Research Paper Medical Science

Spectra,Thermal Study and Biological Screening of Six Co-ordinate Zn (II) Complexes Derived From N (4) Thiosemicarbazone and Heterocyclic Bases.

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ABSTRACT

Zinc (II) complexes have been synthesized by the reaction of zinc (II) chloride with 5-chloro-2-hydroxy acetophenone N(4) phenyl thiosemicarbazone and heterocyclic base like pyridine (py),α/β/γ-picoline in the mole ratio 1:1:1. The synthesized thiosemcarbazone has been characterized by 13C-NMR, 1HNMR,mass spectra as well as IR, electronic spectra.These characteristics confirmed the structure of thiosemicarbazone.Spectral and magnetic measurements indicated octahedral geometry for the six coordinate complexes.The coordinated water molecules were determined by TGA. The thiosemicarbazone and its Zn (II) complexes showed growth inhibitory activity against Citrobactor, Acinetobactor Aspergillus Niger and Candida Albicans.

KEYWORDS N (4) thiosemicarbazone, ZnCl2,antioxidant activity,TGA.

Introduction

The biological properties of thiosemicarbazones and their metal complexes proved that the thiosemicarbazone molecules are planar and a pyridine ring or a NNS tridentate systems are present [1]. The biological activity depends on the parent aldehyde or ketone [2,3].The presence of a bulky group at the terminal nitrogen increases the activity [4].The biological properties of thiosemicarbazones get enhanced due to additional binding site and the presence of bulky group at N (4) position [5-7].The ability of thiosemicarbazone molecules to chelate with metal ions in the biological system is a reason for their biological activity. The lipophilicity, which controls the rate of entry into the cell, is modified on coordination with metal ions and some side effects may be decreased [8,9]. Thiosemicarbazones block DNA synthesis in mammalian cells by inhibiting the enzyme, ribo-nucleosidediphosphatereductase, by chelation with an iron ion required by the enzyme [10,11]. The capacity of thiosemicarbazones to sever the DNA strands have also been reported [12].

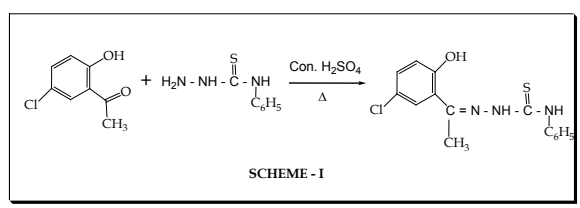
There are some types of cells in the human body which secrete zinc ions. Zinc supports human immune system [13], is needed for wound healing [14], helps to maintain the sense of taste and smell [15] and is needed for DNA synthesis. Zinc also helps in normal growth and development during pregnancy, childhood and adolescence period [16]. Zinc helps in living systems in the formation, growth and metabolism of cells, healing of wounds, activation and secretion of hormones, maintenance of neurotransmission system, ability of memory, stability of retina and crystalline lens, sensitivity in taste and smell, stabilization of cellular membranes, maintenance and activation of immune system, maintenance of normal alcohol metabolism, reduction of hazardous effect of heavy metals. The important features of zinc in these functions and its applications for medical uses are due to zinc ions have small radius and act as a Lewis acid. So it can play crucial role as a catalyst in hydrolysis reactions. The stability of zinc complexes with some ligands present in living system is moderately high. The Zn^{2+} ion is stable because of the fully occupied *3d* orbital, and it is maintained even in highly oxidizing and reducing environments.Zn^{2+} ions have high affinity to the coordinating atoms such as sulfur, nitrogen, and oxygen. Biological activity of thiosemicarbazones is increased on complexation [17], higher activity is with substitution at N(4) position [18].

In this research work the synthesis, spectral characterization and biological studies of six coordinate complexes of zinc (II) with 5-chloro 2-hydroxy acetophenone N (4) phenyl thisemicarbazone have been reported.

