.22 (2.80)	11.18 (11.99)	6.23 (6.86)
Cu-L. 3-Cl py	13.22 (13.60)	38.02 (38.56)	2.12 (2.80)	11.22 (11.99)	6.12 (6.86)
Cu.L.4-Cl py	13.92 (13.60)	38.10 (38.56)	2.02 (2.80)	11.23 (11.99)	6.26 (6.86)

Table 3 .Electronic spectral data (cm^{-1})

Compound	Mode	d-d	L→M	n→π*	π→π*
L	DMF	-	-	25971	40860
Cu-L.Cl	DMF	17800	25600,28300	30064	42843
Cu-L.Py	DMF	17094	25741,28741	31256	42444
Cu-L.2-Cl py	DMF	17692	25974,28550	30560	43486
Cu-L. 3-Cl py	DMF	17500	25841,28562	30781	42553
Cu.L.4-Cl py	DMF	17194	25907,28360	33313	42478

Infrared Spectroscopic data (cm^{-1})

1.L: ν (- OH) 3200; ν (C = N) 1642; ν (- C – S) 790 (s), 1365 (m); ν (N – N) 1060; ν (^{2}N-H) 3250; ν (C – O) 1295.

2 .[Cu-L.Cl]: ν (C = N) 1605; ν (C = N-N=C) 1570, ν (C-S) 702, 1298,ν (N-N) 1110, ν (M - N) 440, ν (M-O) 520, ν (M-S) 320, ν (C - O) 1210.

3 .[Cu-L.Py]: ν (C = N) 1608; ν (C = N-N=C) 1582, ν (C-S) 706, 1308; ν (N-N) 1113, ν (M - N) Base 270, ν (M - N) 455, ν (M - O) 525, ν (M-S) 320, ν (C - O) 1215, Band due to HB 1475.

4.[Cu-L.2-Cl py]: ν (C = N) 1610; ν (C = N-N=C) 1580, ν (C-S) 708, 1311, ν (N-N) 1115, ν (M - N) Base 275, ν (M - N) 458, ν (M - O) 530, ν (M-S) 325, ν (C - O) 1220, Band due to HB 1478.

5.[Cu-L. 3-Cl py]: ν (C = N) 1615; ν (C = N-N=C) 1585, ν (C-S) 710, 1315, ν (N-N) 1120, ν (M - N) Base 280, ν (M - N) 462, ν (M - O) 534, ν (M-S) 328, ν (C - O) 1225, Band due to HB 1482.

6. [Cu.L.4-Cl py]: ν (C = N) 1620; ν (C = N-N=C) 1590, ν (C-S) 718, 1325,ν (N-N) 1125, ν (M - N) Base 280, ν (M - N) 468, ν (M - O) 540, ν (M-S) 335, ν (C - O) 1230, Bands due to HB 1488.

Electron Paramagnetic Resonance Spectral data :

EPR spectrum of complexes was carried out in DMF at 77 K. The values of g_{11}, $g_{\wedge}$, g_{av}, A_{11}, $A_{\wedge}$ R, f, G, a^2, b^2 ,$K_{\|}K_0$ are listed in Table No.4

Table.4

Complex	g_{11}	$g_{\wedge}$	g_{av}	G	A_{11}	$A_{\wedge}$	R	f	a^2	b^2	$K_{\|}$	K_o
Cu-L.Cl	2.15	2.16	2.16	1.45	184	51	0.54	118	0.513	0.720	0.371	0.366
Cu-L.Py	2.18	2.14	2.16	1.62	180	50	0.55	120	0.525	0.725	0.374	0.378
Cu-L.2-Cl py	2.20	2.12	2.16	1.71	182	53	0.53	122	0.520	0.728	0.370	0.370
Cu-L.3-Cl py	2.19	2.13	2.16	1.55	179	55	0.56	125	0.522	0.729	0.372	0.372
Cu.L.4-Cl py	2.17	2.13	2.15	1.60	178	54	0.58	120	0.520	0.724	0.378	0.375

Thermogravimetric analysis:

The TGA curves of complexes were recorded between the temperatures 30 °C to 800 °C

Table.5

Complex	First step	Mass loss %	Second step	Mass loss %	Residue	Temperature	% (Cal) found
Cu-L.Cl	200	2.25	300.15	55.30	CuO	780	20.72(20.44)
Cu-L.Py	200	2.75	380.82	57.80	CuO	780	18.09(18.38)
Cu-L.2-Cl py	211	2.35	319.58	55.60	CuO	778	17.72(17.02)
Cu-L.3-Cl py	210	4.50	300.35	59.60	CuO	778	17.54(17.02)
Cu.L.4-Cl py	214	5.25	318.62	55.72	CuO	780	17.68(17.02)

