International Journal in Physical and Applied Sciences
Volume 07 Issue 4, April 2020 ISSN: 2394-5710 Impact Factor: 4.657
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

SPECTRAL,THERMAL AND BIOLOGICAL STUDIES OF Co(II) AND Cu(II) COMPLEXES OF SUBSTITUTED OF FUROINSEMICARBAZONES

Pushpa. M. Dahikar
Department of Chemistry
Sant Gadgebaba Amravati University, Amravati
Shri.R.R.Lahoti Science College , Morshi, Dist- Amravati

Abstract

Recently, the synthesis of Furoinsemicarbazones with semicarbazide hydrochloride in presence of aqueous sodium hydroxide in DMF-water (80%) medium respectively. The synthesis of Furoinsemicarbazones were carried out by the known literature method. They were characterized by elemental and spectral analysis. The Physico-Chemical data suggested octahedral geometry for Co(II) & Cu(II) complexes. The synthesized complexes were screened for antimicrobial activity at a concentration of 1000µgm/ml. Which was serially diluted to determine their MIC values.

Keywords:- Co(II), Cu(II) complexes , Furoinsemicarbazones, Antimicrobial activity, Sodium hydroxide, DMF-Water(80%) medium, Spectral analysis .

1.Introduction

O-Vanillin semicarbazone have been synthesized and characterized by different physicochemical techniques by Hingorani [1] .Choudhary [2] carried out synthesis and charactarization of new series of mixed ligand complex of Co(II) and Cu(II) with thiosemicarbazone/ Semicarbazone and screened their antibacterial and antifungal activities in detailed.The spectroscopic and biochemical studies of chromium and Mn(II) with p-vanillin containing thiosemicarbazone and semicarbazone ligands reported by chandra[3].Benzoinsemicarbazone are well known for their biological activity Coordination compounds containing ONS as donar atoms are reported to possess antimicrobial activity[4] . Kumar[5] carried out synthesis and characterization of Mn(II), Fe(III) ,Co(II), Ni(II) and Cu(II) complexes of salicyaldehydesemicarbazone . Khan[6] reported synthesis and characterization of Co(II), Ni(II) Cu(II) and Cd(II) complexes with 2-furfuralsemicarbazone (FSC) and 5-methyl-2-furfuralsemicarbazone (MFSC). Physico-chemical and spectral studies of Ni(II) complexes of 2-substituted benzaldehydesemicarbazone, and thiosemicarbazones were carried out by Kumar[7].Investigation on variety of semicarbazones and Schiff bases and their transition metal complexes was carried out by several workers [8-9] Mohapatra [10] reported the complexes of divalent Mn(II), Co(II), Cu(II) with benzyl semicarbazone .In the present work novel transition metal complexes of substituted benzoin semicarbazone are reported.The magnetic moment values of Cr(III),Mn(II) and Fe(III) complexes are in good agreement with the presence of three, four and five unpaired electrons respectively[11].

2.Materials and Methods

The furoinsemicarbazones was prepared by refluxing substituted benzoin with semicarbazide hydrochloride in presence of alkaline medium for 3-4 hours this reaction mixture was kept overnight. This solid products formed were isolated and washed several times with water alcohol mixture the purity was checked by TLC paper. Their structural details were confirmed on the basis of elemental and spectral analysis. Synthesis of complexes the equimolar mixture of each of the ligand(0.01M) and metal salts(0.01M) were refluxed on a water bath for 6,8 hours in presence of sodium acetate in ethanol . The reaction mixtures was kept overnight. The product formed were

isolated washed several times with cold water ethanol mixture. The characterization of synthesized complex was made with elemental analysis, IR and UV-Vis spectra. The melting point of all synthesized compounds was recorded using hot paraffin bath. The carbon and hydrogen analysis were carried out of carlo-Ebra 1106 elemental analyzer. Nitrogen estimation was carried out colman-N-analyzer-29. IR spectra were recorded on perkin Elmer spectra were recorded on Brucker Ac 300F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d_6 as solvent. The purity of compounds was checked on silica Gel-G pellets by TLC with layer thickness of 0.3mm. All chemicals used were of AR grade.

