Original Research Paper Chemistry

Novel synthesis and spectral study of Co (II) complexes derived from ligands containing O,N,S donor atoms

J.R.Gujarathi Associate professor Department of Chemistry*Pratap College, Amalner (M.S.)

ABSTRACT Thiosemicarbazones were synthesized by refluxing 5-chloro 2-hydroxy acetophenone and thiosemicarbazide in the mole ratio 1:1.The complexes of thiosemicarbazoneswith Co(II) were synthesized by refluxing thiosemicarbazone and Co (II) chloride in the mole ratio 1:2.Thethiosemicarbazones and Co (II) complexes were characterized by Elemental analysis, ESI-MS, IRspectroscopy, UV-Visible, Nuclear Magnetic Resonance (1HNMR and 13C-NMR) spectroscopy magnetism and conductivity measurement. The metal complexes and thiosemicarbazone were tested against bacterialparasites. The free radical scavenging activity of synthesized compounds was screened for antioxidant activity. It was found that the complexes are more biologically active than thiosemicarbazone.

KEYWORDS : Bioactivemetalcomplexes, antimicrobialactivity. antioxidant activity,1:2 ratio

I INTRODUCTION

The word 'cobalt' is derived from the German 'kobalt', from kobold, means 'goblin' [1]. Cobalt is an essential trace element for higher organisms. It is required in the active center of coenzymes.Thereare eight cobalt-dependent proteins. Cobalamins are pharmaceutical agents treated in pathologies arising from a lack of vitamin B_{12} [2]. The cobalt complexes have limited medical use compared to copper complexes. Co(III) complexes of bidentate ligands, act as hypoxia-selective agents [3]. Some Cobalt complexes have been found active not only against leukemia and lymphoma cell lines [4] but also against bacteria strains [5]. Cobalt complexes also possess *in vivo* insulin-like properties [6], antifungal [7] and antioxidant activity [8]. Co(III) complex of the known untiulcer drug famotidine have greater antimicrobial activity against *E. coli* and *M. lysodeikticus*than the metal free drug [9]. The pyrazine-2,3-dicarboxylate complexes of 1,10-phenanthroline and alkyl diamines have shown activity against Gram(+) and Gram(-) bacterial strains and fungi *C. albicans*[10]. The cobalt(II) complexes of hinikitiol, 4-isopropyltropolone, are active [11]. Some octahedral cobalt complex possessed good activity against both Gram(+) and Gram(-) bacterial strains but not higher than the free ligand alone [12]. Cobalt (II) complexes not only show antimicrobial but also antifungal activities. The complex of the imidazole-2-carbaldehyde semicarbazone are active against the yeasts *S. cerevisiae* and *C. tropicalis*. Activity was most noticeable against such phytopathogenic fungi as *Alternaria*or *Sclerotinia*[13]. The complexation of the nicotinate derivatives led to an elevation of their biological activity [14]. Research has been done in developing cobalt(II) complexes of the Schiff bases for their antimicrobial [15-17] and antifungal [5] properties. The cobalt(II) complex was found ineffective against Gram(-) bacteria, because of its hydrophobicity and large molecular weight [18].

II.LITERATURE SERVE

The metal complexes formed by salicylaldehydethiosemicarbazone ($ONSH_2$) [19-21].This ligand readily loses a proton from the phenolic group and acts as a singly charged tridentate, coordinating through the oxygen, theimino nitrogen and the thionesulphuratoms.It can also act as a doubly negatively charged tridentate by losing a proton from the mercaptogroup. The Co (III) complexes $[Co(ONSH)_2]Cl$ and $[Co(ONSH)(ONS)]H_2O$ have been synthesized and investigated.Co (III) complexes of anthraldehydethiosemicarbazone (H than) and mixed complex with DMG (DH) have been synthesized and investigated [22]. It was found that in $[Co(than)_2]X.nH_2O$ (X=Cl,Br,I or NCS),the ligand (H-than) is tridentate where as in $[CoCl(DH)_2$ (H-than)].$2H_2O$ or $[Co(DH)_2$ (H-than)].Cl.$4.5H_2O$,it is monodentate and coordinated to Co (III) via S.

