

Biological Evaluation of Six Coordinate Cd (II) Complexes of N (4) Methyl Thiosemicarbazone

J.R.Gujarathi

Associate Professor, Department of Chemistry, *Pratap College, Amalner (M.S.), India

ABSTRACT: Thiosemicarbazone and Cd (II) complexes were synthesized and characterized by means of Elemental analysis,ESI-MS, Fourier Transform Infrared (FT-IR) spectroscopy,Uv-visible spectra, Nuclear Magnetic Resonance (¹HNMR and ¹³CNMR) spectroscopy,room temperature magnetic moment and conductivity.5-chloro 2-hydroxy acetophenone N (4) methyl thiosemicabazone was synthesized by refluxing ketone and thiosemicarbazide in the mole ratio 1:1.The metal complexes and their corresponding thiosemicabazone were tested for bacterial species. It was found that the cadmium complexes synthesized exhibited better bacterial activity than corresponding thiosemicarbazone.

KEYWORDS: Metal salts,Bioactive Cd (II) complexes,antimicrobial activity

I. INTRODUCTION

The thiosemicarbazones molecules have ability to chelate with traces of metals in the biological system and this is a reason for their biological activity. A great clinical challenge in the treatment of cancer with anticancer drugs is that certain tumour cells develop a particular phenotype called multi drug resistance, which makes these cells resistant to other classes of anticancer agents [1]. The palladium complex of phenanthrenequinone thiosemicarbazone has been found potent neoplastic agent possessing selective activity against tumour cells. It is also found effective against drug resistant breast cancer cells [2]. The antitumour activities of Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ chelates of antracene-9-carboxaldehyde thiosemicarbazone and cytotoxic activity of phenyl glyoxal bis (thiosemicarbazone) against Ehrlich ascites carcinoma cells have been studied and reported [3]. Earlier research revealed that the biologically active thiosemicarbazone molecules were planar consisting of pyridine ring or a NNS tridentate system [4]. The biological activity of thiosemicarbazones is also depended on parent aldehyde or ketone [5, 6]. The presence of a bulky group at the terminal nitrogen raises the activity [7]. The presence of bulky groups at the N (4) position of the thiosemicarbazone moiety together with an additional binding site greatly affects biological activity [8-10]. In recent years the biological and medicinal properties of transition metal complexes of thiosemicarbazones, Pd (II) and Pt (II) complexes of 5-chlorosemicarbazones, Pd (II) and Pt (II) complexes of 5-chloro 1-3-dihydro-3-[2-(phenyl)-ethylidene]-2H-indol-2-one-hydrazine carbothiomide have been studied, synthesized and tested for their antimicrobial activity.The results showed that the compounds exhibit antimicrobial properties and the metal chelates show better inhibitory effects than the parent ligands. The study suggests the increased lipophilic character of these complexes may be responsible for their enhanced biological potency [11].

In this research article the synthesis, spectral characterisation and antimicrobial study of six coordinate complexes of Cd (II) with 5-dichloro 2-hydroxy acetophenone N (4) methyl thiosemicarbazone have been reported.

II. LITERATURE SERVE

The biological activity of the two ligands (benzaldehydethiosemicarbazone- BTSC and 3,4-dimethoxybenzaldazine-DMBA) and their zinc(II)-, cadmium(II)- and mercury(II)- complexes having the formula M₂(BTSC)₂(DMBA)₂X₄ and M(BTSC)(DMBA)X (where BTSC=deprotonated BTSC ligand; M = Zn²⁺, Cd²⁺, or Hg²⁺; X = NO₃⁻ or Cl⁻ or I⁻) in dimethylsulphoxide solution have been evaluated [12].Two cobalt(II) complexes [Co(QCT)₂].Cl.1.5H₂O (QCT = quinoline-2-carboxaldehyde thiosemicarbazone) and [Co(QCMT)(CH₃OH)Cl₂] (QCMT = quinoline-2-

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carboxaldehyde N^4 -methyl-thiosemicarbazone) have been synthesized [13]. A series of copper (II) benzoylpyridine thiosemicarbazone complexes have been synthesized and characterized [14]. 2-(2-imino-1-methylimidazolidin-4-ylidene)hydrazinecarbothioamide (IMHC) was synthesized by the reaction of creatinine with thiosemicarbazide [15].

