

Synthesis, Characterization and Study of Some Complexes of Co (Ii) and Ni (Ii) Derived From Schiff Base 3-Hydroxy-4-Methoxybenzaldehyde-3-Oxobutanehydrazone

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ABSTRACT: A Schiff base containing bidenticity 3-hydroxy-4-methoxybenzaldehyde-3oxobutanehydrazone has been prepared by the condensation of 3-hydroxy-4methoxybenzaldehyde & hydrazine. The ligand has been finally prepared and was used for complexation with Co(II) and Ni(II). On the basis of percentage composition and molar conductivity values, the complexes have been formulated as ML₂X₂, where M-stands for Co(II) & Ni(II) while L is m-vanillin-3-oxobutanehydrazone(VBH) and X is Water, Pyridine and \Box -picoline. The mode of coordination of the ligand has been determined by the comparison of the FTIR spectra of the complexes and that of the free ligand. The appearance of some new bands in the FTIR-spectra of complexes confirms the presence of Pyridine, \Box piconine and Water in the coordination sphere of respective complexes. The magnetic moment of Co(II) complexes have been found 4.20-4.21 BM. The octahedral symmetry of Co(II) complexes have further been confirmed by their electronic spectra bands due which display three to ${}^{4}T_{1}g \rightarrow {}^{4}T_{2}g, {}^{4}T_{1}g \rightarrow {}^{4}A_{2}g$ and

 ${}^{4}T_{1}g \rightarrow {}^{4}T_{1}g(P)$ spin allowed transitions. The magnetic moment values of Ni(II) complexes have been found in the range of 3.14-3.17 BM which is also greater than its $\Box_{s} = 2.82$ BM corresponding to two unpaired electrons under octahedral symmetry. The appearance of three bands in their electronic spectra due to ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$, ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)$ spin allowed transitions.

Keywords: vanillin, bidenticity, octahedral, magnetically dilute, Racah Parameter

I. INTRODUCTION

The Schiff base and its transition metal complexes are very fascinating and interesting¹ metal complexes of Schiff base play a central role in the inorganic chemistry of chelate system. Particularly, the Schiff base containing hydrazone moiety are well known and their metal complexes have found vast application in pharmaceutical and industrial chemistry.²⁻¹⁴ In the view of their excellent Metal binding capability last few decades show a plethora of studies in the field of hydrazone and semicarbazone ligands because of their structural properties and broad spectrum of application in various fields. Vanillin hydrazone shows wide range of biological activities.¹⁵⁻¹⁷ Vanillin hydrazone are also potential anti-cancer agent.¹⁸⁻¹⁹ The perusal of literature reveals that the work reported on the complexes of hydrazone of vanillin is very scars. This fact motivated us to pursue research on spectral characterization of complexes of 3-hydroxy-4-methoxybenzaldehyde-3-oxobutanehydrazone with Co(II) and Ni(II) metal ions in which the bidenticity of the ligand may lead to the formation of macromolecules type coordination compounds.

EXPERIMENTAL

All the chemicals used were of Alal.R.Grade and were used as received. Ethylacetoacetate have been procured from Loba Chemie in Maharashtra (India), hydrazine hydrate has been purchased from Fisher Scientific in Maharashtra (India) and 3-hydroxy-4methoxybenzaldehyde (m-vanillin) has been procured from Merck in Ahmedabad (India). First of all 3-oxobutanehydrazide has been prepared by the method reported by D. Kumar, et al.²⁰ It has been given in Scheme-I.



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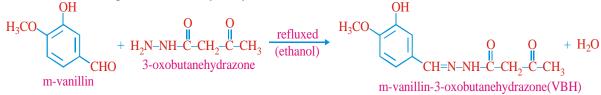
 $OC_2H_5 + H_2N-NH_2 \longrightarrow C_2H_5OH + CH_3$ CH₃--NH-NH₂ Ethylacetoacetate Hvdrazine

Scheme-I

Now. 100 mmol (11.6 g) of 3oxobutanehydrazide and 100 mmol (15.2 g) of 3hydroxy-4-methoxybenzaldehyde dissolved in 50 mL of ethanol. The resulting solution was refluxed on waterbath for two hours and the excess solvent was evaporated. The rest solution was allowed to stand at room temperature whereby a yellow

3-oxobutanehydrazide

compound separated out. It was suctioned filtered and washed with ethanol and finally recrystallised from ethanol. The Schiff base was dried on anhydrous calcium chloride in a desiccator. The Schiff base m-vanillin-3-oxobutanehydrazone, henceforth abbreviated as VBH given as below in Scheme-II.



Scheme-II

The ligand has been used for complexation with Co(II) and Ni(II) by the usual method of reflux. The micro analysis of Carbon, Hydrogen and Nitrogen was carried out by using microanalyser Technique on Carlo Erba Microanalyser-1108. The content of cobalt was determined volumetrically while nickel contents were estimated Gravimetrically. The molar conductance of complexes were measured at room temperature in 10⁻³ M solution in DMSO by Toshniwal Digital Conductivity meter with a deep type cell. FTIR spectra of ligand as well as complexes were recorded in KBr on Perkin Elmer Model Arc RX₁ spectrometer. The magnetic susceptibility was measured at room temperature by Gouy Balance using CuSO₄.5H₂O as a calibrant. The electronic spectra of complexes were recorded on Shimadzu model UV/Vis Spectrophotometer.

