Spectral and Antioxidant Screening of six coordinate Cr (III) Complexes

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Abstract

5-chloro 2-hydroxy acetophenone N (4) ethyl thiosemicarbazone was synthesized by refluxing ketone 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 1:1.The thiosemicarbazones and complexes were characterized by means of Elemental analysis,ESI-MS,FT-IRspectroscopy,refluctance spectra Nuclear Magnetic Resonance (^{1}HNMR and ^{13}C-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,antimicrobial activity.antioxidant activity,1:1 ratio

Introduction

Thiosemicarbazones and their complexes with transition metals have been synthesized and studied widely as they have variety of biological properties such as anticancer, antitumour, antifungal, antibacterial, antimalarial, antitilarial, antiviral and anti-HIV activities [1-8].As per the earlier research 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 activity may arise due to the presence of a bulky group at the terminal nitrogen [12]. The presence of bulky groups at the N (4) position of the thiosemicarbazone together with an additional coordinating sites affect biological activity [13-15].The stereochemistry of many Cr (III) complexes have been studied [16-21].Many Cr (III) complexes exhibit fluoresce and or phosphoresce.luminescene studies of Cr (III) complexes have been of significant importance in understanding of their stereochemistry.J.R.Perumareddi [22] sumarized the theory of cubic and non-cubic ligand fields on Cr (III) complexes.

Considering the above applications the synthesis and characterization of Cr (III) complexes with Schiff base has been reported here.

Experimental

Materials and instrumentation

The thiosemicarbazone was synthesized by refluxing 5-chloro 2-hydroxy acetophenone and N-4 ethyl thiosemicarbazide in ethanol in the mole ratio 1:1 for 3 hours. The pale yellow 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.

SCHEME - I
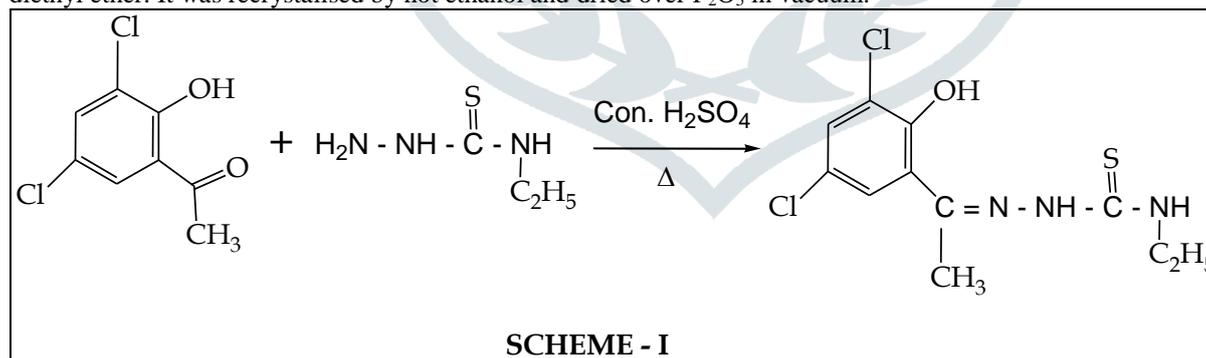
Preparation of complex

CrCl$_3$ salt was dissolved in ethanol.The ethanolic solution of thiosemicarbazone in slight excess over the metal:ligand ratio of 1:1 was added dropwise with constant stirring.One gram sodium acetate was added.The rection mixture was refluxed for one hour.The dark brown product thus obtained was fitered and washed well with cold ethanol and then diethyl ether and dried over P_2O_5 in vacuum.

Preparation of complexes with heterocyclic bases

The complex Cr.L.B (B is heterocyclic base like pyridine, α-picoline, β-picoline,γ-picoline) was synthesized by adding slowly ehanolic solution of CrCl$_3$,heterocyclic base to the hot ehanolic solution of thiosemicarbazone in the ratio 1:1:1and refluxing reaction mixture for one hours. The brown adduct obtained was filtered and washed with hot water, cold ethanol and diethyl ether and dried over P_2O_5 in vacuum.