Experimental

Synthesis of thiosemicarbazone :

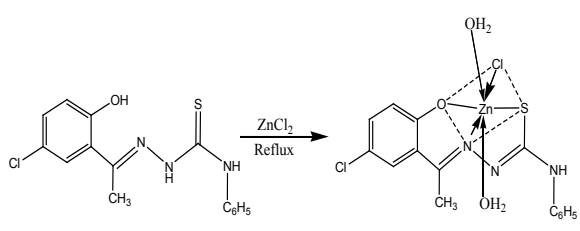
The thiosemicarbazone was synthesized by refluxing ethanolic solutions of 5-chloro 2-hydroxy acetophenone and N (4) phenyl thiosemicarbazide in the mole ratio 1:1 for 3 hours. The pale yellow product obtained after cooling was filtered and washed with hot water then cold ethanol and finally with diethyl ether. It was recrystalized from hot ethanol and dried over P_2O_5 in vacuum.



SCHEME - I

Synthesis of complex:

The complex was synthesized by refluxing ethanolic solutions of thiosemicarbazone, zinc chloride in ratio 1:1 for an hour on a hot water bath.The light yellow product thus obtained was fitered and washed well with hot water,cold absolute ethanol and then diethyl ether and dried over P_2O_5 in vacuum.



Scheme II

Synthesis of adducts:

The complex of the type Zn.L.B (B is heterocyclic base like pyridine, α-picoline, β-picoline,γ-picoline) was synthesized by adding slowly ehanolic solution of ZnCl2 ,heterocyclic base to the hot ehanolic solution of thiosemicarbazone in the mole ratio 1:1:1 and refluxing reaction mixture for one hour. The yellow adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P2O5 in vacuum.(B= pyridine,α-picoline,β-picoline,γ-picoline)

Physical measurements-

Magnetic moment was measured at room temperature by Faraday method. IR spectra were recorded in the range 4000-200 cm^{-1} range Thermo gravimetric analysis was carried out in the temp rnge 30-800°C. UV-Visible spectra were measured on Jasco UV-visible double beam spectrophotometer.Metal in the complex and adducts was estimated by standerdized E.D.T.A using Erichrome black-T as an indicator and PH-10 buffer

solution. Chloride in the complex was determined by Mohr's method.

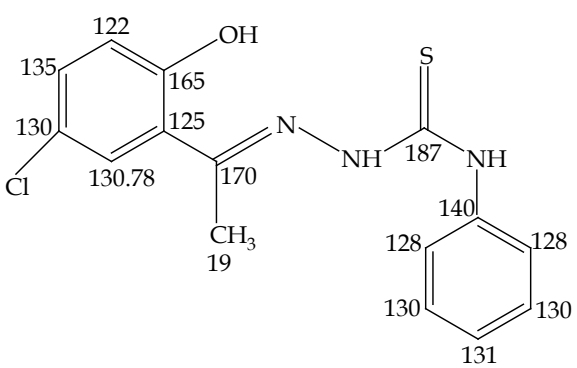
Physical properties:

1. L: Colour- Yellow, Empirical Formula- $C_{15}H_{14}N_3ClOS$.
2. Zn-L.Cl.$(H_2O)_2$:Colour-Yellow,Empirical Formula-$C_{15}H_{16}N_3O_3Cl_2SZn$,Molar conductance-8.40 $Ohm^{-1}cm^2mole^{-1}$, Magnetic Moment (B.M.)- Diamagnetic
3. Zn.L.Py.$(H_2O)_2$:Colour-Yellow,Empirical Formula-$C_{20}H_{21}N_4O_3ClSZn$, Molar conductance-12.20 $Ohm^{-1}cm^2mole^{-1}$, Magnetic Moment (B.M.)- Diamagnetic
4. Zn.α-Pico.$(H_2O)_2$:Colour-Yellow,Empirical ormula-$C_{21}H_{23}N_4O_3ClSZn$,Molar conductance-14.36 $Ohm^{-1}cm^2mole^{-1}$, Magnetic Moment (B.M.)- Diamagnetic
5. Zn.L.β-Pico.$(H_2O)_2$:Colour-Yellow,Empiricalformula-$C_{21}H_{23}N_4O_3ClSZn$,Molar conductance-16.58 $Ohm^{-1}cm^2mole^{-1}$, Magnetic Moment (B.M.)- Diamagnetic
6. Zn.L.γ-Pico.$(H_2O)_2$: Colour-Yellow,Empirical ormula-$C_{21}H_{23}N_4O_3ClSZn$,Molar conductance-19.33 $Ohm^{-1}cm^2mole^{-1}$, Magnetic Moment (B.M.)- Diamagnetic