II. RESULT AND DISCUSSION

The micro analytical data and molar conductivity of ligand and complexes have been given in Table-1. Table-1: Analytical, Melting point, Magnetic Susceptibility, Conductivity measurement of ligand VBH and its metal complexes

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S.	Compounds Colou	Yield	Melting	% Ar	alysis fo	ound / (c	alculated	i)□ _m		
no. (BM)	-	Point (°C)	М	C	Η	Ν	(ohr	n ⁻¹ cm ²	mol-1)
1.	Ligand [VBH] Yellov	v 72	209.5°C	; - (5.61)	57.92 (11.20)		11.00	-	-	
2.	[Co(VBH) 2(H2O)2] Blue	Dark	70 (9.94)	285°Ć (48.54)	9.92 (5.06)	48.72 (9.44)	4.91	9.12	12	4.21
3.	$[Co (VBH)_2(Py)_2]$	Blue	75 (8.25)	288°C (57.06)	8.00 (5.03)	57.48 (11.74)	4.93	11.44	11	4.20
4.	[Co (VBH) ₂ (□-Pico) ₂]	Bright	71 (7.94)	288.8°C	(5.38)		5.12	11.16	12	4.21
5.	[Ni (VBH) ₂ (H ₂ O) ₂] Green	Bright	64 (9.94)	292°C (48.56)	9.60	48.78 (9.44)	4.89	9.20	15	3.14
6.	[Ni (VBH) ₂ (Py) ₂]Green	6 5	294°C (8.25)	8.00 (57.06)	57.34	4.91 (11.70)	11.51	15	3.17	
7.	[Ni (VBH)₂(□-Pico)₂] Green	Dull	65 (7.94)	· · · ·	7.72	58.41 (11.30)	5.10	11.12	13	3.16

CONDUCTIVITY

The low molar conductance values (11-15 ohm⁻¹ cm² mol⁻¹) of 10⁻³ M concentration of complexes in DMSO solution at temperature show their non-electrolytic nature.²¹ The analytical data suggest the formulation of complexes as ML_2X_2 ,

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where M stands for Co(II) and Ni(II), VBH stands for ligand and X stands for H₂O, pyridine and \Box -picoline.

INFRARED SPECTRA

The important and significant IR-bands before and after complexation have been detected and assigned. The free ligand absorbs at 3450 cm^{-1} due to \square_{O-H} stretching vibration of phenolic group of the ligand.²²⁻²³ The band remains intact in complexes that show its non-coordination to the metal ion in the complexes above 3000 cm^{-1} . The spectra of the ligand exhibits more two bands i.e., at 3345 cm⁻¹ due to \square_{N-H}^{24} and at 3090 cm⁻¹ due to \square_{C-H}^{25-26} stretching of aromatic moiety. The band at 3345 cm^{-1} doesn't show any appreciable change in its position in complexes indicating the non participation of N-H group in bonding. The weak band at 2890 cm⁻¹ is assigned to \square_{C-H} of OCH₃ group of the ligand. The strong band at 1680 cm⁻ is assigned to $\square_{C=0}$ of \square , \square unsaturated keto group. It is further substantiated by the appearance of two strong bands at 1215 cm⁻¹ and 1170 cm⁻¹ due to rocking mode of vibration of ketonic group and methyl group respectively attached to it.²⁷ The free ligand doesn't display band at 1650 cm⁻¹ due to amide band i.e. $v_{NH-C=O}$ rather a broad band appears at 3200 cm⁻¹ due to v_{O-H} (Aliphatic) Hbonded with other $v_{C=0}$ group.²⁸ The above supposition is further supported by the appearance of bands at 3040 cm^{-1} , 1590 cm^{-1} , 1440 cm^{-1} and 1240 cm⁻¹ due to \square_{C-H} , $\square_{CH=N-N-C}$, $\square_{C=C}$, and \square_{C-O} , (Enolic) of the free ligand which clearly indicates the existence of the ligand in enolic form.²⁹⁻³⁰ In all the complexes the band at 3200 cm⁻¹ due to hydrogen bonded \square_{O-H} of enolic form is found absent confirming the deprotonation and coordination through deprotonated oxygen to the

metal ion.³¹ A band of medium intensity is observed at 1610 cm⁻¹ due to $\Box_{CH=N}$ (Azomethine) stretching vibration in the ligand.³² This band suffers red shift and appears at 1570–1580 cm⁻¹ in complexes which is indicative of co-ordination through azomethine Nitrogen.³³ The coordination through deprotonated oxygen of O–H group and azomethine Nitrogen is further substantiated by the appearance of new bands in the spectra of complexes. The band near 560 cm⁻¹ is assigned to $\Box_{M=N}$ while the other at 420 cm⁻¹ is assigned to $\Box_{M=0}$.³⁴ Thus the ligand acts as monoanionic bidentate forming a chelate with metal ions.

MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRA

The magnetic moment of complexes have been given in Table-1. The Co(II) complexes exhibit magnetic moment of 4.20-4.21 BM. Which is very close to 3.87 BM due to the presence of three unpaired electrons. It indicates that Co(II) complexes are spin free octahedral. The slightly higher value of magnetic moment may be due to orbital contribution from triply degenerate ${}^{4}T_{1}g$ cubic field ground term. Co(II) complexes displayed three bands in their electronic spectra which may be assigned as below :-

$$v_1 = 9220 - 9250 \text{ cm}^{-1} = {}^4T_1g(F) \rightarrow {}^4T_2g(F)$$

$$v_2 = 18870 - 18995 \text{ cm}^{-1} = {}^4T_1g(F) \rightarrow {}^4T_2g(F)$$

$$v_3 = 20770 - 20810 \, \text{cm}^{-1} = {}^4T_1g(F) \rightarrow {}^4T_1g(P)$$

These three bands are spin allowed transitions.³⁵ The various crystal field parameters derived from electronic spectral bands of Co(II) complexes using Tanabe Sugano diagram have been given in Table-2.

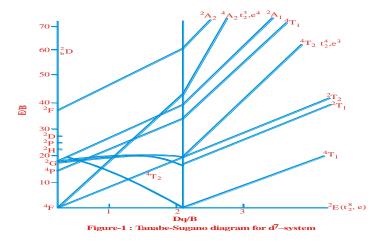




Table-2: Crystal field	parameters of Co(II) Complexes.
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Sl. No.	Complexes	10Dq (cm ⁻¹)	B (cm ^{-1})	□ (%)	\Box_2 / \Box_1
1.	$[Co(VBH)_2(H_2O)_2]$	9250	616.6	37	2.04
2.	$[Co(VBH)_2(Py)_2]$	9188	625	36.6	2.05
3.	$[Co(VBH)_2(\Box-pico)_2]$	9072	630	36	2.06

The values of the various crystal field parameters are in good agreements with values reported for slightly distorted octahedral complexes of Co(II).³⁶ The magnetic moment of Ni(II) complexes are found in between 3.14-3.17 BM, the value greater than \Box_s (2.82 BM) Corresponding to two unpaired electrons in octahedral Ni(II) complexes. This may be due to second order Zeeman effect under which \Box effective is given by

 $\mu_{\text{eff}} = \mu_{\text{s.o}} \left(1 - \frac{4\lambda}{10Dq} \right) \text{BM. Since, a d}^{8}\text{-system}$

is more than half filled, the spin orbit coupling constant λ is negative (-ve) and hence μ_{eff}

becomes greater than $\mu_{s.o}$.³⁷⁻³⁸ The electronic spectra of Ni(II) complexes display three bands which are assigned to the following spin allowed transitions.

$$v_1 = 8400 - 8450 \,\mathrm{cm}^{-1} = {}^3A_2g \to {}^3T_2g$$

$$v_2 = 13410 - 13695 \text{ cm}^{-1} = {}^3\text{A}_2\text{g} \rightarrow {}^3\text{T}_1\text{g}(\text{F})$$

$$v_3 = 21500 - 21880 \,\mathrm{cm}^{-1} = {}^3A_2g \rightarrow {}^3T_1g(P)$$

On the basis of these bands the value of various crystal field parameters of Ni(II) complexes have been given in Table 3.

Table-3:	Crystal f	field	parameters	of Ni(II) Complexes.	
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Sl. No.	Complexes	10Dq (cm ⁻¹)	B (cm ^{-1})	□ (%)	\Box_2 / \Box_1
1.	$[Ni(VBH)_2(H_2O)_2]$	8412.5	673	35.28	1.6
2.	[Ni(VBH) ₂ (Py) ₂]	8498.5	739	28.94	1.62
3.	$[Ni(VBH)_2(\Box-pico)_2]$	8385.5	645.16	37.96	1.59

These values are found in good consonance with the reported values for distorted octahedral symmetry of Ni(II) complexes.³⁹⁻⁴⁰

III. CONCLUSION

The present study reveals that the Schiff base 3-hydroxy-4-methoxybenzaldehyde-3oxobutanehydrazone contains two potential sites for coordination to metal ions. Thus, it behaves as monoanionic bidentate coordinating through one azomethine nitrogen and one dehydrogenated hydroxy oxygen. On the basis of magnetic moment value and electronic spectra of Co^{II} and Ni^{II}, they are found to be octahedral symmetry. The tentative structure of complexes may be given as in Figure 2:-

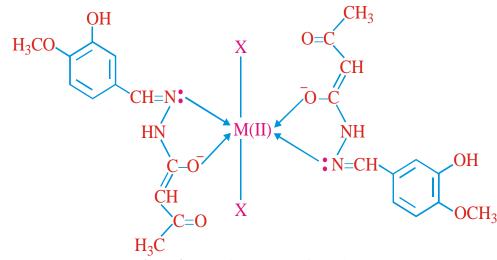


Figure-2 : Tentative structure of complexes



where M = Co, Ni and $X = H_2O$, pyridine and \Box -picoline

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