Physical measurements-

Faraday method was used for magnetic measurement. IR spectra were recorded in the range 4000-200 cm^{-1} range in solid state.Conductivity measurements were carried out on conductivity Bridge at different temperature.Thermo gravimetric analysis was carried out in the temp range 30-800ºC.Electronic spectra was recorded on Jasco double beam spectrophotometer in solid state.Metal in the complexes was estimated by standardized EDTA solution.Chloride in the complex was estimated by Mohr's method.

Table 1 Physical properties:

Compounds	Colour	Empirical Formula	Magnetic Moment B.M.
L	Yellow	$C_{11}H_{13}N_3OSCl_2$	-
Cr-L.Cl.(H$_2$O)$_2$	Brown	$C_{11}H_{15}N_3O_3SCl_3Cr$	3.84
Cr.L.Py.(H$_2$O)$_2$	Brown	$C_{16}H_{20}N_4O_3 SCl_2Cr$	3.87
Cr.α-Pico.(H$_2$O)$_2$	Brown	$C_{17}H_{22}N_4O_3 SCl_2Cr$	3.90
Cr.L β-Pico.(H$_2$O)$_2$	Brown	$C_{17}H_{22}N_4O_3 SCl_2Cr$	3.88
Cr.L.γ-Pico.(H$_2$O)$_2$	Brown	$C_{17}H_{22}N_4O_3 SCl_2Cr$	3.85

Conductivity measurement

The conductivity of complexes was measured in DMF solution and equivalent conductance was calculated.The 0.001 M solution of complexes was prepared in different percentages of DMF-ethanol mixture and the parameter of solution under study was calculated at temperature 298 K,303 K and 308 K.

Equivalent conductance at 298 K					
DMF-Ethanol mixture	Cr.L.Cl(H$_2$O)$_2$	Cr.L.Py(H$_2$O)$_2$	Cr.L. α-Pico (H$_2$O)$_2$	Cr.L.β-Pico (H$_2$O)$_2$	Cr.L.γ-Pico (H$_2$O)$_2$
75%	35.5	38.2	38.3	38.1	38.4
80%	38.6	41.2	40.6	40.3	42.6
85%	45.2	44.7	42.4	42.4	45.2
90%	48.3	49.3	45.2	45.8	48.3
95%	51.3	52.4	48.9	48.6	51.1
100%	54.2	55.2	50.6	51.0	53.2
Equivalent conductance at 303 K					
DMF-Ethanol mixture	Cr.L.Cl(H$_2$O)$_2$	Cr.L.Py(H$_2$O)$_2$	Cr.L. α-Pico (H$_2$O)$_2$	Cr.L.β-Pico (H$_2$O)$_2$	Cr.L.γ-Pico (H$_2$O)$_2$
75%	40.5	40.3	42.3	43.1	43.4
80%	42.6	43.2	44.6	44.0	45.6
85%	47.2	45.7	46.4	47.4	49.2
90%	51.3	50.3	48.2	50.8	52.3

| 95% | 55.3 | 53.4 | 50.9 | 52.6 | 54.1 |
| 100% | 59.3 | 58.4 | 52.5 | 54.6 | 57.7 |

Equivalent conductance at 308 K					
DMF-Ethanol mixture	Cr.L.Cl($H_2O)_2$	Cr.L.Py($H_2O)_2$	Cr.L. α-Pico $(H_2O)_2$	Cr.L.β-Pico $(H_2O)_2$	Cr.L.γ-Pico $(H_2O)_2$
75%	43.5	42.3	43.3	44.1	44.4
80%	45.7	45.2	46.7	45.3	48.3
85%	49.4	47.7	50.4	48.4	52.2
90%	53.3	53.3	52.2	51.8	55.3
95%	58.3	55.4	54.9	53.6	58.1
100%	62.5	59.4	60.3	55.2	60.3

^{1}H-NMR

NMR signals at 12.00 and 2.2 ppm are assigned to – OH and – CH_3 protons respectively. The signals at 2.30, 3.50 correspond to [4]NH and H^4N-C_2H_5 respectively. Signal at 10.0 ppm corresponds to [2]NH. Aromatic protons show multiplets at 7.0, 7.25, 7.45, ppm.