Considering the above research work it is desirable to synthesize and characterize the Co (II) complexes with Schiff base.The present research work reports the synthesis and spectral, characterisation of ligand and metal complexes with Co (II).The biological activities of six coordinate complexes of Co (II) with 5-dichloro 2-hydroxy acetophenonethisemicarbazones and N (4) thiosemicarbazone have also been reported.

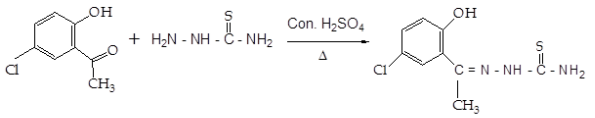
III. MATERIALS AND METHODS

All A.R.gradechemicals 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 thermogravimetricanalysis.Metal in the complexes was estimated by standerdized E.D.T.A.

IV EXPERIMENTAL

Synthesis of thiosemicarbazone L

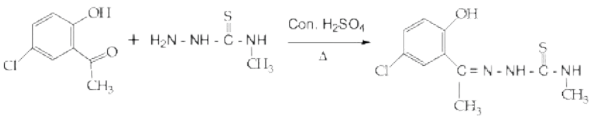
Ethanolic solutions of 5-chloro 2-hydroxy acetophenone and thiosemicarbazide in the mole ratio 1:1 were mixed and refluxed for three hours.. The pale yellow product obtained oncooing was filtered and washed with hot water then cold ethanol and finally with ether. The compound was then filtered and dried in vacuum.



SCHEME - I

Synthesis of thiosemicarbazone L'

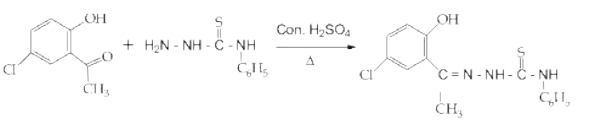
Ethanolic solutions of 5-chloro 2-hydroxy acetophenone was added to ethanolic solution of N(4) methyl thiosemicarbazide in the mole ratio 1:1. The reaction mixture was refluxed for three hours.. The pale yellow product obtainedoncooing was filtered and washed with hot water then cold ethanol and finally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



SCHEME -II

Synthesis of thiosemicarbazone L"

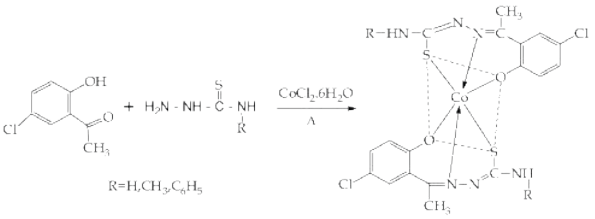
Ethanolic solutions of 5-chloro 2-hydroxy acetophenone was added to ethanolic solution of N (4) phenyl thiosemicarbazide in the mole ratio 1:1.The reaction mixture was refluxed for three hours.. The pale yellow product obtained oncooing was filtered and washed with hot water then cold ethanol and finally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



SCHEME - III

Synthesis of complex ML_2

The complex of the type ML_2 was synthesized by mixingethanolic solutions of thiosemicarbazones (0.01M),$CoCl_2.6H_2O$ in the mole ratio 1:2. The reaction mixture was refluxed for one hours.The dark brown product thus obtained was filtered and washed with a small portion of cold ethanol and was dried in oven.



SCHEME - IV

TABLE 1 PHYSICAL PROPERTIES:

Compounds	Colour	Empirical Formula	Molar conductance $Ohm^{-1}cm^2mole^{-1}$	Magnetic Moment B.M.
L	Yellow	$C_9H_{10}N_3OSCl$	-	-
L′	Yellow	$C_{10}H_{12}N_3OSCl$	-	-
L″	Yellow	$C_{15}H_{14}N_3OSCl$	-	-
Co L_2	Brown	$C_{18}H_{16}N_6O_2S_2Cl_2Co$	40	2.60
Co.L'_2	Brown	$C_{20}H_{20}N_6O_2S_2Cl_2Co$	48	2.65
Co.L''_2	Brown	$C_{30}H_{24}N_6O_2S_2Cl_2Co$	55	2.75