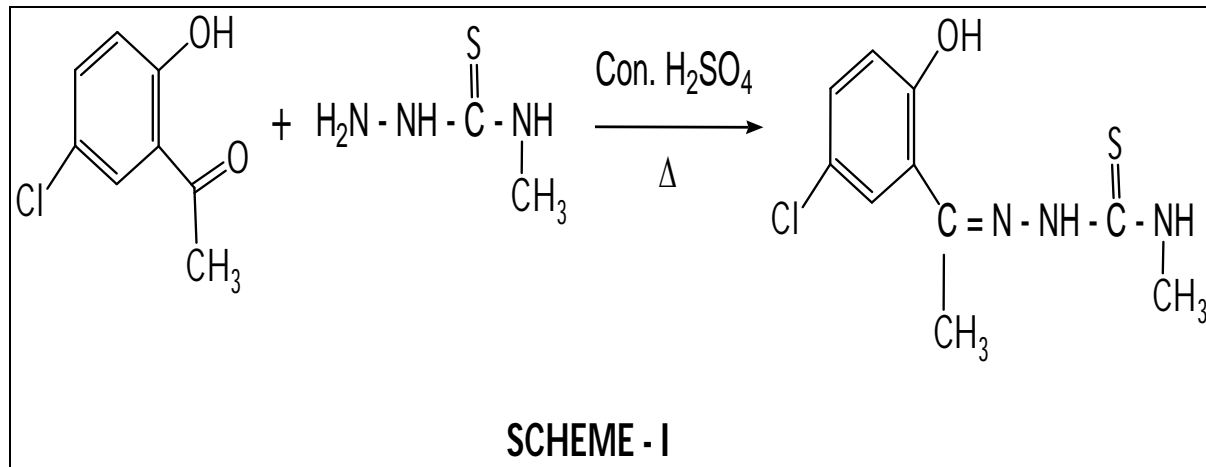
III. MATERIALS AND METHODS

All the chemicals used are of A.R. grade. Magnetic susceptibility measurement was carried out by Faraday method at room temperature. IR spectra were recorded in solid state in the range 4000-200 cm^{-1} range. 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. Thermal analysis was carried out in the temperature range 22-800°C. Metal in the complex and adducts was estimated by standardized E.D.T.A . Mohr's method was used to estimate chloride in the complex.

IV. EXPERIMENTAL

Synthesis of thiosemicarbazone :

Hot ethanolic solutions of 5-chloro 2-hydroxy acetophenone (0.01 mole) and N (4) methyl thiosemicarbazide (0.01 mole) in the mole ratio 1:1 were mixed and the reaction mixture was refluxed for three hours. On cooling the pale yellow product was filtered and washed with hot water then cold ethanol and finally with diethylether. The compound was then purified in ethanol and dried in vacuum.



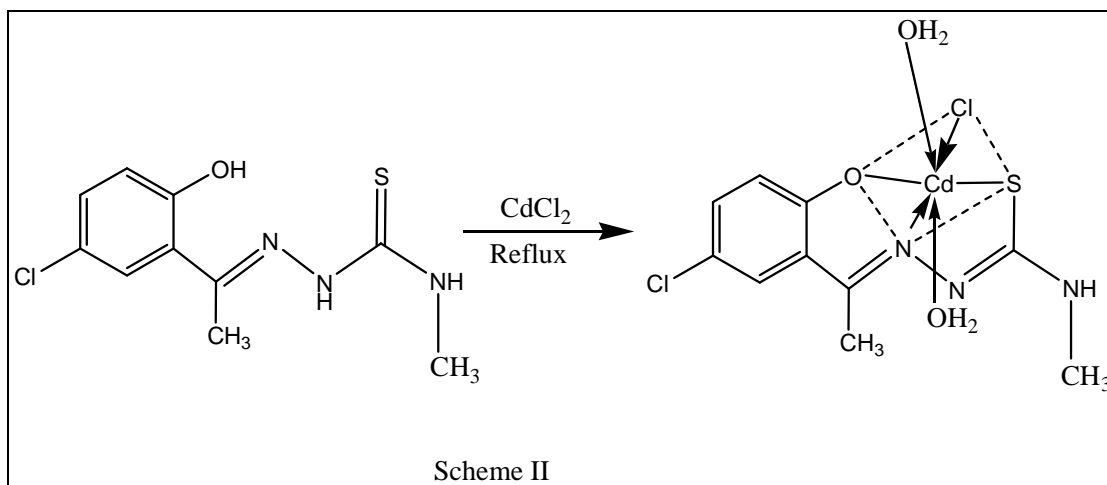
Synthesis of complex M:L:

The complex of the type $\text{M.L.Cl.}(\text{H}_2\text{O})_2$ was synthesized by refluxing hot ethanolic solutions of thiosemicarbazone (0.01mole) and $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ (0.01 mole) in the mole ratio 1:1 for two hours. On cooling the light yellow product was filtered and washed with hot water, cold absolute ethanol and then ether and dried in vacuum.

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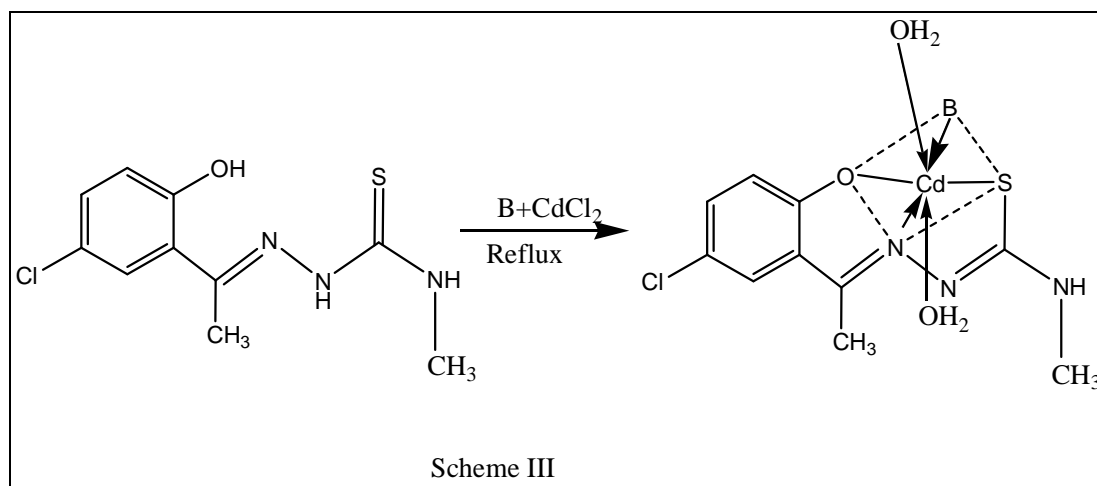
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Synthesis of adducts:

The complexes of the type Cd.L.B (B is heterocyclic base like pyridine, 2-chloro pyridine, 3-chloro pyridine, 4-chloro pyridine) were synthesized by refluxing ethanolic solutions of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.01 mole), heterocyclic base (0.01 mole) and N (4) methyl thiosemicarbazone (0.01 mole) in the ratio 1:1:1 for four hour. On cooling the yellow product was filtered and washed with hot water, cold ethanol and diethyl ether and dried in vacuum.



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

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TABLE 1 PHYSICAL PROPERTIES:

Compounds	Colour	Empirical Formula	Molar conductance Ohm ⁻¹ cm ² mole ⁻¹	Magnetic Moment B.M.
L	Yellow	C ₁₀ H ₁₂ N ₃ O ₃ OSCl	-	-
Cd-L.Cl.(H ₂ O) ₂	Yellow	C ₁₀ H ₁₄ N ₃ O ₃ SCl ₂ Cd	30.4	Diamagnetic
Cd.L.Py.(H ₂ O) ₂	Yellow	C ₁₅ H ₁₉ N ₄ O ₃ SClCd	35.7	Diamagnetic
Cd.2-Cl.py.(H ₂ O) ₂	Yellow	C ₁₅ H ₁₈ N ₄ O ₃ SClCd	38.6	Diamagnetic
Cd.3-Cl.py.(H ₂ O) ₂	Yellow	C ₁₅ H ₁₈ N ₄ O ₃ SClCd	33.4	Diamagnetic
Cd.4-Cl.py.(H ₂ O) ₂	Yellow	C ₁₅ H ₁₈ N ₄ O ₃ SClCd	32.5	Diamagnetic

