

Antioxidant Screening of Cr (III) Complexes Derived from Thiosemicarbazone and N (4) Thiosemicarbazone

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ABSTRACT: Thiosemicarbazone and N (4) thiosemicarbazone were synthesized by refluxing 5-chloro 2-hydroxy acetophenone and thiosemicarbazide in the mole ratio 1:1. The complexes of thiosemicarbazone with Cr (III) chloride were synthesized by refluxing thiosemicarbazone and Cr (III) chloride in the mole ratio 1:3. The thiosemicarbazones and complexes were characterized by means of Elemental analysis, ESI-MS, FT-IR spectroscopy, UV-Visible spectra, EPR spectra, Nuclear Magnetic Resonance (¹H-NMR and ¹³C-NMR) spectroscopy magnetism and conductivity measurement. The metal complexes and thiosemicarbazone were tested against bacterial parasites. The free radical scavenging activity of synthesized compounds was screened for antioxidant activity. It was found that the chromium complexes are more biologically active than thiosemicarbazone.

KEYWORDS: Bioactive metal complexes, EPR, antimicrobial activity, antioxidant activity, 1:3 ratio

I. INTRODUCTION

Thiosemicarbazones and their metal complexes have been studied widely as they generate through a variety of biological properties such as anticancer, antitumour, antifungal, antibacterial, antimalarial, antitubercular, antiviral and anti-HIV activities [1-8]. Earlier research revealed that the biologically active thiosemicarbazone molecules were planar consisting of pyridine ring or a NNS tridentate system [9]. The biological activity of thiosemicarbazones is also depended on parent aldehyde or ketone [10, 11]. The presence of a bulky group at the terminal nitrogen raises the activity [12]. The presence of bulky groups at the N (4) position of the thiosemicarbazone moiety together with an additional binding site greatly affects biological activity [13-15]. In recent years the biological and medicinal properties of transition metal complexes of thiosemicarbazones, Pd (II) and Pt (II) complexes of 5-chloro thiosemicarbazones, Pd (II) and Pt (II) complexes of 5-chloro 1-3-dihydro-3-[2-(phenyl)-ethylidene]-2H-indolizine-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 [16].

II. LITERATURE SURVEY

The stereochemistry of many Cr (III) complexes have been studied [17-22]. Many Cr (III) complexes are known to exhibit fluorescence and or phosphorescence. Luminescence studies of Cr (III) complexes have been of significant importance in understanding of their stereochemistry. J.R. Perumareddi [23] summarized the theory of cubic and non-cubic ligand fields on Cr (III) complexes. The structure of the two six coordinate paramagnetic complexes of Ni (II) with tridentate thiosemicarbazones of isoquinoline-1-carboxaldehyde and pyridine-2-aldehyde have been determined [24,25]. Chromium finds applications in biological systems wherein Cr (III) ion is required in trace amounts for sugar and lipid metabolism [26]. Chromium activates enzymes, maintains protein stability and enhances carbohydrate metabolism [27-30]. Chromium compounds may lower the glucose levels in diabetic patients [31].

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Considering the above applications it is desirable to synthesize and characterize the Cr (III) complexes with Schiff base. The present research work reports the synthesis, spectral characterisation and biological evaluation of six coordinate complexes of Cr (III) with 5-dichloro 2-hydroxy acetophenone thiosemicarbazones.

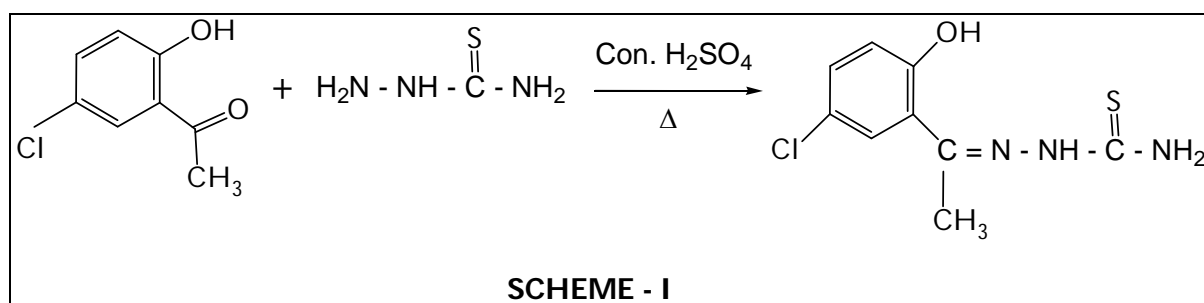
III. MATERIALS AND METHODS

A.R.grade chemicals were used for the synthesis. magnetic moment was measured at room temperature by Faraday method. IR spectra were recorded 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 stability was determined by carrying out thermogravimetric analysis. Metal in the complexes was estimated by standardized E.D.T.A.