^{13}C-NMR (DMSO-D$_6$): δppm
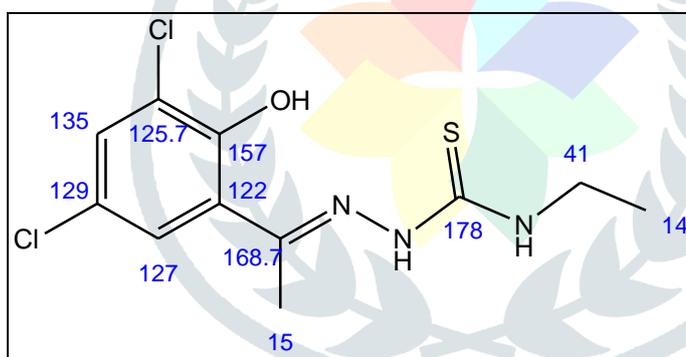
(Calcd) found ESI-MS m/z, ion M^+:$C_{11}H_{13}N_3OSCl_2$ (306.19) 306.71,$C_{11}H_{15}N_3O_3SCl_3Cr$ (424.66) 431.02, $C_{16}H_{20}N_4O_3SCl_2Cr$ (471.30) 471.97,$C_{17}H_{22}N_4O_3SCl_2Cr$ (485.33) 485.94,$C_{17}H_{22}N_4O_3SCl_2Cr$ (485.33) 485.76,$C_{17}H_{22}N_4O_3SCl_2Cr$ (485.33) 485.96.

Analytical data

1.**L:** % C 43.74 (43.15),% H 4.72 (4.28),% N 13.18 (13.72),% S 10.81 (10.47)

2.**Cr-L.Cl.(H$_2$O)$_2$:** % Cr 12.77 (12.16),%Cl 8.93 (8.29),%C 30.11 (30.89),%H 3.01

   (3.54),%N 9.11 (9.82),%S 7.03 (7.50).

3**. Cr.L.Py.(H$_2$O)$_2$:**% Cr 11.66 (11.03),%C 40.11 (40.77),%H 4.98 (4.28),%N 11.09

   (11.89),%S 6.12 (6.80).

4.**Cr.α-Pico.(H$_2$O)$_2$**: % Cr 10.11 (10.71),%C 41.71 (42.07),%H 4.91 (4.57),%N 11.04

   (11.54),%S 6.06 (6.67).

5.**Cr.L β-Pico.(H$_2$O)$_2$**: Cr 10.10 (10.71),%C 42.80 (42.07),%H 4.08 (4.57),%N 11.80

   (11.54),%S 7.04 (6.67).

6.**Cr.L.γ-Pico.(H$_2$O)$_2$**: Cr 10.02 (10.71),%C 42.70 (42.07),%H 4.90 (4.57),%N 11.78

(11.54),%S 7.06 (6.67).

Table 2.**Electronic spectral data (cm^{-1})**

Compound	MLCT	n→π*	π→π*
L	-	28570	40800
Cr-L.Cl.(H$_2$O)$_2$	25600	32452	42882
Cr.L.Py.(H$_2$O)$_2$	25740	32570	42750
Cr.α-Pico.(H$_2$O)$_2$	25775	32690	42870
Cr.L β-Pico.(H$_2$O)$_2$	25680	32750	42860
Cr.L.γ-Pico.(H$_2$O)$_2$	25920	32860	42820