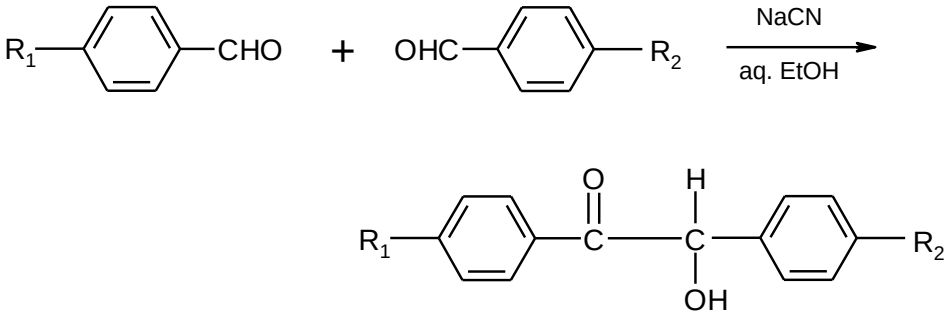
Synthesis of Furoinsemicarbazone

In a 100 ml R.B. flask Furoin (0.1 mol), semicarbazide hydrochloride (0.1 mol), NaOH 10% (5ml) and 80 % dioxane-water mixture (30ml) was refluxed for two hours. It was further heated after colour change for one hour and it was poured in acidified ice-cold water (100 ml) to obtain brown coloured solid product. It was recrystallized from alcohol. Yield 79 %, melting point 195^0C.

General Reaction

For the Preparation of substituted benzoinoxime hydrazone and semicarbazone is given in the slide

i) Preparation of substituted X- benzoin



4,4'-benzoin

R_1 = -OCH_3, -$N(CH_3)_2$, -Cl, -Br, -CH_3, -NH_2, -OH

R_2 = H, -OCH_3, -$N(CH_3)_2$, -Cl, -Br, -CH_3, -NH_2, -OH

Synthesis of complex of Cu(II) with furoinsemicarbazone

Furoinsemicarbazone is dissolved in equimolar ratio of dioxane and ethanol mixture while copper acetate was dissolved in distilled water-ethanol mixture. Separately these two solutions were transferred into 100 ml RB flask and reaction mixture refluxed for five hours.

The reaction mixture was cooled and filter, black coloured crystalline product was separated out. Yield 80%, melting point 278°C.

Properties of complex of Cu(II) with furoinsemicarbazone

1. It is dark black crystalline solid having melting point 278°C.
2. It gave positive test for amide.

3. It gave positive test for alcoholic group.
4. It gave positive test for nitrogen.
5. It gave positive test for copper.
6. It is soluble in alcohol, DMF, CCl_4, chloroform and dioxane.
7. Elemental Analysis :-

Elements	**Found**	**Calculated**
Carbon	44.7821	45.9134
Hydrogen	3.7998	4.1204
Nitrogen	12.0078	12.3613
Copper	7.9874	9.3504

3. Result and Discussion

TABLE-1

THE METAL COMPLEXES COMPOUND, MOLECULAR WEIGHT, COLOUR AND ELEMENTAL ANALYSIS OF VARIOUS METAL IONS

Complexes	**Colour**	**Molecular wt**	**Elemental analysis Found/(calculated)%**			
			C	**H**	**N**	**M**
FUROSC- Cr(III)	Brown	713.84	56.23 (57.15)	4.94 (5.88)	15.68 (15.48)	6.91 (7.82)
FUROSC- Mn(II)	Dark Brown	622.93	41.45 (42.38)	3.54 (4.49)	13.48 (13.48)	7.90 (8.81)
FUROSC- Fe(III)	Grey	587.84	43.98 (44.91)	3.14 (4.08)	14.28 (14.18)	8.55 (9.49)
FUROSC- Co(II)	Red	608.93	42.44 (43.35)	3.32 (4.26)	13.69 (13.69)	8.75 (9.67)
FUROSC- Cu(II)	Red	613.54	41.97 (43.02)	3.31 (4.23)	13.69 (13.69)	9.41 (10.35)

International Journal in Physical and Applied Sciences
Volume 07 Issue 4, April 2020 ISSN: 2394-5710 Impact Factor: 4.657
Journal Homepage: http://ijmr.net.in, Email: irjmss@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal

TABLE-2
IR SPECTRAL DATA OF LIGANDS AND ITS METAL COMPLEXES

Ligands and its Complexes	υ(O-H)	υ(C=N)	υ(C-O)	υ(M-O)	υ(M-N)
FUROSC	3433	1599	1152	-	-
FUROSC- Cr(III)	3399	1579	1128	465	581
FUROSC- Mn(II)	3362	1507	1135	477	586
FUROSC- Fe(III)	3397	1507	1129	469	586
FUROSC- Co(II)	3384	1541	1137	480	587
FUROSC- Cu(II)	3391	1576	1141	484	591