Antimicrobial activity (Agar plate diffusion method)

Table.6 % Activity index of L , Cu(II) complexes,metal salt and standered

Compound % Activity Index	Staphylococcus aureu		Bacilus subtilis		Escherichia Coli		Peudomonas aeruginosa	
	Gram positive				Gram negative			
	800 µg/ml	1000 µg/ml	800 µg/ml	1000 µg/ml	800 µg/ml	1000 µg/ml	800 µg/ml	1000 µg/ml
L	17.80	19.18	17.30	21.30	17.60	21.72	18.35	22.00
Cu-L.Cl	27.00	30.22	28.30	32.16	26.20	32.20	25.30	31.00
Cu-L.Py	32.05	34.40	32.16	34.70	30.21	34.17	31.35	33.10
Cu-L.2-Cl py	33.08	35.68	33.51	36.65	30.95	35.90	31.10	34.12
Cu-L.3-Cl py	33.15	35.32	33.10	36.40	30.60	35.90	31.45	34.35
Cu.L.4-Cl py	33.40	35.44	33.38	36.42	30.15	35.63	32.44	34.00
$CuCl_2.4H_2O$	39.35	40.92	38.35	41.52	38.69	42.20	39.26	42.66
Standered	100	100	100	100	100	100	100	100

(Std-Amphiciline)

% activity index was calculated by the formula

$$\% \text{ Activity Index} = \frac{\text{Zone of inhibition of test compound}}{\text{Zone of inhibition of standard (diameter)}} x100$$

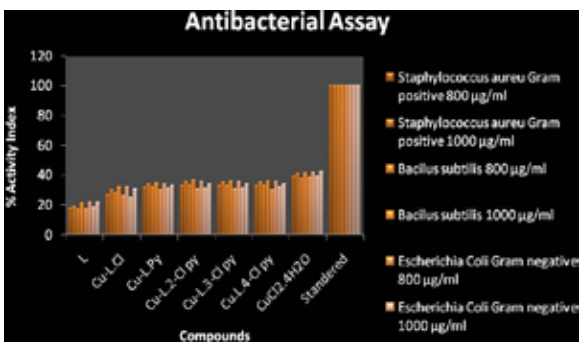


Fig.1 % Activity Index Bar Graph

Results and discussion

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 soluble in DMF in which conductivity measurements were made (27^{0}C), showing all complexes to be non electrolyte [18].

The magnetic susceptibility of complex and adducts carried out at room temperature (27^{0}C) fall in the range of 1.80-1.90 B.M (Table 1). These are very close to the spin-only value of 1.73 B.M. for d^9.

UV-visible spectrum of thiosemicarbazone showed absorption bands n- π* at 25971 cm^{-1}and π- π*at 40,860 cm^{-1} (Table 2). These are shifted to higher side on complexation.The L→M charge transfer bands are observed in the range 25,000-26,000 cm^{-1} and 28,000-29,000 cm^{-1}. The higher energy band is due to S-Cu (II) transitions [19]. The band 22000-29000 cm^{-1} is due to phenoxy O-Cu (II) transitions [20]. The d-d bands of Cu (II) complexes are observed in the range 17,000-18,000 cm^{-1}. This shows square planer structure [21,22].

The IR spectra of L showed ν(OH) vibrations at 3200 cm^{-1} which disappeared in the spectra of complexes. It is confirmed by decrease in ν(CO) and an appearance of a band in the range 520-540 cm^{-1} due to a ν(Cu-O) stretch in the spectra of complexes [23,24,25]. It indicates coordination through phenolic oxygen. ν(C=N) at l642 cm^{-1} in the uncomplexed thiosemicarbazone is shifted to the lower energy side in the spectra of complexes [26] due to the conjugation of the p-orbital on the double bond with the d-orbital on the metal ion with the reduction of force constant. The presence of new band in the range 440-470 cm^{-} is consistent coordination of azomethine nitrogen [27, 28]. The increase in ν (N-N) in the spectra of complexes is due to enhanced double bond character through chelation, thus offsetting the loss of electron density via donation to the metal ion, and it confirms azomethine coordination. The spectral band ν (N-H) of thiosemicarbazones disappeared in the complexes indicating the deprotonation of the N-H proton.The coordination through thiolate sulfur is indicated by a decrease in ν(C-S). The new band in the range 320-335 cm^{-1}is due to (Cu-S) vibration confirms the sulfur bonding [29-31]. IR spectra of the complexes 4, 5, 6, 9 and 10 exhibit bands characteristic of coordinated heterocyclic bases [32].