Infrared Spectroscopic data (cm^{-1})
1.**L**:ν (- OH) 3200; ν (C = N) 1670; ν (- C = S) 785, 1370 ; ν (N – N) 1050; ν (^{2}N-H) 3250; ν (C – O) 1290.
 2 **[Cr-L.Cl.(H$_2$O)$_2$]:** ν (C = N) 1580; ν (C = N-N=C) 1545, ν (C-S) 710, 1302,ν (N-N) 1110, ν(M - N) 422, ν (M-O) 520, ν (M-S) 322, ν (C - O) 1215, ν(Cr-Cl) 350.ν(H$_2$O) 3450,3540.
3.**[Cr.L.Py.(H$_2$O)$_2$] :**ν (C = N) 1588; ν (C = N-N=C) 1550, ν (C-S) 715, 1310; ν (N-N) 1115, ν (M - N) Base 250, ν (M - N) 425, ν (M - O) 522, ν (M-S) 320, ν (C - O) 1222, Band due to HB 1460, ν(H$_2$O) 3440,3510.
4.**Cr.α-Pico.(H$_2$O)$_2$:**ν (C = N) 1590; ν (C = N-N=C) 1545, ν (C-S) 722, 1320,ν (N-N) 1122, ν (M - N) Base 262, ν (M - N) 428, ν (M - O) 528, ν (M-S) 323, ν (C - O) 1231, Band due to HB 1465, ν(H$_2$O) 3542,3550.
5.**Cr.L β-Pico.(H$_2$O)$_2$:**ν (C = N) 1580; ν (C = N-N=C) 1552, ν (C-S) 727, 1328,ν (N-N) 1142, ν (M - N) Base 268, ν (M - N) 435, ν (M - O) 530, ν (M-S) 330, ν (C - O) 1235, Band due to HB 1473, ν(H$_2$O) 3550,3570.
6.**Cr.L.γ-Pico.(H$_2$O)$_2$:**ν (C = N) 1592; ν (C = N-N=C) 1558, ν (C-S) 730, 1338,ν (N-N) 1140, ν (M - N) Base 272, ν (M - N) 440, ν (M - O) 535, ν (M-S) 340, ν (C - O) 1240, Bands due to HB 1477, ν(H$_2$O) 3560,3580.
TGA analysis data:
The TGA curves of complexes were recorded between the temperatures 30 °C to 800 °C
1.Cr-L.Cl.(H$_2$O)$_2$: First step, 112.0 °C, Mass loss 9.60 % second step, 132.0 °C, Mass loss, 17.0 % Third Step 243.0 °C, Mass loss, 38.0 % Fourth Step, 372.0 °C, Mass loss 66.0 %, Residue 775 °C, % of Cr$_2$O$_3$, 35.03 (35.54).
2.Cr.L.Py.(H$_2$O)$_2$**:**First step, 114 °C, Mass loss 6.24 % second step,135.0 °C, Mass loss, 15.0 % Third Step 253 °C, Mass loss, 34.0 % Fourth Step, 370.0°C, Mass loss, 62.0 %, Residue, 790.0 °C, % of Cr$_2$O$_3$, 32.96 (32.20).

3.Cr.α-Pico.(H$_2$O)$_2$**:**First step, 117.0 °C, Mass loss 7.81 % second step,136.0 °C, Mass loss,18.0 % Third Step 258.0 °C, Mass loss, 38.0 % Fourth Step, 377.0°C, Mass loss 64.0 %, Residue 800 °C, % of Cr$_2$O$_3$, 31.96 (31.32).

4.Cr.L β-Pico.(H$_2$O)$_2$**:**First step, 116.0 °C, Mass loss 7.85 % second step, 138.0 °C, Mass loss, 20.0 % Third Step 259.0 °C, Mass loss, 36.0 % Fourth Step, 378.0°C, Mass loss, 67.0 %, Residue, 800.0 °C, % of Cr$_2$O$_3$, 31.90 (31.32).

5.Cr.L.γ-Pico.(H$_2$O)$_2$**:**First step, 117.0 °C, Mass loss 7.90 % second step, 139.0 °C, Mass loss, 20.0 % Third Step 260.0 °C, Mass loss, 38.0 % Fourth Step, 380.0 °C, Mass loss 67.0 %, Residue 790 °C, % of Cr$_2$O$_3$, 31.96 (31.32).
**Antimicrobial Assay(Agar plate diffusion method)**
 Table.3 Absorbance of the L , Cr (III) complexes and standered

Compounds	*Staphylococcus aureu*		*Bacilus subtilis*		*Escherichia Coli*		*Peudomonas aeruginosa*	
	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	0.72	0.36	0.70	0.40	0.71	0.40	0.72	0.42
Cr-L.Cl.(H$_2$O)$_2$	0.67	0.38	0.69	0.26	0.67	0.28	0.67	0.29
Cr.L.Py.(H$_2$O)$_2$	0.64	0.35	0.65	0.24	0.64	0.25	0.65	0.26
Cr.α-Pico.(H$_2$O)$_2$	0.62	0.33	0.63	0.22	0.62	0.23	0.63	0.24

Cr.Lβ-ico.(H₂O)₂	0.63	0.34	0.64	0.23	0.63	0.24	0.64	0.25
Cr.L.γ-co.(H₂O)₂	0.64	0.35	0.65	0.24	0.64	0.25	0.65	0.26
Standered	0.16	0.11	0.13	0.12	0.12	0.11	0.15	0.11
CrCl₃	0.49	0.21	0.20	0.18	0.15	0.18	0.31	0.18