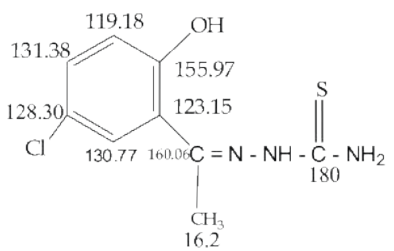
Physical data of ligand and its complexes is presented in Table 1.The complexes are soluble in DMF. Molar conductance measured in DMF solution of these complexes indicates non electrolyte.The Co (II) ion,d7 case has three unpaired electrons and observed magnetic moments are found to be 30 % higher than the spin only value in case of magnetically dilute Co (II) complexes.The higher magnetic moment is generally attributed to incomplete quenching of the orbital contribution to the magnetic moment due to inverted multiplet levels.In some cases abnormally low magnetic moments are also observed.

^{1}H-NMR L

Signals at 13, 3.40 ppm are assigned to – OH, - CH_3 protons respectively. Thiosemicarbazone does not show any peak corresponds to S-H proton, indicating it exists in thioketo form. Absence of ^{2}NH proton signal suggests enolisation of ^{2}NH – C = S group to ^{2}N=C-SH. Little low field position of ^{4}NH (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.

^{13}C-NMR L

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-CH_3).

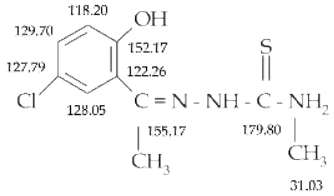


^{1}H-NMR L′

NMR signals at 13.00 and 3.00 ppm are assigned to – OH and – CH_3 protons respectively. The signals at 2.19, 2.25 correspond to ^{4}NH and H^{4}N-CH_3 respectively. Absence of ^{2}NH proton signals suggests enolisation of ^{2}NN – C = S group to ^{2}N = C – SH. Aromatic protons show multiplet at 6.9, 7.255, 7.45, ppm range.

^{13}C-NMR L′

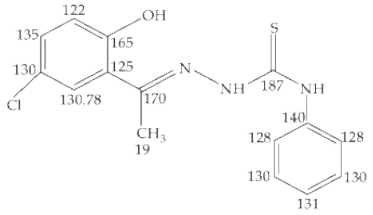
118.20 (C = C), 129.70 (C = C), 127.79 (C = C – Cl), 128.05 (C = C), 122.26 (C= C), 152.17 (C = C – OH), 155.39 (C = N), 179.80 (C = S), 31.03 (NH- Ch_3)



^{1}H-NMR L″

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).

13C-NMR L″



(Calculated) found ESI-MS

L:$C_9H_{10}N_3OSCl$(243.70) 243.11,**L′**:$C_{10}H_{12}N_3OSCl$(257.72) 257.15,**L″**:$C_{15}H_{14}N_3OSCl$(319.79) 319.41, **Co.L_2**: $C_{18}H_{16}N_6O_2S_2Cl_2Co$ (542.20)542.79,**Co.L'_2**:$C_{20}H_{20}N_6O_2S_2Cl_2Co$(570.35)570.02,**Co.$L''_2$**:$C_{30}H_{24}N_6O_2S_2Cl_2Co$ (694.24) 694.93.

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

V ANALYTICAL DATA

1.**L:**% 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.**L′**% 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.L″ :% 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. **Co.L_2:** % Co 10.17 (10.87), %C 39.12 (39.87), %H 2.31 (2.97), %N 15.13 (15.50)%O 5.13 (5.90), %S 11.20 (11.81).

5**. Co.L'_2:** % Co 10.97 (10.33), %C 42.91 (42.11), %H 3.53 (3.81), %N 14.21 (14.73), %O 5.03 (5.61 %S 11.72 (11.24).

6.**Co.L''_2**: % Co 8.72 (8.49), %C 51.03 (51.90), %H 3.02 (3.48), %N 12.72(12.11), %O 4.87 (4.61) %S 9.93 (9.24).

On the basis of elemental analysis data,thecomplexes have 1:2composition.The calculated and therotical values are matched.