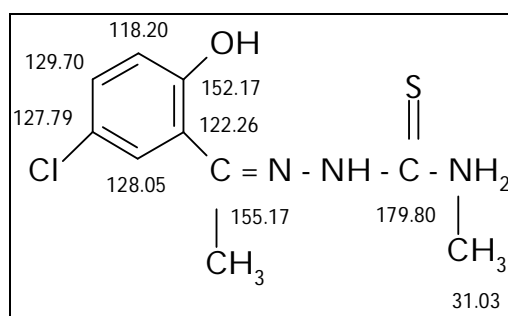
Physical properties of thiosemicarbazone and its complexes are presented in Table 1. The complexes are soluble in DMF in which conductivity measurements were carried out (25^oC), showing all complexes are non electrolyte in nature [16]. The magnetic moment measurement was carried out by Faraday method at room temperature showed diamagnetic behavior expected for d¹⁰ configuration.

¹H-NMR

NMR signals at 13.00 and 3.00 ppm are assigned to – OH and – CH₃ protons respectively. The signals at 2.19, 2.25 correspond to ⁴NH and H⁴N-CH₃ respectively. Absence of ²NH proton signals suggests enolisation of ²NN – C = S group to ²N = C – SH. Aromatic protons show multiplet at 6.9, 7.255, 7.45, ppm range.

¹³C-NMR (DMSO-D₆): 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- CH₃)



(Calcd) found ESI-MS m/z, ion M⁺

C₁₀H₁₂N₃O₃OSCl (257.91) 257.10, C₁₀H₁₄N₃O₃SCl₂Cd (439.37) 439.91, C₁₅H₁₉N₄O₃SClCd (482.84) 482.10, C₁₅H₁₈N₄O₃SCl₂Cd (517.28) 567.72, C₁₅H₁₈N₄O₃SCl₂Cd (517.28) 517.72, C₁₅H₁₈N₄O₃SCl₂Cd (517.28) 517.77.

The structure of the thiosemicarbazone and complexes is confirmed from Mass spectral data as indicated by molecular ion peak (M + 1) corresponding to their molecular weights.

V. ANALYTICAL DATA

- L:** % C 46.72 (46.57), % H 4.05 (4.69), % N 16.96 (16.36), % S 12.01 (12.43)
- Cd-L.Cl.(H₂O)₂:** % Cd 27.11 (27.77), % Cl 8.91 (8.07), % C 27.10 (27.53), % H 3.81

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(3.21), % O 10.21 (10.92) %N 9.97 (9.60), %S 6.99 (7.30).

3. **Cd.L.Py.(H₂O)₂**: % Cd 23.78 (23.20), %C 37.84 (37.31), %H 3.10 (3.97), %N 11.02,O 9.12 (9.94), %S 6.19 (6.64).

4. **Cd.2-Cl.py.(H₂O)₂**: % Cd 21.07 (21.65), %C 34.07 (34.83), %H 3.03 (3.51),% O 9.72 (9.29) %N 10.21 (10.83), %S 6.20 (6.83).

5. **Cd.3-Cl.py.(H₂O)₂** % Cd 21.15 (21.65), %C 34.11 (34.83), %H 3.81 (3.51), % O 9.81(9.29) %N 9.20 (10.83), %S 6.10 (6.83).

6. **Cd.4-Cl.py.(H₂O)₂**: % Cd 21.18 (21.65), %C 34.13 (34.83), %H 3.09 (3.51),% O 9.55 (9.29) %N 10.25 (10.83), %S 6.09 (6.83).