IV. EXPERIMENTAL

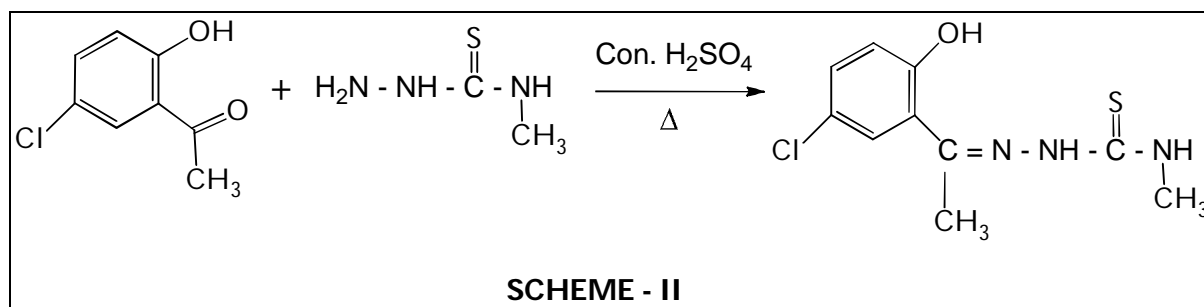
Synthesis of thiosemicarbazone L_1

Ethanol solutions of 5-chloro 2-hydroxy acetophenone was added to ethanol solution of thiosemicarbazide in the mole ratio 1:1. The reaction mixture was refluxed for three hours. The pale yellow product obtained on cooling was filtered and washed with hot water then cold ethanol and finally with ether. The compound was then purified in ethanol and dried in vacuum.



Synthesis of thiosemicarbazone L_2

Ethanol solutions of 5-chloro 2-hydroxy acetophenone was added to ethanol solution of N(4) methyl thiosemicarbazide in the mole ratio 1:1. The reaction mixture was refluxed for three hours. The pale yellow product obtained on cooling was filtered and washed with hot water then cold ethanol and finally with ether. The compound was then purified in ethanol and dried in vacuum.



Synthesis of thiosemicarbazone L_3

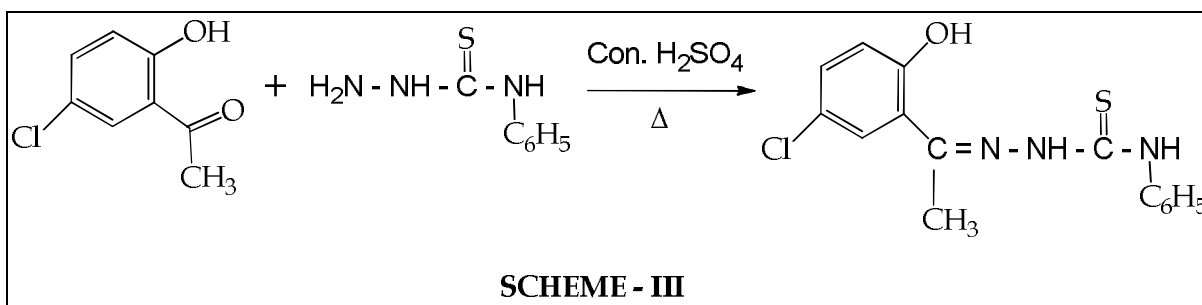
Ethanol solutions of 5-chloro 2-hydroxy acetophenone was added to ethanol solution of N(4) phenyl thiosemicarbazide in the mole ratio 1:1. The reaction mixture was refluxed for three hours. The pale yellow product

