

## 'Spectral Elucidation Of Structure Of Some Complexes'

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**Abstract:** Schiff Base, 3- Hydroxy 4-Methoxy Benzaldehyde 3-Oxobutanehydrazone (VBH) Has Been Prepared By The Condensation Of 3- Oxobutanehydrazide And 3-Hydroxy- 4 Methoxy benzaldehyde. The Schiff Base Has Been Used For Complexation With Co (II), Ni (II), Zn(II) And Cd(II). The Percentage Composition Of Complexes Has Been Determined By Their Micro Analysis. The Molar Conductivities Values Of Complexes Have Been Found In Between 11 To 15  $\text{Ohm}^{-1} \text{cm}^2\text{mol}^{-1}$  In DMF Solution Of  $10^{-3}$  Concentration Which Indicates Their Non Electrolytic Nature. The I.R. Spectra Of Complexes Have Been Compared With That Of The Free Ligand To Trace Out The Point Of Ligation Of The Ligand To The Metal Ions. The Electronic Spectra Of Complexes With Their Magnetic Movement Values Lead To The Octahedral Structure Of The Complexes. The Appreciable Decrease In The Value Of Racah Parameter In All The Complexes Have Been Taken As The Strong Evidence In The Favour Of Co-Valency In M-L Bond In All The Complexes. The Value Of  $10Dq$  Been Derived Using Tanabe-Sugano Diagram.

**Key Word:**  $10Dq$ , Ligation, Racah Parameter

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### I. Introduction

The Chemistry Of Schiff Base And Their Transition Metal Complexes Is Very Fascinating And Interesting<sup>(1)</sup>. Metal Complexes Of Schiff Base As They Have Played A Central Role In The Inorganic Chemistry Of Chelate System. Schiff Base Containing The Hydrazone Moiety Are Well Known And Their Metal Complexes Have Found Vast Application In Pharmaceutical And Industrial Chemistry<sup>(2-14)</sup>.

Semicarbazone And Hydrazone Have Emerged As Promising Ligand In Co-Ordination Chemistry. 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<sup>(15-17)</sup>. Vanillin Hydrazone Are Potential Anti Cancer Agent<sup>(18-19)</sup> Also.

The Perusal Of Literature Reveals That No Work Has Been Reported On The Schiff Base Derived From Meta-Vanillin And Substituted Hydrazide.

This Prompted Us To Pursue Our Research On The Schiff Base Derived From Meta Vanillin And 3-Oxobutanehydrazide And Its Complexes With Co (II), Ni (II), Zn(II) And Cd(II) Metal Ions.

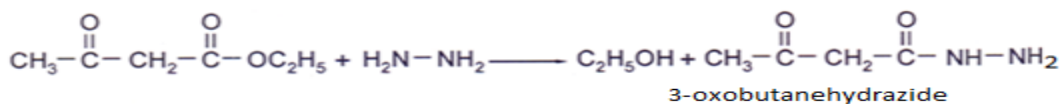
### II. Materials And Methods

#### 2.1 Materials

All The Reagents Used Were Of AR Grade And Were Used As Received. Ethyl Aceto Acetate, Co(II) Acetate Ni (II) Acetate, Zn(II) Acetate And Cd(II) Acetate Were Procured From Laba Chemic And Hydrazine Hydrate And DMF Were Purchased From Fischer Scientific.

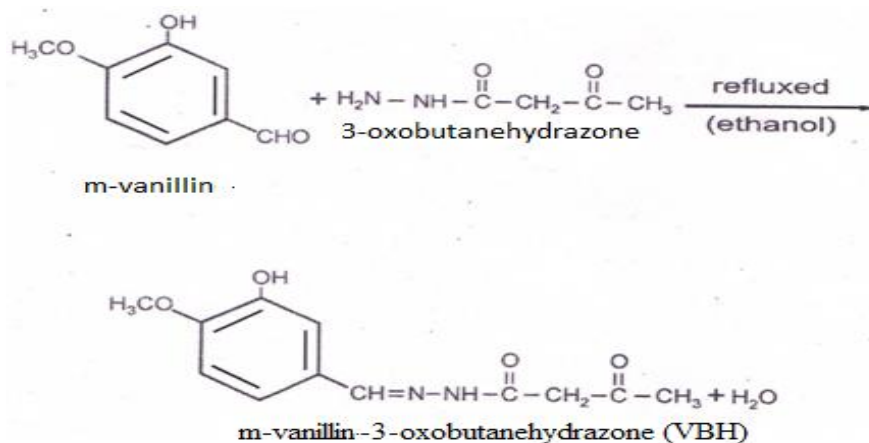
#### 2.2 Methods

At First 3- Oxobutanehydrazide Was Prepared By The Method Reported By D. Kumar. Et Al<sup>(20)</sup>. It Has Been Given In (Scheme I).



Scheme - I

It Has Been Used For Condensation With M-Vanillin (3-Hydroxy 4-Methoxy Benzaldehyde) To Form The Schiff Base, M-Vanillin-3-Oxobutanehydrazone, Hence Forth Abbreviated As VBH (Scheme II).



