

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-3-oxobutanehydrazone has been prepared by the condensation of 3-hydroxy-4-methoxybenzaldehyde & 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 ML_2X_2 , where M-stands for Co(II) & Ni(II) while L is m-vanillin-3-oxobutanehydrazone(VBH) and X is Water, Pyridine and π -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, π -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 which display three bands due to ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ 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 $\mu_s = 2.82$ BM corresponding to two unpaired electrons under octahedral symmetry. The appearance of three bands in their electronic spectra due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ spin allowed transitions.

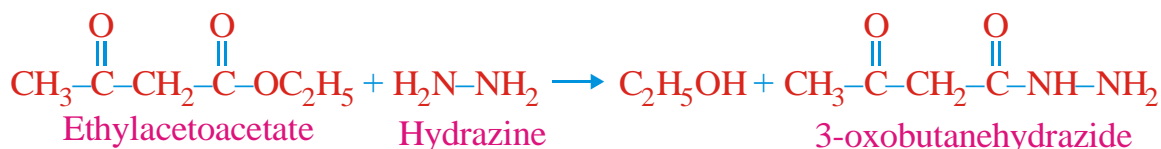
Keywords: vanillin, bidenticity, octahedral, magnetically dilute, Racah Parameter

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

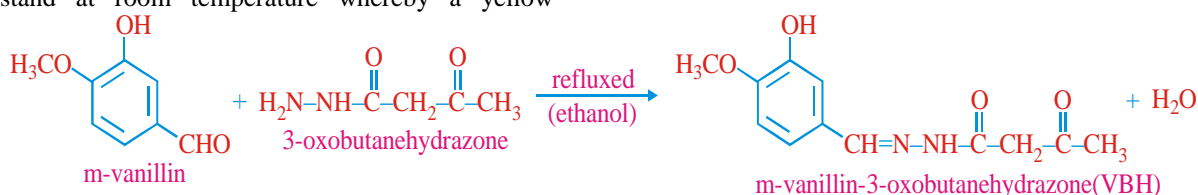
All the chemicals used were of Alal.R.Grade and were used as received. Ethylacetoacetate have been procured from Loba Chemie in Maharashtra (India), hydrazine hydrate has been purchased from Fisher Scientific in Maharashtra (India) and 3-hydroxy-4-methoxybenzaldehyde (m-vanillin) has been procured from 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.



Scheme-I

Now, 100 mmol (11.6 g) of 3-oxobutanehydrazide and 100 mmol (15.2 g) of 3-hydroxy-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

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

S. no. (BM)	Compounds	Colour	Yield	Melting Point (°C)	% Analysis found / (calculated)				κ _m	
					M	C	H	N	(ohm ⁻¹ cm ² mol ⁻¹)	□
1.	Ligand [VBH]	Yellow	72	209.5°C (57.61)	—	57.92 (5.61)	5.24 (11.20)	11.00	—	—
2.	[Co(VBH) ₂ (H ₂ O) ₂]	Dark Blue	70	285°C (9.94)	9.92 (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	288°C (8.25)	8.00 (57.06)	5.03 (5.03)	57.48 (11.74)	4.93	11.44	11 4.20
4.	[Co (VBH) ₂ (□-Pico) ₂]	Bright	71	288.8°C (7.94)	7.69 (58.14)	5.38 (5.38)	58.39 (11.30)	5.12	11.16	12 4.21
5.	[Ni (VBH) ₂ (H ₂ O) ₂]	Bright Green	64	292°C (9.94)	9.60 (48.56)	5.05 (5.05)	48.78 (9.44)	4.89	9.20	15 3.14
6.	[Ni (VBH) ₂ (Py) ₂]	Green	65	294°C (8.25)	8.00 (57.06)	5.03 (5.03)	57.34 (11.70)	4.91	11.51	15 3.17
7.	[Ni (VBH) ₂ (□-Pico) ₂]	Dull Green	65	282°C (7.94)	7.72 (58.14)	5.38 (5.38)	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 ML₂X₂,

Table-2: Crystal field parameters of Co(II) Complexes.

Sl. No.	Complexes	10Dq (cm ⁻¹)	B (cm ⁻¹)	□ (%)	□ ₂ /□ ₁
1.	[Co(VBH) ₂ (H ₂ O) ₂]	9250	616.6	37	2.04
2.	[Co(VBH) ₂ (Py) ₂]	9188	625	36.6	2.05
3.	[Co(VBH) ₂ (□-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 μ_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 \square effective is given by $\mu_{\text{eff}} = \mu_{s,o} \left(1 - \frac{4\lambda}{10Dq} \right)$ BM. Since, a d⁸-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.

$$\nu_1 = 8400 - 8450 \text{ cm}^{-1} = {}^3A_{2g} \rightarrow {}^3T_{2g}$$

$$\nu_2 = 13410 - 13695 \text{ cm}^{-1} = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$$

$$\nu_3 = 21500 - 21880 \text{ cm}^{-1} = {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$$

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 field parameters of Ni(II) Complexes.

Sl. No.	Complexes	10Dq (cm ⁻¹)	B (cm ⁻¹)	□ (%)	□ ₂ /□ ₁
1.	[Ni(VBH) ₂ (H ₂ O) 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 (□-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-3-oxobutanehydrazone 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:-

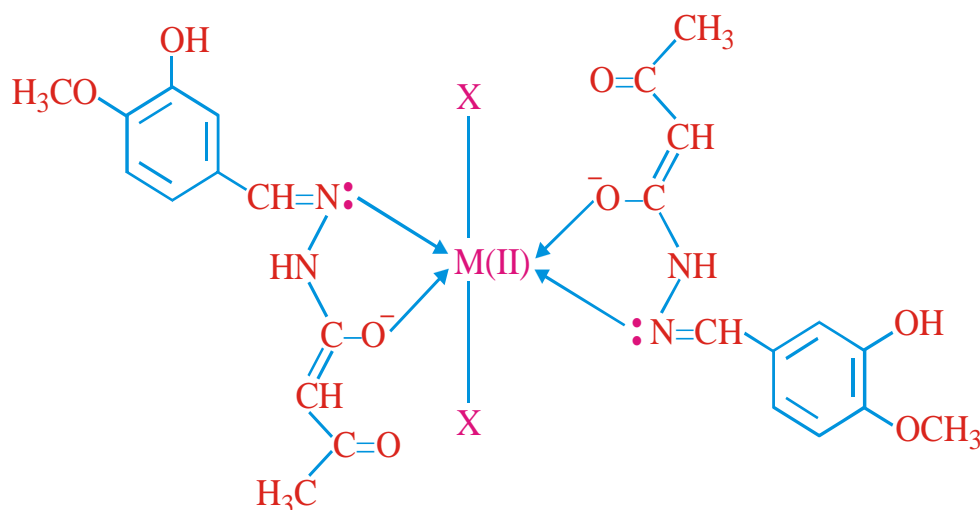


Figure-2 : Tentative structure of complexes

where M = Co, Ni and X = H₂O, pyridine and π -picoline

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