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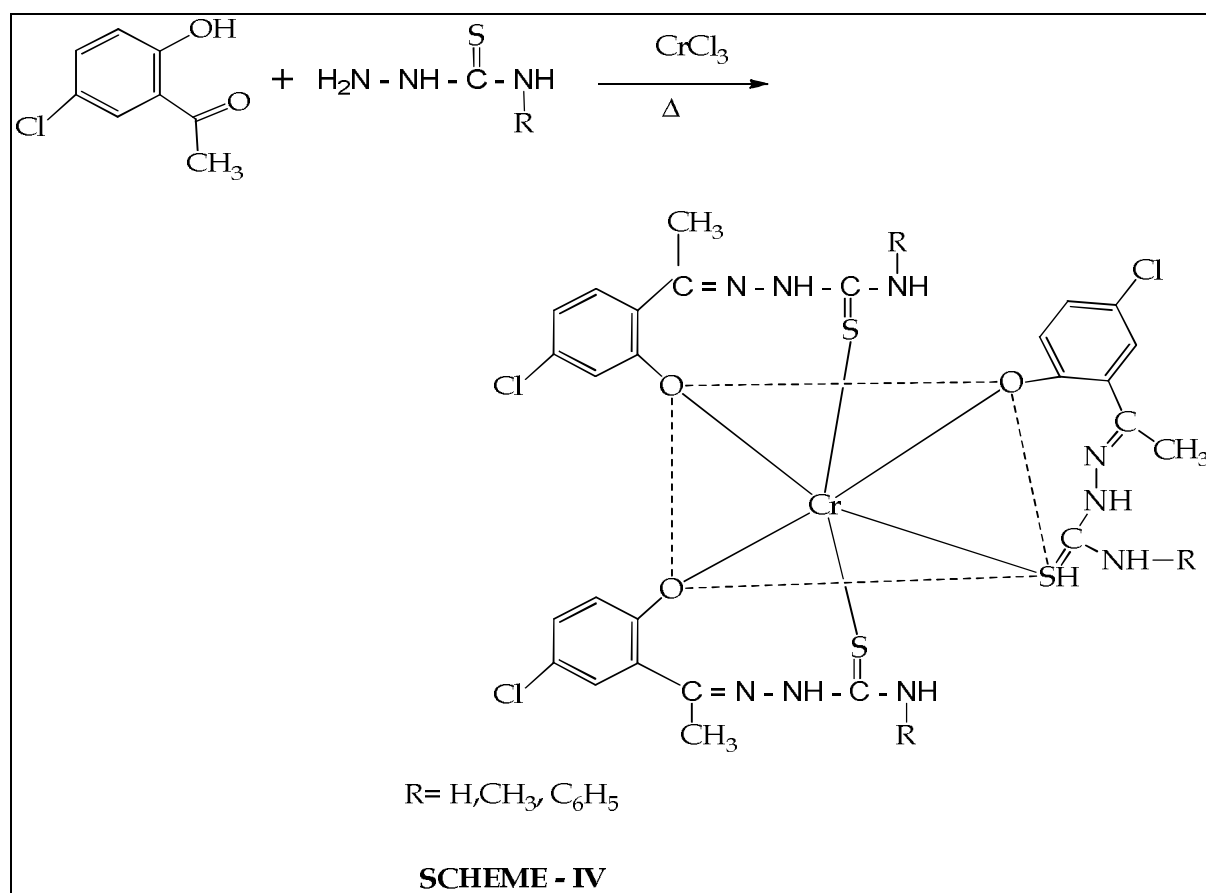
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obtained on cooling was filtered and washed with hot water then cold ethanol and finally with ether. The compound was then purified in ethanol and dried in vacuum.



Synthesis of complex ML₃

The complex of the type ML₃ was synthesized by refluxing ethanolic solutions of thiosemicarbazones (0.01mole), CrCl₃.6H₂O in the mole ratio 1:3 for four hours. One gram of sodium acetate was added. The brown product obtained was filtered and washed with hot water, cold absolute ethanol and then ether and dried in vacuum.



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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 ₁	Yellow	C ₉ H ₁₀ N ₃ O SCl	-	-
L ₂	Yellow	C ₁₀ H ₁₂ N ₃ O SCl	-	-
L ₃	Yellow	C ₁₅ H ₁₄ N ₃ O SCl	-	-
Cr L ₁	Brown	C ₂₇ H ₂₇ N ₉ O ₃ S ₃ Cl ₃ Cr	40	3.83
Cr L ₂	Brown	C ₃₀ H ₃₃ N ₉ O ₃ S ₃ Cl ₃ Cr	45	3.89
Cr L ₃	Brown	C ₄₅ H ₃₉ N ₉ O ₃ S ₃ Cl ₃ Cr	54	3.94

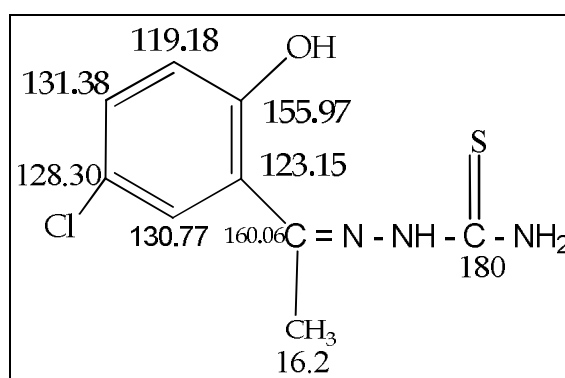
Physical data of ligand and its complexes is presented in Table 1. The complex and all adducts are in soluble in ethanol and soluble in DMF. Molar conductance measured in DMF solution of these complexes indicates non electrolyte. The electronic ground state is ⁴F and the ground state in an octahedral field is ⁴A_{2g}. The moments, as expected, lie between spin-only value and that predicted by the equation. The magnetic moments do not vary appreciably with temperature.