Analytical data showed that the calculated and experimental percentages are matched and hence confirmed 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.

VI. INFRARED SPECTROSCOPIC DATA (cm⁻¹)

1.L: ν (- OH) 3225; ν (C = N) 1638; ν (- C - S) 795, 1358; ν (N - N) 1049; ν (²N-H) 2925; ν (C - O) 1388.

2 Cd.L.Cl.(H₂O)₂: ν (C = N) 1555; ν (C = N-N=C) 1520, ν (C-S) 710, 1305, ν (N-N) 1145, ν (M - N) 420, ν (M-O) 520, ν (M-S) 320, ν (C - O) 1215, ν (H₂O) 3400,3500.

3 Cd.L.Py.(H₂O)₂: ν (C = N) 1560; ν (C = N-N=C) 1525, ν (C-S) 715, 1310; ν (N-N) 1150, ν (M - N) Base 250, ν (M - N) 425, ν (M - O) 525, ν (M-S) 325, ν (C - O) 1220, Band due to HB 1410, ν (H₂O) 3420,3520.

4. Cd.2-Cl.py.(H₂O)₂: ν (C = N) 1565; ν (C = N-N=C) 1530, ν (C-S) 720, 1315, ν (N-N) 1155, ν (M - N) Base 260, ν (M - N) 430, ν (M - O) 530, ν (M-S) 345, ν (C - O) 1225, Band due to HB 1420, ν (H₂O) 3430,3530.

5. Cd.3-Cl.py.(H₂O)₂: ν (C = N) 1570; ν (C = N-N=C) 1540, ν (C-S) 730, 1325, ν (N-N) 1160, ν (M - N) Base 260, ν (M - N) 435, ν (M - O) 535, ν (M-S) 350, ν (C - O) 1230, Band due to HB 1425, ν (H₂O) 3435,3540.

6. Cd.4-Cl.py.(H₂O)₂: ν (C = N) 1580; ν (C = N-N=C) 1545, ν (C-S) 735, 1335, ν (N-N) 1170, ν (M - N) Base 270, ν (M - N) 440, ν (M - O) 550, ν (M-S) 360, ν (C - O) 1240, Bands due to HB 1430, ν (H₂O) 3440,3550.

The bands in IR spectra due to ν (N-H) appear at 2925 cm⁻¹ for thiosemicarbazone, disappeared in the spectra of all the complexes. The band at 1638 cm⁻¹ due to ν (C = N) of the thiosemicarbazone shifted to lower side upon coordination. This shows the coordination of azomethine nitrogen. The presence of a band in the range 420-440cm⁻¹, assignable to ν (Cd-N) for the complexes confirm the coordination of azomethine nitrogen. A shift in the absorption bands due to the ν (N- N) from 1049 cm⁻¹ to higher region is due to the increase in double bond character off-setting the loss of electron density via donation to the metal. This also confirms the coordination through the azomethine nitrogen. The coordination via thiolate sulfur is indicated by decrease ν (C=S). The bands at 320-360 cm⁻¹ assignable to ν (Cd-S) in the complexes confirm sulfur coordination. The peaks observed in the range 520-550 cm⁻¹ are due to the Cd-O (phenolic) bond. This is indicated by decrease in ν (C-O).

VII ELECTRONIC SPECTRAL DATA (cm⁻¹):

Compound	State	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	MLCT
L	DMF	37240	30150	-
Cd-L.Cl.(H ₂ O) ₂	DMF	32100	28200	22030
Cd.L.Py.(H ₂ O) ₂	DMF	32210	28180	22100
Cd.2-Cl.py.(H ₂ O) ₂	DMF	32150	28150	22150
Cd.3-Cl.py.(H ₂ O) ₂	DMF	32170	28130	24500
Cd.4-Cl.py.(H ₂ O) ₂	DMF	32180	28120	24300

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The ligand and charge transfer transitions are presented in table No.1. The spectra are recorded in DMF. The bands in the thiosemicarbazone are 37240 and 30150 cm^{-1} . These are assignable to $\pi \rightarrow \pi^*$ transitions of phenyl ring [17-19] and $n \rightarrow \pi^*$ transitions of azomethine and thioamide [20,21]. The energy of these bands is shifted on complexation. The shifting of $\pi \rightarrow \pi^*$ transition to higher side is due to C=S bond which is weakened and the conjugation system becomes enhanced on complexation [22]. The $n \rightarrow \pi^*$ bands in the complexes are due to donation of lone pair of electrons to the metal. The broad bands in the complexes in the region 22100-24500 cm^{-1} are due to Cd-S transitions.