^{1}H-NMR

NMR signals at 13.00 and 3.1 ppm are assigned to – OH and – CH_3 protons respectively. Absence of ^{2}NH proton signal suggests enolisation of ^{2}NH – C = S group to ^{2}N=C-SH. Signal at 3.9 ppm cooresponds to ^{4}NH Aromatic protons show multiples at 6.9, 7.20 , 7.60,7.65,7.77,7.30,6.20,7.29 ppm range.

^{13}C-NMR (DMSO-D_6): δppm 122 (C=C), 135 (C=C), 130 (C=C-Cl), 130.78 (C=C), 125(C=C),165 (C=C-OH),170 (C=N),19 (=C-CH_3),187 (C=S),140 (NH-C=C),128 (C=C),130 (C=C),131 (C=C),130 (C=C),128 (C=C).



(Calcd) found ESI-MS m/z, ion M^+ : $C_{15}H_{14}N_3ClOS$ (319.79) 319.05, $C_{15}H_{16}N_3O_3Cl_2SZn$ (454.66) 454.10, $C_{20}H_{21}N_4O_3ClSZn$ (498.30) 498.92, $C_{21}H_{23}N_4O_3ClSZn$ (512.33) 512.80, $C_{21}H_{23}N_4O_3ClSZn$ (512.33) 512.89, $C_{21}H_{23}N_4O_3ClSZn$ (512.33) 512.91.

Analytical data

1. **L:** % C 56.07 (56.33),% H 4.87 (4.41),% N 13.80 (13.14),% S 10.89 (10.03)
2. **Zn-L.Cl.$(H_2O)_2$:** % Zn 14.72 (14.38), %Cl 7.08 (7.80), %C 40.02 (39.62), %H 3.07 (3.55), %N 9.87 (9.24), %S 7.77 (7.05).
3. **Zn.L.Py.$(H_2O)_2$:** % Zn 13.91 (13.12), %C 48.70 (48.20), %H 4.78 (4.25), %N 11.64 (11.24), %S 7.12 (7.43).
4. **Zn.α-Pico.$(H_2O)_2$**: % Zn 12.26 (12.77), %C 49.81 (49.23), %H 4.12 (4.52), %N 10.32 (10.94), %S 6.71 (6.26).
5. **Zn.L β-Pico.$(H_2O)_2$**: % Zn 12.21 (12.77), %C 49.84 (49.23), %H 4.20 (4.52), %N 10.04 (10.94), %S 6.80 (6.26).
6. **Zn.L.γ-Pico.$(H_2O)_2$**: % Zn 12.30 (12.77), %C 49.25 (49.23), %H 4.02 (4.52), %N 10.10 (10.94), %S 6.90 (6.26).

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

Compound	Mode	MLCT	n→π*	π→π*
L	DMF	-	30800	35806
Zn-L.Cl.$(H_2O)_2$	DMF	25346	32416	34553
Zn.L.Py.$(H_2O)_2$	DMF	25453	32426	34536
Zn.α-Pico.$(H_2O)_2$	DMF	25336	32479	34564
Zn.L β-Pico.$(H_2O)_2$	DMF	25351	32480	34510
Zn.L.γ-Pico.$(H_2O)_2$	DMF	25425	32460	34565

Infrared Spectroscopic data (cm^{-1})