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

1.L: ν (- OH) 3147,ν (C = N) 1620, ν (- C – S) 750 (s), 1370 ;ν (^{2}N-H) 3250, ν (N – N) 1050, , ν (C – O) 1280.

2.L′: ν (- OH) 3225, ν (C = N) 1630, ν (- C – S) 755 , 1358 , ν (^{2}N-H) 3255,ν (N – N) 1045, ν(C– O) 1282.

3. **L″**: ν (- OH) 3240; ν (C = N) 1635; ν (- C = S) 760, 1360 ;ν (^{2}N-H) 3260, ν (N – N) 1055, ν (C – O) 1285.

4Co-L_2:ν (C = N) 1550 ν (C = N – N = C) 1570,ν (C-S) 710, 1301,ν (N–N) 1140,ν(M - N) 430, ν (M-O) 520, ν (M-S) 320, ν (C - O) 1205.

5 Co.L'_2:ν (C = N) 1560,ν (C = N – N = C) 1575,ν (C-S) 705, 1305,ν (N–N) 1145, ν (M - N) 440, ν (M - O) 525, ν (M-S) 330, ν (C - O) 1210.

6. Co.L''_2: ν (C = N) 1565,ν (C = N – N = C) 1580,ν (C-S) 715, 1310,ν (N–N) 1150,ν (M - N) 445, ν (M - O) 530, ν (M-S) 335, ν (C - O) 1215.

VII.Tabe 2 ElecronicSpectraincm^{-1}

Compound	State	d-d	LMCT	n→π*	π→π*
L	DMF	-	-	29750	36205
L′	DMF	-	-	29610	36402

L"	DMF	-	-	30110	37503
Co. L_2	DMF	17540	26702	31500	38202
Co. L'_2	DMF	17650	26805	31750	38530
Co. L''_2	DMF	17850	26908	31440	38900

VIII TGA ANALYSIS DATA:

1.**Co-L_2:** First step, 150 °C, Mass loss 20 % second step, 215 °C, Mass loss, 35 % Third Step 360 °C, Mass loss, 45 % Fourth Step, 660°C, Mass loss 65 %, Residue 790 °C, % of CoO, 13.21 (13.82).

2.**Co.L'$_2$:**First step, 155 °C, Mass loss 25 % second step,217 °C, Mass loss, 39 % Third Step 370 °C, Mass loss, 48 % Fourth Step, 670°C, Mass loss, 68%, Residue, 790 °C, % of CoO, 13.71 (13.14).

3. **Co.L"$_2$:** First step, 160 °C, Mass loss 28% second step,220 °C, Mass loss, 40 % Third Step 375 °C, Mass loss, 55 % Fourth Step, 675°C, Mass loss 70 %, Residue 790 °C, % of CoO, 10.12 (10.79).

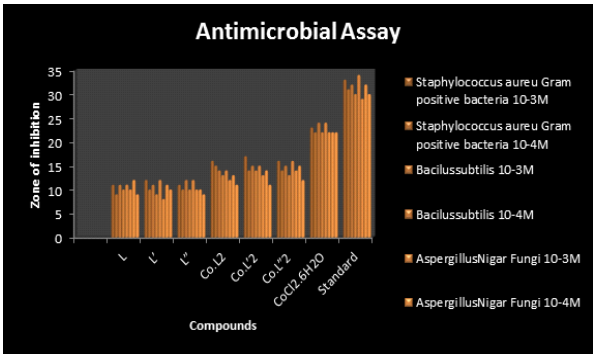
IX ANTIBACTERIALACTIVITY(WELL DIFFUSION METHOD)

Table.3 Zone of inhibition in mm L,L',L"and Co (II) complexes and standered

Compound	*Staphylococcus aureu*		*Bacilussubtilis*		*AspergillusNigar*		*Candida Albicans*	
	Gram positive bacteria				Fungi			
	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	11	9	11	10	11	10	12	9
L'	12	10	11	9	12	8	11	10
L"	11	10	12	10	12	10	10	9
$Co.L_2$	16	15	14	13	14	12	13	11
$Co.L'_2$	17	14	15	14	15	13	14	11
$Co.L''_2$	16	14	15	13	16	14	15	12
$CoCl_2.6H_2O$	23	22	24	22	24	22	22	22
Standard	33	31	32	30	34	29	32	30