¹H-NMR L₁

Signals at 13, 3.40 ppm are assigned to - OH, - CH₃ protons respectively. Thiosemicarbazone does not show any peak corresponds to S-H proton, indicating it exists in thioketo form. Absence of ²NH proton signal suggests enolisation of ²NH - C = S group to ²N=C-SH. Little low field position of ⁴NH (7.8 ppm) could be attributable to the deshielding caused by - N = C< of the system N=CSH = NH). Aromatic protons show multiples at 7.00, 7.25 and 7.50 ppm range.

¹³C-NMR L₁

119.18 (C = C), 131.38 (C = C), 128.27 (C = C - Cl), 130.77 (C = C), 123.15 (C = C), 155.97 (C = C - OH), 160.06 (C = N), 180.0 (C=S), 16.2 (C-CH₃).



¹H-NMR L₂

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.

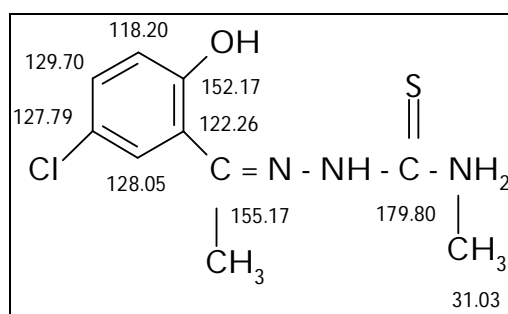
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¹³C-NMR L₂

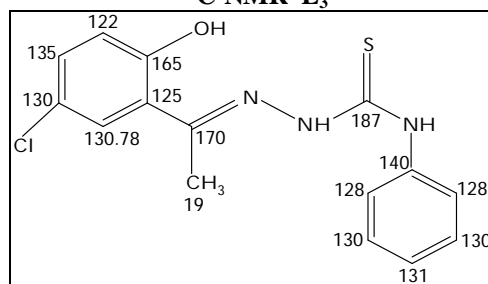
118.20 (C = C), 129.70 (C = C), 127.79 (C = C - Cl), 128.05 (C = C), 122.26(C = C), 152.17 (C = C - OH), 155.39 (C = N), 179.80 (C = S), 31.03 (NH- CH₃)



¹H-NMR L₃

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-CH₃),187 (C=S),140 (NH-C=C),128 (C=C),130 (C=C),131 (C=C),130 (C=C),128 (C=C).

¹³C-NMR L₃



(Calcd) found ESI-MS

L₁:C₉H₁₀ N₃O₃SCl(243.70) 243.11,L₂:C₁₀H₁₂ N₃O₃SCl(257.72) 257.15,L₃:C₁₅H₁₄ N₃O₃SCl(319.79)

319.41,Cr.L₁:C₂₇H₂₇N₉O₃S₃Cl₃Cr(780.07) 780.91,Cr.L₂ :C₃₀H₃₃N₉O₃S₃Cl₃Cr(822.15)

822.98,Cr.L₃:C₄₅H₃₉N₉O₃S₃Cl₃Cr(1008.35) 1008.72.

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

V. ANALYTICAL DATA

- 1.L₁:% C 44.91 (44.35),% H 4.88 (4.14),% N 17.92 (17.24), %O 6.06 (6.57) % S 13.71 (13.16)
- 2.L₂% C 46.02 (46.60),% H 4.04 (4.69),% N 16.91 (16.30),%O 6.78 (6.21)% S 12.87 (12.44)
- 3.L₃ :% C 56.81 (56.33),% H 4.92 (4.41),% N 13.82 (13.14),%O 5.81 (5.00)% S 10.54 (10.03)
4. Cr.L₁: % Cr 6.03 (6.67), %C 41.07 (41.57), %H 3.96 (3.55), %N 16.81 (16.16)%O 6.81 (6.15), %S 12.74 (12.33).
5. Cr.L₂: % Cr 6.93 (6.32), %C 43.12 (43.82), %H 4.82 (4.04), %N 15.86 (15.33), %O 5.13 (5.84) %S 11.01 (11.70).
- 6.Cr.L₃: % Cr 5.72 (5.16), %C 53.98 (53.60), %H 3.10 (3.90), %N 12.92(12.50), %O 4.10 (4.76) %S 9.04 (9.54).

On the basis of elemental analysis data,the complexes were found to have 1:3 composition.The calculated and theoretical values are matched.

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VI. INFRARED SPECTROSCOPIC DATA(cm^{-1})

1.L₁: ν (- OH) 3147; ν (C = N) 1624; ν (- C - S) 758 (s), 1374 ; ν (N - N) 1049; ν (²N-H) 2943; ν (C - O) 1281.