1. L: ν (- OH) 3340; ν (C = N) 1678; ν (- C = S) 790, 1375 ; ν (N – N) 1075; ν (^{2}N-H) 3240; ν (C – O) 1285.
2. **[Zn-L.Cl.$(H_2O)_2$]:** ν (C = N) 1585; ν (C = N-N=C) 1553, ν (C-S) 715, 1310,ν (N-N) 1135, ν(M - N) 475, ν (M-O) 535, ν (M-S) 330, ν (C - O) 1230, ν(H_2O) 840.
3. **[Zn.L.Py.$(H_2O)_2$]:** ν (C = N) 1590; ν (C = N-N=C) 1550, ν (C-S) 715, 1318; ν (N-N) 1125, ν (M - N) Base 270, ν (M - N) 470, ν (M - O) 539, ν (M-S) 332, ν (C - O) 1235, Band due to HB 1465, ν(H_2O) 860.
4. **[Zn.α-Pico.$(H_2O)_2$]:** ν (C = N) 1595; ν (C = N-N=C) 1555, ν (C-S) 720, 1319, ν (N-N) 1124, ν (M - N) Base 279, ν (M - N) 475, ν (M - O) 530, ν (M-S) 335, ν (C - O) 1238, Band due to HB 1470, ν(H_2O) 880.
5. **[Zn.L β-Pico.$(H_2O)_2$]:** ν (C = N) 1597; ν (C = N-N=C) 1558, ν (C-S) 726, 1310,ν (N-N) 1125, ν (M - N) Base 280, ν (M - N) 479, ν (M - O) 538, ν (M-S) 338, ν (C - O) 1240, Band due to HB 1473, ν(H_2O) 890.
6. **[Zn.L.γ-Pico.$(H_2O)_2$]:** ν (C = N) 1590; ν (C = N-N=C) 1560, ν (C-S) 722, 1318,ν (N-N) 1129, ν (M - N) Base 278, ν (M - N) 480, ν (M - O) 539, ν (M-S) 340, ν (C - O) 1239, Bands due to HB 1475, ν(H_2O) 885.

TGA analysis data:

1. **[Zn-L.Cl.$(H_2O)_2$]**: First step, 112 °C, Mass loss 7.95 % second step, 210 °C, Mass loss, 30.22 % Third Step 360.40 °C, Mass loss, 40.23 % Fourth Step, 660.66 °C, Mass loss 63.5 %, Residue 778 °C, % of ZnO, 17.08 (17.90).
2. **[Zn.L.Py.$(H_2O)_2$]:**First step, 113 °C, Mass loss 7.26 % second step,200 °C, Mass loss, 32.39 % Third Step 360 °C, Mass loss, 41.02 % Fourth Step, 670.30 °C, Mass loss, 64.01 %, Residue, 779 °C, % of ZnO, 16.81 (16.34).
3. **[Zn.α-Pico.$(H_2O)_2$]:** First step, 114 °C, Mass loss 7.08 % second step,230 °C, Mass loss, 30.26 % Third Step 365 °C, Mass loss, 40.46 % Fourth Step, 670.15 °C, Mass loss 63.5 %, Residue 778 °C, % of ZnO, 15.10 (15.89).
4. **[Zn.L β-Pico.$(H_2O)_2$]:**First step, 114 °C, Mass loss 7.06 % second step, 232 °C, Mass loss, 32.25 % Third Step 362 °C, Mass loss, 40.02 % Fourth Step, 671 °C, Mass loss, 62.28 %, Residue, 778 °C, % of ZnO, 15.18 (15.89).
5. **[Zn.L.γ-Pico.$(H_2O)_2$]:**First step, 113 °C, Mass loss 7.08 % second step, 230.22 °C, Mass loss, 32.25 % Third Step 365 °C, Mass loss, 40.28 % Fourth Step, 670 °C, Mass loss 61.78 %, Residue 780 °C, % of ZnO, 15.20 (15.89).

Antimicrobial Assay (Well diffusion method)

Table.2 % Activity index of L , Zn (II) complexes and standered

Compound % Activity Index	*Citrobactor*		*Acinewbacior*		*Asper gillus Nigar*		*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	23.28	20.30	42.12	35.30	56.63	42.32	65.68	51.03
Zn-L.Cl.$(H_2O)_2$	46.114	35.28	50.12	35.63	69.24	63.23	83.33	65.10
Zn.L.Py.$(H_2O)_2$	50.90	41.86	52.03	37.71	73.22	68.20	85.36	67.13

