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Synthesis, Characterization, Thermal and Antibacterial studies of Isonicotinoyl hydrazone Schiff base Complexes of Cobalt(II), Nickel(II), Copper(II) and Zinc(II)

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ABSTRACT

A newly synthesized series of transition metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 2-hydroxy-5-bromo-3 nitroacetophenone hydrazone Schiff base [LH_2] derived from 2-hydroxy-5-bromo-3-nitroacetophenone and isonicotinoyl hydrazide have been synthesiz

ed and characterized on the basis of molar conductance, magnetic susceptibilities, elemental analysis, infrared, ^1H NMR, electronic spectra and thermogravimetric analysis. The Schiff base acts as monobasic bidentate ligand commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. Which is confirmed by IR spectral data. Thermal analysis indicates the coordinated and lattice water molecules in the complexes which is also IR spectral data. The bioefficacy of the ligands and therir complexes have been examined against the growth of bacteria to assess their antimicrobial potential.

Keywords: Schiff base, Magnetic susceptibility, Thermal, Antimicrobial studies.

1. INTRODUCTION

The study of a range of coordination compounds is linked to the coordination of metals with the Schiff base ligands. The hydrazone Schiff bases are widely used ligands to synthesize their metal complexes due to their facile synthesis, significant and good solubility in common organic solvents. Thus, they have played a important applicable role in research and development of coordination chemistry as they readily form stable metal complexes in different oxidation states[1]. Schiff bases or their metal complexes have many applications in different fields[2] Hydrazones, heteroaroyl hydrazones ligands and their metal complexes are biologically active. Heteroaroyl hydrazones forms stable metal complexes with transition metal ions and inner transition metal ions due to complexing ability of ligand through keto-enol tautomerism and availability of other donar sites in the ligand i.e. isonicotinoyl hydrazide is one of the drug in chemotherapy of tuberculosis[3]. Due to its biological potency, pharmacological properties and synthetic flexibility of Schiff base derived from isonicotinic acid hydrazide [4,5].

The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-bromo-3-nitroacetophenone and isonicotinoyl hydrazide.

2. Material and Methods

All the chemicals used were of AR grade and used as received isonicotinoyl hydrazide(IH) was obtained from E.Merck. 2-hydroxy-5-bromo-3-nitro acetophenone (HBNA) was prepared by known method [6]. The solvents were purified by standard methods [7].

2.1. Synthesis of 2-hydroxy-5-bromo-3-nitroacetophenone isonicotinoyl hydrazone [HBNAIH]

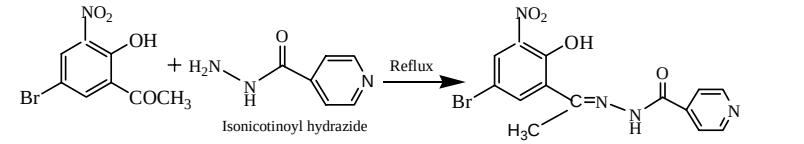
A solution of isonicotinoyl hydrazide (0.02M) in 25ml of ethanol was added to an ethanolic solution (25ml) of 2-hydroxy-5-bromo-3-nitroacetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 3h. Then cooled to room temperature. The resulting pale yellow coloured solid was washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and melting point. It was also characterized by IR and ^1H NMR spectral studies. Yield: 65% MP: 275 ^0C .

2.2. Preparation of complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HBNAIH (0.02M) in 25ml of ethanol a suspension of respective metal salts

[acetates of Co (II), Ni (II), Cu (II), and Zn (II)] was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6h. The precipitated complexes were filtered, washed with ethanol. Followed by ether and dried over fused calcium chloride. Yield: 40-45%

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods[8]. The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}. Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermo gravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0 min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.



2-hydroxy-5-bromo-3-nitroacetophenone

2-hydroxy-5-bromo-3-nitroacetophenone isonicotinoyl hydrazone

Scheme 1-Synthesis of the ligand (LH_2)

Table - 1: Analytical data of the Ligands.

Ligand	Molecular Formula	Formula Weight	Colour and nature	Elemental Analysis		
				C% found (Cal.)	H% Found (Cal.)	N% Found (Cal.)
HBNAIH	$C_{14}H_{11}N_4O_4Br$	379.2	Yellow Crystalline	43.79 (44.35)	02.65 (02.92)	14.34 (14.78)

Table - 2: Analytical data and molar conductance of the compounds.