2.L₂: ν (- OH) 3225; ν (C = N) 1638; ν (- C - S) 795 , 1358 ; ν (N - N) 1049; ν (²N-H) 2925; ν (C - O) 1388.

3. L₃: ν (- OH) 3340; ν (C = N) 1678; ν (- C = S) 790, 1375 ; ν (N - N) 1075; ν (²N-H) 3240; ν (C - O) 1285.

4Cr-L₁: ν (C = N) 1624, ν (C-S) 708, 1310, ν (M - N) 430, ν (M-O) 525, ν (M-S) 325, ν (C - O) 1210.

5 Cr.L₂: ν (C = N) 1638, ν (C-S) 715, 1315, ν (M - N) 435, ν (M - O) 530, ν (M-S) 335, ν (C - O) 1215.

6. Cr.L₃: ν (C = N) 1678, ν (C-S) 720, 1320, ν (M - N) 440, ν (M - O) 540, ν (M-S) 340, ν (C - O) 1225.

The bands in IR spectra of thiosemicarbazones at 3147, 3225, 3340 cm^{-1} are due to -OH group. The bands at 2943, 2925 and 3240 cm^{-1} are due to ν (N-H). The bands at 1624, 1638, 1678 cm^{-1} due to ν (C = N) of the thiosemicarbazone moiety remain unaffected upon coordination. This shows the no coordination of throughazomethine nitrogen. The coordination via thiolate sulfur is indicated by decrease ν (C=S) [32,33]. The bands at 325-340 cm^{-1} assignable to ν (Cr-S) in the complexes confirm sulfur coordination. The new peaks observed in the range 525-540 cm^{-1} are due to the Cr-O(phenolic) bond [34-41]. This is indicated by decrease in ν (C-O).

VII. ELECTRONIC SPECTRA

The electronic spectra were recorded in DMF solution. There are spin allowed transitions in high spin states. The ground state is ⁴A_{2g}. The spin allowed transitions are ⁴A_{2g} (F) → ⁴T_{2g} (F), ⁴A_{2g} (F) → ⁴T_{1g} (F) and ⁴A_{2g} (F) → ⁴T_{2g} (P). These transitions are ν_1 , ν_2 and ν_3 . The absorption band at 34,500 cm^{-1} is a higher energy band. The bands at 31,250, 27,777 and 25,641 cm^{-1} are due to charge transfer. All transitions indicate octahedral geometry for the complexes [42-45].

VIII. EPR SPECTRA

Compounds	λ_{max} in cm^{-1}	g values
Cr.L ₁	17220, 25445, 35202	1.92
Cr.L ₂	17600, 25402, 35650	1.94
Cr.L ₃	17802, 25330, 35200	1.97

The EPR spectra of the complexes were recorded at liquid nitrogen temperature. The value of λ_{max} suggested covalent character in all complexes. The values of g are found in the range 1.92-1.97 indicating σ -coordinated geometry [46-48].

IX TGA ANALYSIS DATA

1. Cr-L₁: First step, 150 °C, Mass loss 15 % second step, 200 °C, Mass loss, 30 % Third Step 350 °C, Mass loss, 40 % Fourth Step, 650 °C, Mass loss 65 %, Residue 800 °C, % of Cr₂O₃, 19.92 (19.49).

2. Cr.L₂: First step, 148 °C, Mass loss 17 % second step, 200 °C, Mass loss, 32 % Third Step 355 °C, Mass loss, 50 % Fourth Step, 660 °C, Mass loss, 67%, Residue, 800 °C, % of Cr₂O₃, 18.86 (18.49).

3. Cr.L₃: First step, 150 °C, Mass loss 20 % second step, 210 °C, Mass loss, 35 % Third Step 365 °C, Mass loss, 48 % Fourth Step, 660 °C, Mass loss 65 %, Residue 800 °C, % of Cr₂O₃, 15.88 (15.07).

The hydrated layer was removed below 100 °C. The TGA data indicated that the decomposition proceeded in four steps. The compounds are stable up to about 300 °C. In the second step the loss is up to 35%. The organic molecule was lost up to 650 °C. The mass lost corresponding to this step is about 65%. The decomposition was complete and metal oxide was formed at a temperature about 800 °C. The coordination of metal and increase in coordination number in the complexes may give thermal stability.