The IR spectra of ligand shows a strong band at 1599cm^{-1} due to (C=N) group broad band around 3433cm^{-1} in the spectra of complexes is assignable of water. FUROSC-Cr(III) shows band at 3399(O-H).Which decreases 3362cm^{-1} inducting that attached to oxygen .However 1579 (C=N) significantly decrease to 1507 cm-1 showing linkage through azido nitrogen.The υ(M-O)& υ(M-N) vibration are verified to existing by the appearance of new weak bands in the spectra of complexes at 465&581 respectively. The IR spectra of ligand shows a strong band at 1599cm^{-1} due to (C=N) group broad band around 3433cm^{-1} in the spectra of complexes is assignable of water. FUROSC-Co(II) shows band at 3433(O-H).Which decreases 3384cm^{-1} inducting that attached to oxygen .However 1599 (C=N) significantly decrease to 1541 cm-1 showing linkage through azido nitrogen. The υ(M-O)& υ(M-N) vibration are verified to existing by the appearance of new weak bands in the spectra of complexes at 480&587 respectively.

TABLE-3
ELECTRONIC SPECTRAL DATA,MAGNETIC MOMENT AND LIGAND FIELD PARAMETER OF THE METAL COMPLEXES

Complexes	μeff (B.M.)	λ max (cm-1)	Dq	B'	B	CFSE	ν_2/ν_1	% Cova	$(\Lambda_M)\Omega^{-1}$ Cm^2 Mol^{-1}
FUROSC-Cr(III)	5.81	13769,19794 ,22620	1504	675	0.735	206	1.43	26.05	12.8
FUROSC-Mn(II)	5.99	14084,19390 ,21840	1527	596	0.620	349	1.37	38.00	17.8
FUROSC-Fe(III)	5.83	13793,18518 ,22471	1505	662	0.652	344	1.34	34.08	12.4
FUROSC-Co(II)	5.20	13087,17953 ,20616	1421	577	0.594	195	1.37	40.06	11.4
FUROSC-Cu(II)	1.84	14075,19194 ,22094	1421	577	0.594	195	1.37	46.53	12.8

The electronic spectrum of Cr(III) complexes exhibits three bands at 13769,19794 and 22620 cm^{-1} which may be assigned to $^4A_{2g} \dashrightarrow {}^4T_{2g}(F)$,$^4A_{2g}$--›^4T_1g (F) and $^4A_{2g}$--›$^4T_1g(P)$,transition, respectively for an octahedral stereochemistry[11] .The magnetic moment value of 5.81 B.M for Cr(III) complex is consistent with octahedral geometry around metal centre. Fe(III) Complexes three bands are observed in case of Fe(III) complexes at 13793, 1818, 22471 cm^{-1} which may be assigned to $^6A_{1g} \dashrightarrow {}^4T_{1g}(F)$,$^6A_{1g}$--›$^4T_2g(F)$ and $^6A_{1g}$--›^4Eg, belongs to transition respectively, indicating octahedral geometry of Fe(III)complexes [12-13]. The value of 5.83 B.M. would suggest high spin six coordination for Fe(III) complexes. The Mn(II) complex shows three bands in the regions 14084,19390,21840 cm^{-1} ·while Co(II) complexes is characterized by three absorption bands at 13087,17953 and 20616 cm^{-1} · while Cu(II) complexes is characterized by three absorption bands at 14075,19194 and 22094 cm^{-1} · Various ligand field parameters 10Dq,B,β, CFSE and conductance along with different d-d transitions for the complexes,are calculated and presented in table-3.The ligand field parameters are consistent with octahedral geometry.The Racha inter-electronic repulsion parameter B is less than free ion value suggesting a considerable covalent character of the bond.The calculated values of ν_2/ν_1 ratio is within the range expected for an octahedral geometry.On the basis of elemental analysis, molar conductivity,magnetic measurements,IR and electronic spectral data an octahedral geometryhave been proposed for Cr(III),Fe(III),Mn(II),Co(II) and Cu(II) are assigned octahedral geometry respectively.