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 decomposition of complexes proceeded in several steps. Hydrations of water molecules were lost in between 30-100^{0}C. No change was seen up to ~ 200^{0}C.The break in the curves observed due to evaporation of molecules of organic ligand.The complete ligand was removed from the coordination sphere at ~ 600^{0}C. Finally CuO was formed above 600^{0}C. The decomposition was complete at ~ 780^{0}C.

It has been found that Cu (II) complexes were stable up to 200^{0}C. The second step temperatures are in the range of 300-400^{0}C. The solid residue was CuO [33].

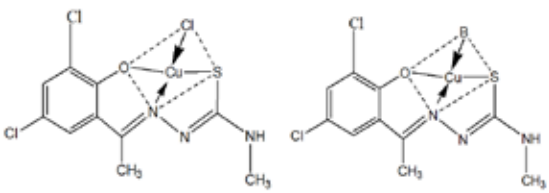
The complexes prepared with different metals decompose in two steps. It is evaluated that the coordination of metal ion to ligand in the complexes is responsible for the thermal stabilities of metal complexes [34].

EPR spectra of complexes showed well resolved four copper hyperfine lines, characteristic of monomeric Cu (II) complexes and nine superhyperfine lines due to azomethine nitrogen and nitrogen atom of the coordinated heterocyclic base in frozen DMF. Since superhyperfine coupling by nitrogen of the heterocyclic base is observed, the coordinated heterocyclic base is found to be coplanar with the ONS bichelate rings [35]. Hence a square planar structure can be assigned for CuLB (B = py,2-chloro pyridine,3-chloro pyridine,4-chloro pyridine) The variations in g values indicate that the geometry of the compound is affected by the nature of the coordinating gegenions. The geometric parameter G is calculated by the relation G = $(g_{11-2}/g_{\wedge-2})$ is a measure of the exchange interaction between copper centres in the polycrystalline compound. If G > 4, the exchange interactions is negligible and if it is less than 4 exchange interaction is indicated in the complex. All complexes have values $g_{11} > g_{\wedge} > 2$ and G values falling within this range 1 to 3 are consistent with a $dx^2 - y^2$ ground state corresponding to square planer or square pyramidal geometry. For all complexes the lowest g value is 2.12 indicating a rhombic square coplanar geometry. The rhombic spectral values R is calculated by the relation $R = g_2 - g_1/g_3 - g_2$. If R > 1, a predominant $dx^2 - y^2$ ground state is present and when R= 1 then the ground state is an approximately equal mixture of dz^2 and $dx^2 - y^2$, the structure is intermediate between square planar and trigonal bipyramidal geometries. For all complexes R < 1 suggests a distorted square planar geometry with a $dx^2 - y^2$ ground state. The empirical factor $f = g_{11}/A_{11}$ (cm) is an index of tetragonal distortion. The value may vary from 118 to 125 for square planer complexes. The orbital reduction factor K_{11} was calculated by the relation $K_{\|} = \alpha^2 \beta^2$. For all compounds $K_{\|}$ » 0.370 ~ 0.378. The contribution of s electrons to the hyperfine interaction can be estimated by the value of Fermi contact hyperfine interaction term (K_0). K_0 is a dimensionless quantity and is generally found to have a value of 0.3. The values calculated for all complexes are in the range of 0.366 to 0.378.The bonding parameters α^2, β^2 are regarded as measures of the covalency of the in plane σ bonds, in plane p bonds α^2, β^2 values are much less than 1.0 which is expected for 100 % ionic character of the bonds, and become smaller with increasing covalent bonding. The evaluated values of α^2, β^2 of the complexes are consistent with both strong in plane σ and in–plane p bonding. For all complexes, the g_{11} values are nearly same indicating that the bonding is dominated by the thiosemicarbazone moiety rather than the heterocyclic bases. The g_{11} values are less than 2.3, is an indication of significant covalent bonding in the complexes [36, 37].

The bacterial assay was carried out by the agar plate diffusion method. The activity was determined by measuring the diameter of the inhibition zone (in mm). Activity was measured in two different concentrations (800µg/ml, 1000µg/ml). The adducts showed good activ-

ity against bacterial species than free ligand. The results of % activity index are given in Table 6. In these six compounds tested, adducts were found to be more active against four bacterial cultures. The thiosemicarbazone was found less active than its complex and adducts. The increase coordination number increases on complexation,this increases microbial activity. Thus it is evaluated that the coordination of metal ion to ligand enhances biological activity.More activity was observed at 1000µg/ml concentration.The minimum inhibitory concentration is 800µg/ml.Below this no activity was observed. Gram positive species showed better activity than gram negative pecies. It has been observed that the % activity index for free metal ion is higher than metal in binded form.

Expected structures



(B = pyridine, 2-chloro pyridine, 3-chloro pyridine, 4-chloro pyridine)

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