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XANTIBACTERIAL ACTIVITY(WELL DIFFUSION METHOD)

Table.2 % Activity Index L₁,L₂,L₃ , Cr (III) complexes and standered

Compound	<i>Staphylococcus aureu</i>		<i>Bacilussubtilis</i>		<i>Escherichia Coli</i>		<i>Peudomonasaeruginosa</i>	
	Gram positive				Gram negative			
	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 ₁	25	19	27	20	24	19	29	18
L ₂	28	21	25	21	27	18	28	16
L ₃	29	22	27	22	28	17	30	17
Cr.L ₁	51	42	49	40	52	45	55	46
Cr.L ₂	58	44	52	42	54	47	58	48
Cr.L ₃	60	45	55	45	58	19	67	51
CrCl ₃ .6H ₂ O	112	106	115	108	117	109	120	118
Standard	100	100	100	100	100	100	100	100

(Std-Amphiciline)

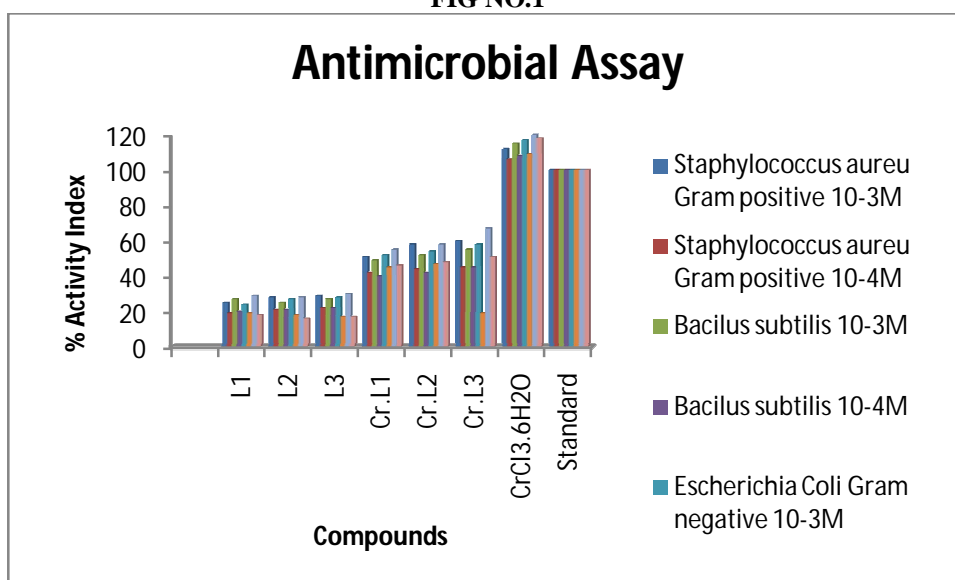
$$\% \text{ Activity Index} = \frac{\text{Zone of inhibition of test compound}}{\text{Zone of inhibition of standard (diameter)}} \times 100$$

The antibacterial activity was determined using the well diffusion method. Activity was measured in two different molar concentrations, 10⁻³M, 10⁻⁴ M. The results indicated that the synthesized compounds exhibited antibacterial activity at low and high concentrations. The complexes showed maximum activity against bacterial species than free ligand. 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 lipid layer of the bacterial membranes. The increased lipophilic character of this molecule may be responsible for its enhanced potent antibacterial activity. The thiosemicarbazones were found less active than their complexes. The delocalization of π-electrons increases lipophilicity and this facilitates the penetration into lipid membranes, further restricting proliferation of the microorganisms [49]. In complexes coordination number increases which increases antimicrobial activity. *Staphylococcus aureu* and *Bacilussubtilis* are gram +ve bacterial species and *Escherichia Coli*, *Peudomonasaeruginosa* are Gram (-). 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 chromium chloride salts were found more effective than complexes. The Cr²⁺ ions have small size having d⁴ configuration. This increases the permeability to cell membrane. But use of metal ion solution to treat bacterial 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 i.e. it is more in concentrated solution.

FIG NO.1



The above bar graph indicates maximum activity at higher concentration than at lower concentration. More activity was observed in case of Gram (-) bacteria than gram positive bacteria. The activity index was more in Gram (-) bacteria.

XI. ANTIOXIDANT STUDY

Antioxidant studies on the thiosemicarbazone metal complexes have been analysed by DPPH assay. DPPH is stable free nitrogen radical and the assay determines the ability of the compound to reduce DPPH radical. The antioxidants can act by converting the unpaired electrons to paired ones. The decrease in absorbance at 517 nm is the measure of test compound to reduce DPPH radical that acts as an antioxidant which is indicated by the formation of yellow colour.