(Std-Amphiciline,Fluconazole)

FIG NO.1



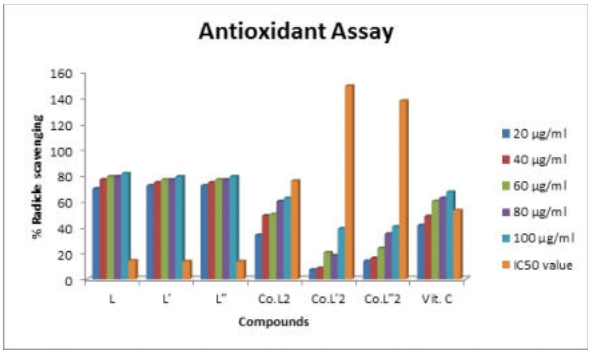
Maximum activity is obtained at higher concentration than at lower concentration. More activity was observed Gram (+) bacterial species than fungal species.

X ANTIOXIDANT STUDY

Table.4 % RADICAL SCAVENGING EXHIBITED BY L,L',L"and Co(II) COMPLEXES

Compound	20 µg/ml	40 µg/ml	60 µg/ml	80 µg/ml	100 µg/ml	IC_{50} value
L	69.76	76.74	79.06	79.06	81.39	14.33
L'	72.09	74.41	76.74	76.74	79.06	13.87
L"	72.09	74.41	76.74	76.74	79.06	13.87
$Co.L_2$	34.00	49.00	50.00	60.00	62.50	75.72
$Co.L'_2$	7.35	8.52	20.52	18.32	39.02	148.87
$Co.L''_2$	14.00	16.20	24.00	35.00	40.50	137.35
Vit. C	41.55	48.53	60.15	62.48	67.13	53.02

Fig No.2



More activity % radical scavenging activity was observed in the complexes

Result and Discussion

IR spectra of L,L',L" show bands at 3147,3225 and 3240 cm^{-1} due to phenolic –OH groups.These bands disappeared in the spectra of the complexes. The band in the range 3250-3260 cm^{-1} in the ligands due to the $\nu(^2NH)$ disappeared in the spectra of complexes. This indicates the coordination of thiosemicarbazone around the Ni(II) ion in its deprotonated form. It is confirmed by decrease in ν(CO) frequency and appearance of a band in the range 520-530cm^{-1} due to a ν (Co-O) in the spectra of complexes [23]. It indicates coordination through phenolic oxygen. There is negative shift of ν(C=N) of the ligands at 1620-1635 to 1550-1565 cm^{-1}. It is confirmed with coordination of azomethine nitrogen with the presence of new band in the range 430-445cm^{-1}due to ν(Co-N) in the complexes [23, 24-28].The ν(N-N) of the thiosemicarbazones is found in the range the 1045-1055cm^{-1}. It is shifted to higher side in the spectra of the complexes, due to the increase in the bond strength.It confirms the coordination via the azomethine nitrogen. The bands in the range I358-1370 and 750-760cm^{-1}due to thioamide stretching and bending vibrations in thiosemicarbazones are shifted to lower side, indicating coordination of the thiolate sulfur to the Co(II) ion. It is again confirmed with the presence of new band in the range 320-335cm^{-1}, assignable to ν(Co-S) in the complexes [25].

UV-spectra was carried out in DMF. Each thiosemicarbazone and its Co (II) complex show a ring π→π* band in the range 36000-39000 cm^{-1} and an n→π* band in the range29000-32000 cm^{-1}, involving transitions within the thiosemicarbazone moiety [29]. These bands are slightly shifted to higher side upon complexation. The shift of the π→π* bands to longer wavelength region in complexes is due to weakening of the C=S bond and the conjugation system enhanced on complexation [30, 31]. In the case of complexes having ONS donor ligands, the shift of two ligand to metal charge transfer bands are observed in the range 26000-27000 cm^{-1}. Each complex has a d-d combination bands are found in the range 17000-18000 cm^{-1}.