Compounds	Colour	Mol.wt.	Analysis %, Found (calc.)				μ_{eff} B.M.	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)
			M	C	H	N		
$[Co(LH)_2\,2H_2O]\,H_20$	Brown	869.3	5.80 (6.77)	38.35 (38.65)	2.35 (2.99)	12.48 (12.88)	4.7	3.2
$[Ni(L)H_2O]\,H_20$	Green	471.9	12.28 (12.43)	35.30 (35.60)	2.24 (2.75)	11.13 (11.86)	Dia	6.19
$[Cu(LH)_2]\,3H_20$	Brown	873.9	7.12 (7.26)	37.45 (38.44)	3.13 (3.20)	12.34 (12.81)	1.61	5.23
$[Zn(LH)_2 2H_2O]\,2H_20$	Red	893.8	7.08 (7.14)	37.22 (37.59)	3.16 (3.35)	12.12 (12.53)	Dia	---

3. RESULTS AND DISCUSSION

The ligand HBNAIH and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, diffused reflectance spectra, molar conductance, magnetic succeptibility measurements and thermogravimetric analysis.

The ^1H NMR spectra of ligand HBNAIH shows signals [9-12] at δ 12.85, (1H, s, phenolic OH); 12.44, (1H, s, imino); 9.15 and 9.18 (4H, d, isonicotine); 7.85 and 7.35, (2H, m, phenyl) and 3.15 ppm, (3H, s, methyl)

All these values and analytical data is consistent with proposed molecular formula of

ligand. All the compounds are coloured solid and stable in air. All the compounds are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF (10^{-3} M) solution at room temperature (Table.2) shows all the complexes are non electrolytes.

IR spectra of ligand shows[13-17] V(C=N) peaks at 1618 cm^{-1} and absence of C=O peak at around 1700 – 1750 cm^{-1} indicates the Schiff base formation. Other reported peaks are V(N-H) at 3181 cm^{-1} , V(OH) at 2994cm^{-1} V(C=O) phenolic at 1535 cm^{-1}, pyridyl ring breathing peak at 1072 cm^{-1}, V(N-N) peak at 991 cm^{-1} and V(C=N) peak at 1618 cm^{-1}, The V(C=N) peak of ligand is found to be shifted to lower frequencies in the spectra of complexes indicating the coordination via the azomethine nitrogen, which is also confirmed by appearance of bands in the range of 540 – 345 cm^{-1} which have been assigned to V(M-N) band.

Thermogravimetric techniques have a very wide field of application. The results from thermogravimetric analyses are usually reported in the form of curves relating the mass lost from the sample against temperature. In this metal complexes all the complexes except Cu (II) show two stage decomposition pattern and Cu (II) show three stage decomposition pattern. Thermogravimetric study indicates all the complexes are stable up to 60-70^{0}C. The percentage weight loss data (Table 3) up to 140^{0}C indicates the loss of one water molecule from Co (II) and Ni (II) complexes each, loss of two water molecule from Zn (II) complexes and loss of three water molecules (lattice) from Cu (II) complexes each. Further loss in weight up to 220-240^{0}C was observed. The percentage weight loss data indicates loss of one coordinated water molecule from Ni (II), complexe each, loss of two coordinated water molecule from Co (II) and Zn (II) complexes each. There is no weight loss at 220-240^{0}C in Cu (II) complexe indicates the absence of coordinated water molecule in this complex [18-25].

3.1. Antimicrobial activity

Antimicrobial Screening assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis the agar diffusion method has been employed. In this study the ligand and their metal complexe were tested for their effect on certain human pathogenic bacteria such as Gram-positive. The inhibition effect of the ligand and its metal complexes on the growth of various bacterial species *B.subtilis*, *P.vulgaris*, *S.aureus*, *E.coli*, *P.fluorescen*, *A.aerogenes*, *B.megatherium*. are summarized in Table 4 [26-29].

Table -3: The percentage weight loss data of complexes of HBNAIH

Complexes	The percentage weight loss at 110-140^{0}C observed (Calc.)	220-240^{0}C Observed (Calc.)	Half decomposition Temperature (^{0}C)
Co(II)	2.23 (2.40)	4.62 (4.68)	432.5
Ni(II)	4.12 (4.30)	4.21 (4.36)	468.0
Cu(II)	6.55 (6.80)	-	444.0
Zn(II)	4.8 (4.5)	5.1 (4.6)	412.0