VIII. THERMAL GRAVIMETRIC ANALYSIS DATA

1. **Cd-L.Cl.(H₂O)₂**: First step, 115 °C, Mass loss 8.50 % second step, 210 °C, Mass loss, 25.50 % Third Step 340 °C, Mass loss, 50.25 % Fourth Step, 640°C, Mass loss 65.5 %, Residue 800 °C, % of CdO, 29.92 (29.13).
2. **Cd-L.Py.(H₂O)₂**: First step, 114 °C, Mass loss 7.96 % second step, 230 °C, Mass loss, 26.30 % Third Step 350 °C, Mass loss, 70.02 % Fourth Step, 650 °C, Mass loss, 70.00 %, Residue, 800 °C, % of CdO, 26.98 (26.51).
3. **Cd-2-Cl.py.(H₂O)₂**: First step, 114 °C, Mass loss 6.96 % second step, 240 °C, Mass loss, 27.10 % Third Step 360 °C, Mass loss, 72.40 % Fourth Step, 660 °C, Mass loss 75.5 %, Residue 800 °C, % of CdO, 24.03 (24.74).
- 4 **Cd-3-Cl.py.(H₂O)₂**: First step, 115 °C, Mass loss 6.90 % second step, 245 °C, Mass loss, 30.25 % Third Step 370 °C, Mass loss, 75.02 % Fourth Step, 670 °C, Mass loss, 80.27 %, Residue, 790 °C, % of CdO, 24.03 (24.74).
- 5 **Cd-4-Cl.py.(H₂O)₂**: First step, 116 °C, Mass loss 6.60 % second step, 250 °C, Mass loss, 32 % Third Step 375 °C, Mass loss, 80.28 % Fourth Step, 675 °C, Mass loss 82.70 %, Residue 800 °C, % of CdO, 24.08 (24.74).

The hydrated water layer was removed below 100°C. There are two water molecules in the complexes in coordination. These two coordinated water molecules were eliminated at relatively temperature less than 117°C. The two coordinated water molecules in complexes were removed in one step. The decomposition proceeded in four steps. The compounds are stable up to about 250°C. The complexes containing pyridine are more stable. The decomposition took place in three steps after the removal of coordinated water molecules in complexes. In the second step the loss is up to 32%. The organic molecule in coordination lost up to 675°C. The mass lost corresponding to this step is about 80%. The decomposition was complete and metal oxide was formed at a temperature about 800 °C. It is concluded that increase in coordination number in the complexes may be responsible for the thermal stability.

IX BIOLOGICAL ACTIVITY (AGAR PLATE DIFFUSION METHOD)

Table.4 Minimum Inhibitory concentration L , Cd (II) complexes and standard

Compound	<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>		<i>Escherichia Coli</i>		<i>Pseudomonas aeruginosa</i>	
	Gram positive				Gram negative			
	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml
L	0.74	0.53	0.73	0.55	0.76	0.59	0.78	0.58
Cd-L.(H ₂ O) ₃	0.61	0.33	0.63	0.25	0.64	0.22	0.65	0.23
Cd-L.Py.(H ₂ O) ₂	0.63	0.28	0.59	0.22	0.63	0.20	0.60	0.21
Cd-2-Cl.py.(H ₂ O) ₂	0.64	0.26	0.56	0.21	0.61	0.21	0.59	0.20
Cd-3-Cl py.(H ₂ O) ₂	0.63	0.27	0.54	0.22	0.62	0.20	0.58	0.22
cd-4-Cl py.(H ₂ O) ₂	0.65	0.24	0.53	0.23	0.63	0.21	0.55	0.20
CdCl ₂ .2.5H ₂ O	0.22	0.15	0.24	0.16	0.13	0.22	0.11	0.24
Standard	0.15	0.11	0.15	0.14	0.25	0.12	0.15	0.12