TGA data indicated that in the complexes hydrated layer was removed below 100°C. The decomposition of the complexes proceeded in four steps. The complexes are stable up to about 360-375°C.In the second step the loss in mass is upto 35-40%.The organic molecue was lost up to 660-675°C.The mass lost cooresponding to this step is about 65-70%. The decomposition was complete and metal oxide was formed at a temperature about 790 °C.No coordinated water molecule/molecules was found in the analysis. The more thermal stability of the compexes is due to the coordination of metal.

The antimicrobial activity was determined using the well diffusion method. Activity was measured in two different molar concentrations ,10^{-3}M, 10^{-4} M. The zone of inhibition was measured in mm.It is found that the synthesized compounds exhibited microbil activity at low and high concentrations. The synthesized complexes showed maximum activity against bacterial species than free ligands. 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 antimicrobial activity. The thiosemicarbazones were found less active than theircomplexes. The delocalization of π-electrons increases lipophilicity and this facilitates the penetration into lipid membranes, further restricting proliferation of the microorganisms [32]. In complexes coordination number increases. This may be responsible for enhanced antimicrobial activity. ***Staphylococcusaureu*** and ***Bacilussubtilis*** are gram +ve bacterial species and ***AspergillusNigar***, ***Candida - Albicans*** are fungal species.The metal chloride salt was found more growth inhibitory than complexes. The Co^{+2}ions have small size having d^7configuration.This increases the permeability to cell membrane.But use of metal ion solution to treat bacterial diseases may be toxic,so it can be used in coordination with ligand.The general sequence of of inhibitory activity can be represented as - Metal salt > Standard > complexes > free ligand.

The growth inhibition decreases on dilution ie it is more in concentrated solution.

Antioxidant study was carried out by DPPH assay. DPPH is stable free nitrogen radical and the assay determines the ability of the compound to reduce DPPH radical. The antioxidants play important role of converting unpaired electrons to paired ones. There is decrease in absorbance at 517 nm.This measures the abiity of test compound to reduce DPPH radical that acts as an antioxidant which is then 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 40 min, the absorbance of each solution was determined at 517 nm using doube beam 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 absorbance of the reaction mixture indicated higher free radical scavenging activity [33]. The results of antioxidant activity are presented in Table No. 4.
Lower the absorbance of the reaction mixture indicated higher free radical scavenging activity. Complexes showed better % scavenging activity at higher concentration.

XII CONCLUSION

The thiosemicabazones are found tridentate having ONS donor atoms.The spectral data indicates octahedral geometry for complexes.The complexes are paramagnetic.TGA indicates thermal stability of the complexes. The compounds are thermally stable upto360-375^{0}C.The decomposition took place in four steps.The complexes showed growth inhibitory activity against gram +ve bacterial and fungal species.The activity is more at 10^{-3}M concentration.The metal salts showed better growth inhibition at higher concentration.The complexes are found ntioxidants.