Table - 4: Antimicrobial activity

Ligand and its Complexes	Zone of inhibition (in mm)						
	B.subtilis (mm)	*P.vulgas* (mm)	*S.aureus* (mm)	*E.coli* (mm)	*P.fluorescen* (mm)	*A.aerogenes* (mm)	*B.megatherium* (mm)
HBNAIH	S_{10}	R	S_{11}	R	S_8	R	S_7
Co-HBNAIH	S_{11}	S_{11}	R	S_{12}	R	S_9	R
Ni-HBNAIH	R	R	S_8	S_{14}	R	R	R
Cu-HBNAIH	S_{12}	S_{10}	R	S_{16}	R	S_6	S_{11}
Zn-HBNAIH	S_{13}	R	R	R	S_{15}	S_{13}	S_{12}

S-Sensitive, R-Resistant

4. CONCLUSION

The analysis of magnetic moment, thermal analysis and electronic spectral data shows characterization and structural changes in metal complexes. All the complexes contain lattice water and shows weight loss up to 320^{0}C indicates decomposition of ligand molecule. Further a horizontal curve was observed beyond 640^{0}C suggest the formation of final decomposition products i.e. stable metal oxides of respective metals. On the basis of half decomposition temperature the order of thermal stability is found to be Ni(II)>Cu(II)> Co(II) > Zn(II). The structural changes of all complexes have marked effect on the sensitivity and sensitivity varies with organisms.

5. REFERENCES

1. Prasad KS, Shiva Kumar L, Chandan S, Jayalakshmi B, and Revanasiddappaa HD Spectrochim. Acta, Part A, 2011; 81:276.
2. Ramesh M, Chandrashekar KB and Hussain R. Indian J. Chem., 2000;39A:1337.
3. Sharma RP, Kothari AK and Sharma NK. Indian J. Derm. Vener. Lepr., 1995;61: 26.
4. Jahagirdar JA, Patil BG, and Havinale BR. Indian J. Chem.,1990; 29A: 924.
5. Hawlader MBH and Begum MS. Indian J. Chem., 2004; 43A: 2352.
6. Ballchausen CJ and Gray HB. Inorg. Chem., 1962; 1: 11.
7. Furniss BS, Hannaford AJ, Smith PWG and Tatchell AR. Vogel's practical organic chem. 5thEd.(Logman Scientific Technical, John Wiley and Sons),1989.
8. Vogel AI. A Text book of quantitative inorganic chemistry 3rdEd., (ELBS,London), 1961.
9. Maurya MR and Gopinathan C. Indian J. Chem., 1996; 35A: 701.
10. Jayaramadu M and Reddy KH. Indian J. Chem., 1999; 38A: 1173.
11. Sastry PS and Rao TR. Proc. Indian Acad. Sci.(Chem. Sci.), 1995; 107(1): 25.
12. Mahajan RK and Patial VP. J. Indian Council Chem., 2001; 18(1): 4.
13. Maurya MR, Antony DC, Gopinathan, S and Gopinathan C. Bull. Chem. Soc. Jpn. 1995; 68: 554.
14. Viroopakshapp J and Vithalrao D. J. Indian Chem. Soc., 1996; 73: 531.
15. Figgis BN, "Introduction to ligand field", weley Estern Ltd. 1976.
16. Sacconi L. J. Ame. Chem. Soc., 1954; 76: 3400.
17. Panda AK, Dash DC, Mishra P and Mohnaty H. J. Indian Chem. Soc., 1996; 35A: 324.
18. Mishra AP and Sharma N. J. Ind. Council Chem., 2009; 26(2): 125.
19. Mallikarjun K. E. J. Chem., 2004; 1(2): 105.
20. Horowitz H. and Metzger G. Anal. Chem., 1963; 35: 1464.
21. Broido A. J. Polym. Sci. Part, A2, 1964; 1761.
22. Lucia HS, Terra A, Guekezian M, Gaubeur I, Matos JR, Maria E and Suarez-Iha V. J. Polyhedron, 2002; 21: 2375.
23. Abdo MF, Abdel-Ghani, NT, Badr Y and El-Borady OM. ISESCO Sci. and Tech., 2007; 3(3): 58.
24. Potange VN, Mane PS, Mane VG and Arbad BR. J. Indian Chem. Soc., 2008; 5: 792.
25. Mishra P. Int. J. Pharma. Sci. Rev. and Res., 2010; 2(2): 87.
26. Singh V. and Singh A. Russian J. Coord. Chem., 2008; 34(5): 374.
27. Sutariya B, Mohan S, Sambasiva S and Rao S. Indian j. Chem., 2007; 46B: 884.
28. Venkatesh P. Asian J. Pharm. Hea. Sci., 2011; 1(1): 8.
29. Kaura AK and Kaura M. Int. J. Chem. and Pharm. Sci., 2012; 3(4): 24.