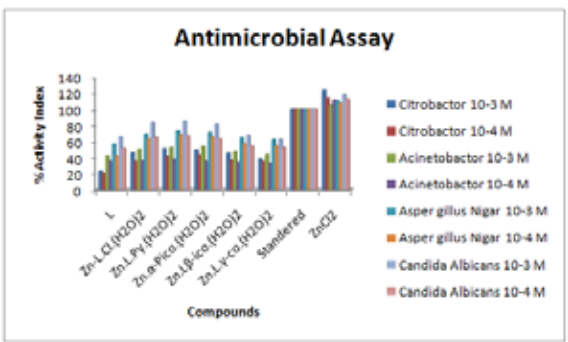
Zn.α-Pico.$(H_2O)_2$	49.26	43.69	53.64	35.42	71.25	65.73	81.11	63.11
Zn.L.β-ico.$(H_2O)_2$	45.21	36.38	47.24	34.42	64.61	56.91	67.35	54.34
Zn.L.γ-co.$(H_2O)_2$	38.14	35.11	44.14	33.12	62.12	54.12	62.41	52.00
Standered	100	100	100	100	100	100	100	100
$ZnCl_2$	123.5	113.57	104.35	111.32	110.22	107.08	118.33	112.23

(Standered -Cefodoxine,Fluconazole)

% 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 Antimicrobial Assay



Results and discussion

It is found that the molar conductance values of the complexes in DMF (10^{-3}M) at room temperature are in the range of 8-20 ohm-1cm^2 mol^{-1}. Very low values indicate that these complexes behave as non electrolytes in DMF and are neutral in nature [19]. The complexes are colored, non hygroscopic and are stable in air . They are insoluble in water and slightly soluble in ethanol, methanol and completely soluble in DMF.

Elemental analysis data are consistant with 1:1 mole ratio of metal ion, thiosemicarbazone for complex and 1:1:1 mole ratio for metal, thiosemicarbazone and heterocyclic base for all adducts. The magnetic moments were measured at room temperatur by Faraday method showed diamagnetic behavior expected for d^{10} configuration. Mass spectral data confirmed the structure of the thiosemicarbazone and complexes as indicated by molecular ion peak (M + 1) corresponding to their molecular weights.

UV-visible spectra were measured in DMF (Table 1). The UV-visible spectrum depends on the energy of metal d orbitals, their degeneracy and the number of electrons distributed in these orbitals.It is controlled by the oxidation state of the metal, number and kind of the ligand and the geometry of the complex [20].The electronic spectrum of thiosemicarbazone showed π- π* transition band [21-23] at 35,860 cm-1 and n- π*transition band[24,25] at 30,800 cm^{-1}. The d-d bands are not observed in the spectra of complexes. The π- π*absorption bands are shifted to higher energy side in complexes due to the weakening of the C=S bond and conjugation system gets enhanced upon complexation [26,27]. The lone pair of electrons is transfered to the metal ion on complexation.As a result of this,there is reduction in intensity of n- π* transition indicating coordination of azomethine nitrogen. MLCT bands in the complexes are found in the range 25000-26000 cm^{-1} which are assignable to Zn→S transitions.

The shifting of ν(^{7}C=N^1) to the lower side indicating coordination of the azomethine nitrogen [28]. The new band in the range 470-480 cm^{-1} confirms the coordination of azomethine nitrogen [29,30]. The increase in ν(^{1}N-^{2}N) may be due to the increase in double bond character off-sets the loss of electron density via donation to the metal. This confirms the coordination through the azomethine nitrogen atom. The band ^{2}N-H of thiosemicarbazone disappears in the complexes due to the deprotonation of the ^{2}N-H . Thiosemicarbazone shows ν(C=S) band at 1360 and 785cm^{-1}, shifted to lower side in complexes indicating coordination through thiolate sulfur [31].The appearance of new band in the range 330-340 is due to participation of thiolet sulfur. The phenolic oxygen occupies the third coordination on loss of OH proton.This shifts ν(C-O) band 1290 cm^{-1}in uncomplexed thiosemicarbazone to lower side in the complexes. The apperence of new band in complexes in the range 525-540 cm^{-1} is due to Zn-O confirmed coordination through oxygen. The heterocyclic base nitrogen atom occupies fourth coordination site in adducts. The band in the range 275-280 cm^{-1} is assigned for ν (Zn-N).The bands due to coordinated heterocyclic bases have also been observed in IR spectra of all complexes [32-34].Bands approximately at 870-950cm^{-1} suggests the coordination of water molecules in the complexes.