(Standered -Cefodoxine,Fluconazole)

Fig 1 Antimicrobial Assay
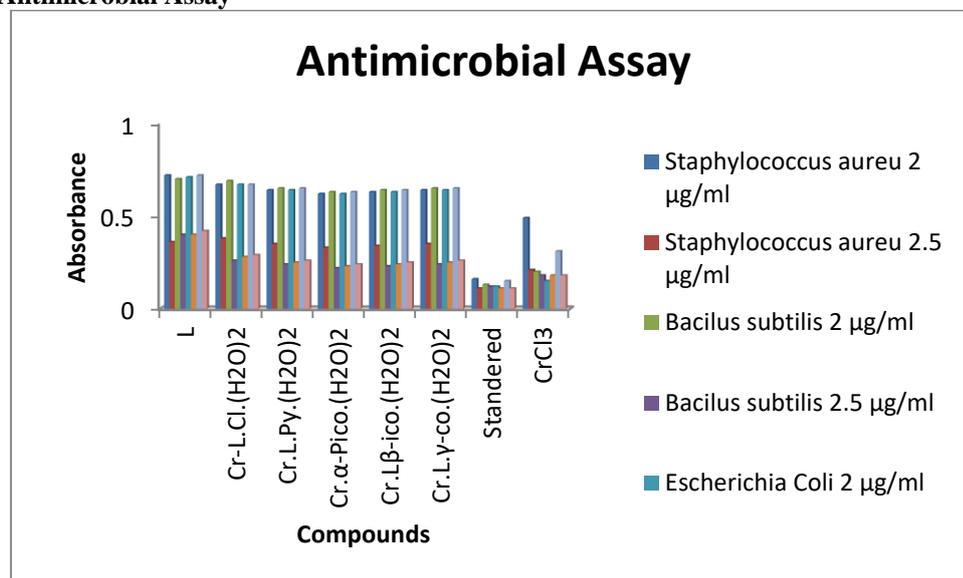
% RADICAL SCAVENGING EXHIBITED BY L and Cr (III) COMPLEXES

Table.4

Complex	20 µg/ml	40 µg/ml	60 µg/ml	80 µg/ml	100 µg/ml
L	72.09	74.41	76.74	76.74	79.06
Cr-L.Cl.(H₂O)₂	30.00	45.00	45.00	55.00	52.50
Cr.L.Py.(H₂O)₂	32.33	40.50	42.50	48.50	53.00
Cr.α-Pico.(H₂O)₂	35.10	42.32	45.0	49.50	54.80
Cr.Lβ-ico.(H₂O)₂	36.12	43.22	52.36	51.40	52.30
Cr.L.γ-co.(H₂O)₂	35.0	42.20	50.23	49.36	55.60
Vit. C	39.53	46.51	58.13	60.46	65.11

Results and discussion

Elemental analysis data confirmed 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 complexes are soluble in DMF.

The equivalent conductance of electrolyte solution depends on concentration of electrolyte solution and varies with increase in concentration of the electrolyte.It is found that equivalent conductance of an electrolyte increases with decrease increase in dilution.In dilute solution conductance is more.All complexes show increasing value of conductance with increase in the dilution at 298 K, 303K,308 K.The conductivity of an electrolyte depends upon the temperature.The conductivity of an electrolyte increases with increase in temperature.This may be due to at higher temperature the mobility of ions increases and hence more conductivity is observed.

The electronic ground term is ^4F and the ground state in an octahedral field is ^4A_2g .The magnetic moments may reduce below spin-only values because 1-4λ/10dq effect.Because of the low value of the spin-orbit coupling constant,the reduction is rather small.In fact,the accuracy of the determination of the magnetic susceptibility is generally not high enough to allow the actual degree of reduction to be used to estimate the amount by which orbital angular moment is reduced by electron delocalization.The moments,as expected,lie between spin-only value and that predicted by the above equation,but the difference between the two quantities is only 4% high-spin complexes.For the ground term in an octahedral; field there is no reduction of the moment below the spin-only value by spin -orbit coupling with higher liquid field terms.