Each extract or standard (from 21 mg/ml to 21 g/ml) was added to 2 ml of DPPH in methanol solution in a test tube. After incubation at 37°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. IC₅₀ 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 [50]. The results of antioxidant activity are presented in Table No. 3

Table.2 % RADICAL SCAVENGING EXHIBITED BY L₁,L₂,L₃Cr (II) COMPLEXES

Complex	20 µg/ml	40 µg/ml	60 µg/ml	80 µg/ml	3100 µg/ml	IC ₅₀ value
L ₁	69.76	76.74	79.06	79.06	81.39	14.33
L ₂	72.09	74.41	76.74	76.74	79.06	13.87
L ₃	72.09	74.41	76.74	76.74	79.06	13.87
Cr.L ₁	30.00	45.00	45.00	55.00	62.50	72.72
Cr.L ₂	3.33	7.50	17.50	17.50	35.00	142.85
Cr.L ₃	10.00	12.50	20.00	30.00	37.50	133.33
Vit. C	39.53	46.51	58.13	60.46	65.11	51.00

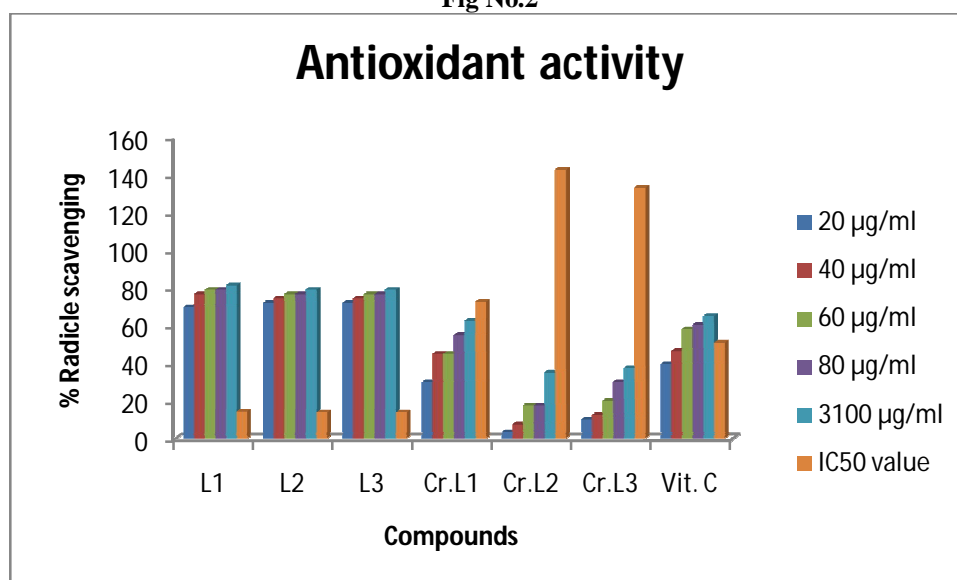
Lower the absorbance of the reaction mixture indicated higher free radical scavenging activity [51]. Complexes showed better % scavenging activity at higher concentration.

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Fig No.2



The above bar graph indicates % radical scavenging activity. More activity was observed in the complexes

XII. CONCLUSION

The thiosemicabazones synthesized are tridentate ONS donors. The spectral data indicates octahedral geometry for complexes. The complexes are paramagnetic. TGA data indicates thermal stability of the complexes. The compounds are thermally stable upto 200°C. The decomposition took place in four steps. The EPR spectral data indicate covalent character and σ -coordination in the complexes. The complexes showed growth inhibitory activity against gram +ve and (-) bacterial species. The activity is more at 10^{-3} M concentration. The metal salts showed more inhibition. The complexes showed radical scavenging.

REFERENCES

- Philip V, Suni V, Kurup M.R.P, M. Nethaji, *Polyhedron* 25 **2006** 1931.
- French F.A, Blanz E.J, Jr. *J. Med. Chem.* 9 **1996**, 585.
- Das M, Livingstone S.E, Br. J. Cancer. 37 **1978**, 466.
- Dobek A.S, Klayman D.L, Dickson L.T, Scovill J.P, Tramont E.C, *Antimicrob Agents Chemother* 18 **1980** 27.
- Usman A, Razak I.A, Chantrapromma S, Fun S.K, Sreekanth, Sivakumar S, Kurup M.R.P, *Acta. Cryst. C* **2002**, 461.
- Klayman D.L, Lin A.J, Mc Call J.W.J. *Med. Chem.*, 34 **1991** 1422.
- Shipman Jr C, Smith H, Drach J.C, Klayman D.L, *Antiviral. Res.* 6 **1986** 197.
- EI-Sawaf A.K, west D.X, EI-Bahnasawy R.M, EI-Saied F.A, *Transition Met. Chem.* 23 **1998**, 227.
- Tojal J.G, Orad A.G, Serra J.L, Pizarro J.L, Lezama L, Arriortua T, Rojo. *J. Inorg. Bichem.* **45** **1999**, 75.
- Padhye S, Kauffman G.B. *Coord. Chem. Rev.* **63** **1985** 127.
- Lukevics E, Jansone D, Rubina K, Abele E, Gennane S, Leite L, Shymaska M.J, Popelis, *Eur. J. Med. Chem.* 30 **1995** 983.
- Joseph M, Kuriakose M, Kurup M.R.P, Suresh E, Kishore A, Bhat S.G, *Polyhedron* 25 **2006**, 25 61.
- Jain S.K, Garg B.S, Bhoon Y.K, *Spectrochim. Acta A*, 42 **1986**, 959.
- Hossain M.E, Alam M.N, J. Begum, Ali M.A, Nazimudhin M, Smith F.E, Hynes R.C. *Inorg. Chim. Acta.* **1996**, 249, 207.
- Hu-W, Zhou W, Xia-C X, Wen. *Bioorg. and Med. Chem. Lett.* **2006**, 16, 2213.
- Singh R.V, Fahmi N, Biyala M.K, *J. Iranian. Chem. Soc.* **2005**, 2, 40.
- Palm A, Werbin H, *Can. J. Chem.* 32 **1954** 858
- Palm A, Werbin W, *Can. J. Chem.* 31 **1953** 1004
- Califano and Luttke *Z. Phys. Chem.* 5 **1955** 204
- Birladeanu L *J. R. spectra of Organic Compounds. New York* **1972** 333
- Blink AR Hadzi *J. Chem. Soc.* **1958** 4536
- Mahmoud M.R. Abdel-Hamide El.M. *Thaty Ind. J. Chem.* 19A **1980** 345
- Mahmoud M.R. Abdel-Hamide El.M. *Thaty Ind. J. Inorg. Nucl. Chem* 42 **1980** 349