(Std-Amphiciline)

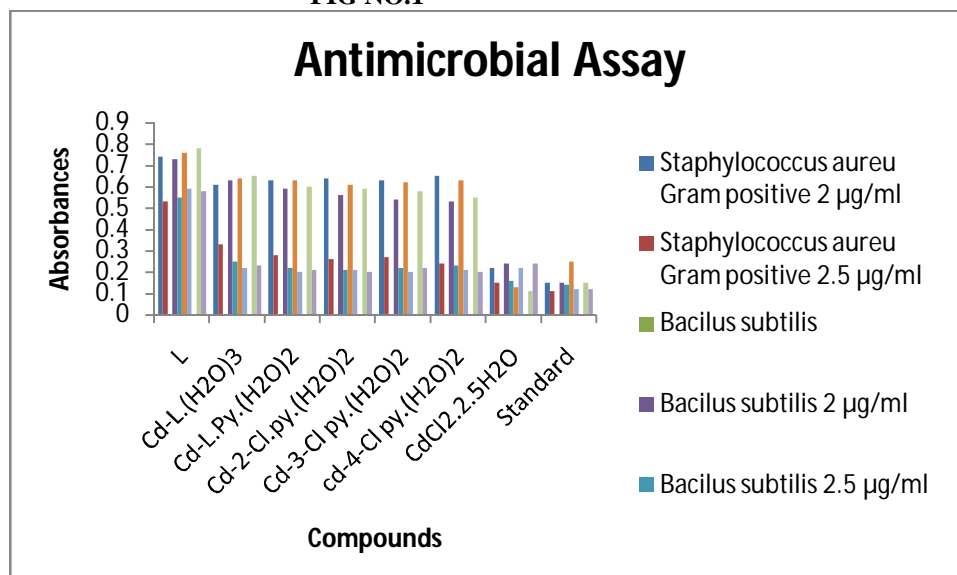
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The antimicrobial assay was carried out by agar plate. The complexes containing heterocyclic bases exhibited better activity against bacterial species than thiosemicarbazone. The solutions of thiosemicarbazone and complexes with 2 $\mu\text{g/ml}$, 2.5 $\mu\text{g/ml}$ and 3 $\mu\text{g/ml}$ concentrations were prepared in DMF. The solution of standard drug ampicillin was also prepared in the same concentration. Inoculums of the overnight culture were prepared. 0.2 ml of the inoculums was added to the test tubes containing the solutions of the compounds of different concentrations. After the addition of sterile water to each of the test tubes, these were incubated for 24 hours and observed for turbidity. The absorbance of the turbid solutions was measured at 520 nm. The same method was used for standard Ampicillin [23]. More absorbance was observed at 2 $\mu\text{g/ml}$ the absorbance is more. Less absorbance was observed at 2.5 $\mu\text{g/ml}$ and no absorbance at 3 $\mu\text{g/ml}$. The inhibitory activity is more at 2.5 $\mu\text{g/ml}$. The metal salt solution showed better inhibition than ligand and complexes. The inhibitory concentration is 2.5 $\mu\text{g/ml}$. The free metal is more effective than complexes. Thus increase in coordination number in complexes and heterocyclic bases increase microbial activity.

FIG NO.1



The above bar graph shows less absorbances at the higher concentration. The metal salts solution showed more inhibitory activity than the complexes. At higher concentration complexes containing heterocyclic bases showed more inhibitory activity than the complex.

X. CONCLUSION

The synthesized thiosemicarbazone is tridentate ONS donor. The spectral data indicate octahedral geometry for complexes. The complexes are found diamagnetic. Thermal analysis indicates two water molecules in coordination. The compounds are thermally stable up to 250⁰C. The decomposition took place in four steps. The complex showed growth inhibitory activity against gram +ve bacterial species. The absorbances are more at 2 $\mu\text{g/ml}$ concentration than 2.5 $\mu\text{g/ml}$ concentration.

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