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

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 v_1, v_2 and v_3.The absorbtion bands in the range 42000-43000cm⁻¹ are of higher energy bands.The bands at in the region 25000-26000

$cm^{-1}$are due to charge transfer.All transitions indicate octahedral geometry for the complexes [23-26].

The band in IR spectra of thiosemicarbazone at 3200 cm^{-1} is due to –OH group.The band at 3250 $cm^{-1}$is due to v(N-H). It is disappeared in the spectra of complexes.The band at 1670 cm^{-1} due to v (C = N) of the thiosemicarbazone moiety is shifted to ower side upon coordination.This shows coordination of throughazomethine nitrogen.The coordination via thiolate sulfur is indicated by decrease in v (C=S) [27,28]. The bands in the range 320-340 cm^{-1}assignable to v (Cr-S) in the complexes confirm sulfur coordination. The new peaks observed in the range 52-535 cm^{-1} are due to the Cr- O(phenolic) bond [29-36].This is indicated by decrease in v (C-O). The band is assigned for v (Cr-N) due to heterocyclic base in 250-275 cm^{-1} range in the spectra of all complexes. The characteristics bands due to coordinated heterocyclic bases are also observed in IR spectra of all complexes[37-39].The heterocyclic base nitrogen atom occupies fourth coordination site.

The TGA curves of Cr (III) complexes were recorded within a temperature range 30-800^{0}C.Hydrated layer was lost in between 30-110^{0}C.Then two coordinated water molecules were lost in the temperature range 112-117^{0}C.Mass lost at this stage is about 4-10 %.Break observed in the curves due to removal of part of thiosemicarbazone molecule.The remaining part of thiosemicarbazone removed from the coordination sphere at ~ 600-650^{0}C.The metal oxides were formed above 600^{0}C.The decomposition was complete at ~ 800^{0}C.Cr (III) complexes are thermally stable up to 120^{0}Cand decomposition started at this temperature.The complexes prepared with different metals decompose in steps.It is concluded that the thermal stability of the complexesis due to the coordination of metal ion to thiosemicarbazone [40].

The antibacterial assay was carried out by the agar plate diffusion method.The minimum inhibitory concentration was determined by liquid dilution method [41].The absorbance of the turbid solutions was measured at 520 nm.The same method was used for standard [42].Less ctivity was observed with thiosemicarbazone.This might be due to coordintion which reduces the polarity of the central metal atom because of the partial sharing of its positive charge with donor groups and possible π-electron delocalisation within the whole chelating ring.So the lipophilic nature of the central metal atom increases,which favours the permeation of the solution of complexes through the lipid layer of the cell membrane[43].It is found that complexes containing heterocyclic bases show better activity than the thiosemicarbazone and the complex.The absorbance is more at 2µg/ml and less at 2.5 µg/ml and no absorbance observed at 3µg/ml.The inhibition is more at 2.5 µg/ml.The chelation theory explains the reason behind the better activity of these thiosemicarbazone complexes[44].The polarity of the metal ion is minimized to an advanced level, due to the ligand and positive charge of the metal ion with donor groups especially with sulfur-nitrogen donors.

Thiosemicarbazone metal complexes have been analysed for antioxidant activity 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 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. 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 [45].Lower the absorbance of the reaction mixture indicated higher free radical scavenging activity [46].It is found that complexes showed better % scavenging activity at higher concentration.

CONCLUSION

Thiosemicabazone is tridentate ONS donor lignd.The spectral data indicates octahedral geometry for complexes.The complexes are paramagnetic.Two coordinated water molecues are found.The complexes found thermally stable.All complexes exhibited growth inhibitory activity against gram +ve bacterial species.Finally,antibacterial activity for all compounds is in the order of Standered >metal salt>Cr.α-Pico.(H$_2$O)$_2$> Cr.Lβ-ico.(H$_2$O)$_2$>Cr.L.γ-co.(H$_2$O)$_2$=Cr.L.Py.(H$_2$O)$_2$>Cr-L.Cl.(H$_2$O)$_2$>L.The presence of –CH$_3$ group with heterocyclic bases may affect ntibacteria activity**The minimum inhibitory concentration is 2.5 µg/ml.**The equivalent conductance increases on dilution.The equivalent conductance increases with increase in temperature.At higher concentration antioxidant ctivity is more.

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