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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22. Akbar M Ali Teoh S.G *J.InorgNuclChem* 41 **1979** 809
23. Singh R V Tondon J P *Ind J Chem* 19A **1980** 602
24. Koing E *Structure and Bonding Vol 9* springer Verlag Berlin Heidelberg
25. Prece E R wasson J R *J InorgNuclChem* 36 **1974** 67
26. Cronin R J *The Chromin Controversy Alternative and complementary Therapies* 10 **2004** 39
27. Vincent J B *Acc chem. Res* 33 **2000** 503
28. Anderson R A *ClinPhysiolBiochem* 4 **1986** 31
29. Davis C M Vincent J B *J BiollnorgChem* 2 **1997** 675
30. Mertz W *Nutr Rev* 56 **1998** 174
31. Morris B W Kouta S sadwal S *Int J Pharm Res and Sci* **2014** 56
32. West.D.X., Whyte A.C., Sharif F.D., Gabremedhin H., Liberta A.E, *Trans.Met. Chem.* 18, **1993**, 238.
33. Campbell M.J.M, *Coord. Chem. Rev.* 15, **1975**, 279.
34. Gerioh M, Mason R. *J ChemSoc* 296 **2007**
35. Hathaway b J Billing D E. *Coord.Chem.Rev* 5 **1970** 143
36. A B P Lever *Inorg.ElectronicSpec.* 1st ed. Elsevier, Amsterdam **1968**
37. Chandra S, Shweta *Spectrochim. Acta A* 71 **2008** 720
38. Figgis B N "Introduction to Ligand Fields", 1st ed. Wiley Eastern limited **1966**
39. Chandra S, Jain D, Sharma A K Sharma P *Molecules* 14 **2009** 174
40. Chandra S, Kumar R *Trans. Met. Chem.* 29 **2004** 269
41. Percy G.C., Thornton D.A, *J. Inorg. Nuclear. Chem.* 34, **1972**, 3351.
42. Kumar U, Chandra S *Journal of Saudi Chemical Society* 15 2011 187
43. Chandra S Raizada S Tyagi M Sharma P K *Spectro.Chimi A* 69 2008 816
44. Chandra S Kumar A *Journal of Saudi chemical society* 14 2012 12
45. Sulekh Chandra Smriti Raizada Sangeeta Sadwal *International Journal of advanced Engineering Research and Technology* 2014 115
46. Chandra S Tyagi M Agrawal S *Journal of Saudi chemical Society* 15 2011 49
47. Mabbs F E, Collison D *Electron Paramagnetic Resonance of Transition Metal Compounds* Elsevier Amsterdam 1992
48. Owen J, *Proc Roy Soc London A* 227 1955 183
49. Ahmed A Al-Amiery, Yasmien K Al-Majedy, Heba H Ibrahim and Ali A Al-Tamimi. *Al-Amiery et al. Organic and Medicinal Chemistry Letters* **2012**, 2:4.
50. Rai S, Wahile A, Mukherjee K, Saha B.P, Mukherjee P.K, *J. Ethnopharma*, 104 **2006**, 312.
51. Bottari B, Maccari R, Monforte F, Ottana R, Rotondo E, Vigorita M.G, *Bioorg. Med. Chem. Lett*, 10 **2000**, 657.