Thermo gravimetric studies

Thermo gravimetric study indicates all the complexes are stable 120^0C.Allthe complexes shows a gradual weight loss in fragments. The TG analysis of Co(II),Mn(II) and Fe(III) complexes shows three step decomposition while the ligand and its Cr(III),Cu(II) complexes undergo two step decomposition. All the complexes are stable up to 120^0C except Cr(III),Cu(II). The elimination of one water molecule in the first stage of Co(II),Mn(II) ,Fe(III)and Cu(II) complexes and in second stage loss of two water molecules of Cu(II) complexes indicates the presence of lattice water molecules. In the presence of two co-ordinated water molecule of all these complexes as well as Cr(III) complex weight loss up to220^0C.After 220^0C there is rapid weight loss which indicates decomposition of free parts of co-ordinated ligands. After this there is no weight loss up to 560-670^0C whis suggest the absence of any other water molecule (lattice/co-ordinated) in all these complexes. Finally, above 650^0C a constant level is obtained corresponding to metal oxides such as Cr_2O_3,CoO,MnO_2,Fe_2O_3 and CuO respectively.The half decomposition temperature of complexes are given (Table:3).The comparative thermal stability order of complexes is found to be Cu(II)<Co(II) <Fe(III) <Mn(II) <Cr(III).The analysis of magnetic moment, thermal analysis and electronic spectral data indicate octahedral geometry for the complexes.

TABLE-4

THE PERCENTAGE WEIGHT LOSS DATA OF COMPLEXES OF FUROSC

Complexes	The percentage weight loss at		Half decomposition Temparature^{0}C
	120^0C-140^0C Observed(Calc.)	220^0C-240^0C Observed(Calc.)	
Cr(III)	_	6.92(6.86)	708
Co(II)	2.95(2.93)	8.88(8.80)	618
Mn(II)	6.45(6.40)	12.90(12.86)	662
Fe(III)	4.03(4.00)	12.16(12.13)	632
Cu(II)	5.86(5.80)	_	612

Antimicrobial activity of complexes

The compounds were assayed for their antimicrobial activities[14] against four test organisms E.coli, S. aureus, Ps.aeruginosa, B. subtilis at a concentration of 1000µgm/ml by agar well technique[15]. Further their MIC value against these organisms were determined by serial dilution method using DMF as a solvent. On the basis of MIC values, FUROSC-Cr(III) is found to be most effective antimicrobial agent followed by FUROSC-Mn(III) and FUROSC-Cu(III). The enhance antimicrobial activity in case of the compounds. FUROSC-Co(III) may be attributed to the presence of furanyl group. The results obtained are given in table-5

TABLE-5
MIC VALUES IN µgm/ml OF COMPOUNDS

Complexes	***E.coli***	***S.aureus***	***P. aeruginosa***	***B.Subtilis***
FUROSC- Cr(III)	63	125	125	250
FUROSC- Mn(II)	125	250	250	125
FUROSC- Fe(III)	250	250	125	250
FUROSC- Co(II)	250	125	63	63
FUROSC- Cu(II)	125	125	250	250

Acknowledgment

The authors are thankful to the SAIF,CDRI, Lukhnow for IR SAIF Chandigarh .Department of Physics, SGBAU, Amravati for magnetic measurements of the compounds respectively.

References

[1] S. Hingorani, K. singh, B.V. Agrawal, J.Ind chem.soc, 7, (1994), 183-186
[2] A. Choudhari, R.Sharma, M. Nagar, Int. Research J. pharmacy and pharmacology,1, (2011) ,172-187
[3] S. Chandra and M. Tyagi, J. Ind. Chem, Soc., 85, 42 - 47, 2008
[4] H.G. pettering and J.A. crime, cancer Res, 27, (1967) 1278
[5] Y. Kumar, S. Chandra; R.P. Singh; A.K. Singh, synthesis and reactivity in Inorganic, Metal -organic and Nano- metal chemistry, 14(2), 185-189, 1984.
[6] M.A. Khan and G.M.Bouet, Transition Met. Chem., 24, 294 - 298, 1999.
[7] B. Kumar, S.K. Sangal; A. Kumar, J. Ind. Chem., Soc., 86, 514 - 517, 2009
[8] R.C. Mehrotra, G.wilkinson, R.D. Gillard and J.S. Mccleverty comprehensive coordination chemistry , pergaman press, New york, 2,(1988), 269
[9] E. Tas, M. ulusoy and M. guler transition met chem., (2004),180
[10] R.C. Mishra, and B.K. Mohapatra, J.Indian chem. Soc, vol LIX, (1982), 836-838
[11]S.Chandra and M.Tyagi,J.Ind.Chem.Soc.,85,45,2008

[12] A.A. El- Asmy; M.E. Khalifa; M.M. Hassanian, Ind. J. of Chem; 43(A), 92 - 97,2004.
[13] M.A. Monshi, J. Ind. Chem. Soc., 75, 158 - 159, 1998.
[14] K. Nakamoto, "Infrared and Raman spectra of Inorganic and coordination compounds" willeyInterscience, New York, 3rd Ed. 171 1978
[15] S. Chandra, L.K. Gupta; K.K. Sharma, J. Saudi Chem. Soc., 9(1), 131 - 136,2005.