REFERENCES

1. Andreini C.; Bertini I.; Cavalarro G.; Holliday G.L.; Thornton J.M. J. Biol. Inorg. Chem. 13,2008 1205
2. Hui Chao; Liang-NianJi John Wiley & Sons Ltd., Chichester, England Chapter 11,2005 201.
3. Ott I.; Kircher B.; Gust R. J. Inorg. Biochem. 98,2004 485.
4. Lopez-Sandoval H.; Londono-Lemos M.E.; Garza-Velasco R.; Poblano-Melendez I.;Granada-Macias P.; Gracia-Mora I.; Barba-Behrens N. . J. Inorg. Biochem. 102,2008 1267.
5. Matsumoto K.; Yamamoto S.; Yoshikawa Y.; Doe M.; Kojima Y.; Sakurai H.; HashimotoH.; Kajiwara M.N. .B. Chem. Soc. Jpn. 78,2005 1077.
6. Lv J.; Liu T.; Cai S.; Wang X.; Liu L.; Wang Y. J. Inorg.Biochem. 100, 2006 1888.
7. Takeuchi T.; Bottcher A.; Quezada C.M.; Meade T.J.; Gray H.B. Bioorg. Med.Chem. 7, 1999 815.
8. Dimiza F.; Papadopoulos A.N.; Tangoulis V.; Psycharis V.; Raptopoulou C.P.;Kessissoglou D.P.; Psomas G. Dalton Trans. 39, 2010 4517.
9. Miodragovic D.U.; Bogdanovic G.A.; Miodragovic Z.M.; Radulovic M.D.; NovakovicS.B.; Kaluderovic G.N.; Kozlowski H. J. Inorg. Biochem. 100,2006 1568.
10. Yesilel O.Z.; Mutlu A.; Darcan C.; Buyukgungor O. J. Mol. Structure 964,2010 39.
11. Nomiya K.; Yoshizawa A.; Tsukagoshi K.; Kasuga N.C.;Hirakawa S.; Watanabe J. J. Inorg.Biochem. 98,2004 46.
12. Dixit R.B.; Vanparia S.F.; Patel T.S.; Chandresh L.J.; Doshi H.V.; Dixit B.C. Appl. Organometal. Chem. 24,2010 408.
13. Rodriguez-Arguelles M.C.; Mosquera-Vazquez S.; Sanmartin-Matalobos J.; Garcia-DeibeA.M.; Pelizzi C.; Zani F. Polyhedron 29, 2010 864.
14. Segl'a P.; Miklovic J.; Miklos D.; Titis J.; Herchel R.; Moncol J.; Kalinakova B.; HudecovaD.; Mrazova V.; Lis T.; Melnik M. Transition Met. Chem. 33, 2008 967.
15. Singh V.P.; Katiyar A.; Singh S. Biometals21, 2008 491.
16. Avaji P.G.; Patil S.A.; Badami P.S.33, 2008 275.
17. Yadawe M.S.; Patil S.A. Transit. Metal. Chem. 22,1997 220.
18. Dorkov P.; Pantcheva I.N.; Sheldrick W.S.; Mayer-Figge H.; Petrova R.; Mitewa M. J. Inorg. Biochem.102, 2008 26.
19. Ablov A V,Gerbeleu N V Russ.J.Inorg.Chem .9 1964 1260.
20. Ablov A V,Gerbeleu N V Russ.J.Inorg.Chem .10 1965 33.
21. Ablov A V,Gerbeleu N V Russ.J.Inorg.Chem .10 1965 624.
22. Ablov A V,Gerbeleu N V,Shopron M V Zh.J.Neorg.Khim.15 1970 1875.
23. R.P. John, A. Sreekanth, M.R.P. Kurup, S.M. Mobin, Polyhedron 21 2002 2515.
24. N.C. Saha, A. Seal, R.J. Butcher, N. Saha, J. Indian Chem. Soc. 78 2001 601.
25. D.K. Sau, N. Saha, R.J. Butcher, S. Chaudhuri, Trans. Met. Chem. 28 2003 229.
26. P. Bera, R.J. Butcher, S. Chaudhuri, N. Saha, Polyhedron 21 2002 1.
27. A. Mitra, T. Banerjee, P. Roychowdhuri, S. Chaudhuri, P. Bera, N. Saha, Polyhedron 16 1997 3735.
28. A.L. Balch, L.A. Fosset, R.R. Guimerans, M.M. Olmstead, P.E. Reed, F.E. Wood, Inorg. Chem. 25 1986 1248.
29. D.X. West, M.M. Salberg, G.A. Bain, A.E. Liberta, Trans. Met. Chem. 22 1997 180.
30. V. Philip, V. Suni, M .R.P. Kurup, Polyhedron 25 2006 1931.
31. 1.-X. Li, H.A. Tang, Yi-Zhi Li, M. Wang, L.-F. Wang, C.-G. Xia, J. Inorg.Biochem. 78 2000 167.
32. Ahmed A Al-Amiery, Yasmien K Al-Majedy, Heba H Ibrahim and Ali A Al-Tamimi. Al-Amiery et al. Organic and Medicinal Chemistry
33. 27.Rai S, Wahile A, Mukherjee K, Saha B.P, Mukherjee P.K, J. Ethnopharma, 104 2006, 312.