The prepared complexes were subjected to thermal analysis. Mass loss considerations of the decomposition indicate that the complexes have been converted to corresponding metal oxides. The curves were recorded in the temperature range 30-800^{0}C. Hydrations of water molecules were lost in between 30-110^{0}C. The two coordinated water molecules were lost in the temperature range 112-115^{0}C.At this stage corresponding mass loss is about 7-8 %.This confirms the coordination of two water molecules.The coordination of water molecules in all complexes is same. No change is observed up to ~ 200^{0}C. There is break in the curves due to evaporation of a molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 600-700^{0}C. Finally the metal oxides were formed above 700^{0}C. The decomposition was complete and metal oxide is formed at ~ 780^{0}C.The complexes decompose in steps. It is found that the coordination of metal ion to ligand is responsible for thermal stabilities of metal complexes [35].

The antibacterial activity was determined using the well diffusion method. Biological activity was measured in two different molar concentrations ,10^{-3}M, 10^{-4} M. The results of antibacterial activity study for compounds indicated that the new molecules exhibited antibacterial activity against the bacteria at low and high concentrations. The adducts showed maximum activity against bacterial and fungal species than free ligand and Zn.L.Cl.$(H_2O)_2$ complex. The increased activity of the synthesized compounds may be due to electron delocalization over the whole molecule. This increases the lipophilic character of the molecule and favors its permeation through the lipoid layer of the bacterial membranes. The increased lipophilic character of this molecule may be responsible for its enhanced potent antibacterial activity. The thiosemicarbazone was found less active than its zinc complex and adducts.Lipophilicity is an important factor to control the antifungal activity.The delocalization of π-electrons increases lipophilicity and this facilitates the penetration into lipid membranes, further restricting proliferation of the microorganisms [36]. In complexes coordination number increases which increases antimicrobial activity.*Acinetobactor* and *Citrobactor* are gram –ve bacterial species. In gram negative bacteria the outer membrane is thin and they possess outer membrane. So, it might not be easy for the complexes to diffuse inside the bacterial cell. The zinc chloride salts were found more effective than complexes. The Zn^{2+} ions have small size having d^{10}configuration. This increases the permeability to cell membrane..But use of metal ion solution to treat bacterial and fungal diseases is toxic,so it can be used in coordination with ligand. The general sequence of % activity index can be represented as -

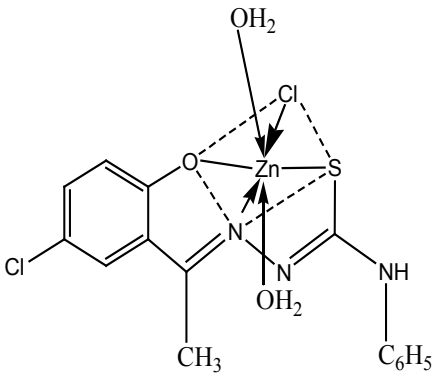
Metal salt > Standard > complexes > ligand.

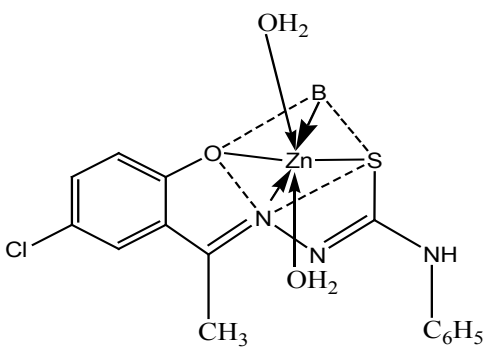
The % activity index decreases on dilution ie it is more in concentrated solution.

Conclusion: Ligand shows tridentate nature in each complex. It is coordinated to metal ion through phenolate oxygen,a-

zomethine nitrogen and thiolet sulfur.The fourth coordination site is occupied by chlorine atom in complex and heterocyclic base in adducts.TGA and IR spectra confirm the coordination of two water molecules.The synthesized complex and adducts showed good inhibitory activity against bacterial and fungal species.

Expected structure





(B = pyridine, α-picoline, β-picoline,γ-picoline)

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