The Ligand Has Been Used For Complexation With Co (II), Ni (II), Zn(II) And Cd(II) By The Usual Method Of Reflux.

The Micro Analysis Of Carbon, Hydrogen And Nitrogen Was Carried Out By Using Micro Analyser Technique On Carbo Erba Micro Analyser 1108. Cobalt Content In Complex Was Determined Volumetrically While Ni, Zn, Cd Contents Were Estimated Gravimetrically. The Molar Conductance Of Complexes Was Measured At Room Temperature In  $10^{-3}$  M Solution In DMSO By Toshniwal Digital Conductivity Meter With A Deep Type Cell. I.R. Spectra Of Ligand As Well As Complexes Were Recorded In KBr On Perkin Elmer Model Arc Rx<sub>1</sub> Spectrometer. The Magnetic Susceptibility Was Measured At Room Temperature By Gouy Balance Using CuSO<sub>4</sub>·5H<sub>2</sub>O As Calibrant. The Electronic Spectra Of Complexes Were Recorded By Shimadzu Model UV 150-150.02. Spectrophotometer.

### III. Result And Discussion

#### 3.1 Physical And Analytical Data

The Physical And Analytical Data Of Complexes Have Been Recorded In Table - I.

**Table - I**

Elemental Analysis Data And Physical Properties % Found/ (Calculated).

| Compound  | Colour       | Yield | M.Pt.                | M              | C                | H              | N                | $\lambda$<br>Ohm <sup>-1</sup> cm <sup>2</sup><br>Mol <sup>-1</sup> | $\mu$<br>BM |
|---|--------------|-------|----------------------|----------------|------------------|----------------|------------------|---|-------------|
| Ligand  | Yellow       | 72    | 209.5 <sup>0</sup> C | --             | 57.92<br>(57.61) | 5.24<br>(5.61) | 11.00<br>(11.20) | -   | -           |
| Co <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>   | Dark Blue    | 70    | 285 <sup>0</sup> C   | 9.92<br>(9.94) | 48.72<br>(48.54) | 4.91<br>(5.06) | 9.12<br>(9.44)   | 12  | 4.21        |
| Co <sub>2</sub> (Py) <sub>2</sub>                 | Blue         | 75    | 288 <sup>0</sup> C   | 8.00<br>(8.25) | 57.48<br>(57.06) | 4.93<br>(5.03) | 11.44<br>(11.74) | 11  | 4.20        |
| Co <sub>2</sub> ( $\alpha$ -Picolin) <sub>2</sub> | Bright       | 71    | 288.8 <sup>0</sup> C | 7.69<br>(7.94) | 58.39<br>(58.14) | 5.12<br>(5.38) | 11.16<br>(11.30) | 12  | 4.21        |
| Ni <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>   | Bright Green | 64    | 292 <sup>0</sup> C   | 9.60<br>(9.94) | 48.78<br>(48.56) | 4.89<br>(5.05) | 9.20<br>(9.44)   | 15  | 3.14        |
| Ni <sub>2</sub> (Py) <sub>2</sub>                 | Green        | 65    | 294 <sup>0</sup> C   | 8.00<br>(8.25) | 57.34<br>(57.06) | 4.91<br>(5.03) | 11.51<br>(11.70) | 15  | 3.17        |
| Ni <sub>2</sub> ( $\alpha$ -Picolin) <sub>2</sub> | Dull Green   | 65    | 282 <sup>0</sup> C   | 7.72<br>(7.94) | 58.41<br>(58.14) | 5.10<br>(5.38) | 11.12<br>(11.30) | 13  | 3.16        |

|  |                 |    |                    |                  |                  |                |                  |    |             |
|--|-----------------|----|--------------------|------------------|------------------|----------------|------------------|----|-------------|
| ZnL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>   | Cream           | 68 | 263 <sup>0</sup> C | 10.64<br>(10.85) | 48.32<br>(48.08) | 4.90<br>(5.00) | 9.14<br>(9.34)   | 14 | Diamagnetic |
| ZnL <sub>2</sub> (Py) <sub>2</sub>                 | Yellowish Cream | 67 | 264 <sup>0</sup> C | 8.91<br>(9.01)   | 56.78<br>(56.58) | 4.64<br>(4.99) | 11.42<br>(11.65) | 13 | Diamagnetic |
| ZnL <sub>2</sub> ( $\alpha$ -Picolin) <sub>2</sub> | Yellowish Cream | 68 | 264 <sup>0</sup> C | 8.42<br>(8.67)   | 57.83<br>(57.67) | 5.12<br>(5.34) | 11.00<br>(11.21) | 13 | Diamagnetic |
| CdL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>   | White           | 72 | 268 <sup>0</sup> C | 17.06<br>(17.33) | 44.81<br>(44.58) | 4.36<br>(4.64) | 8.41<br>(8.66)   | 12 | Diamagnetic |
| CdL <sub>2</sub> (Py) <sub>2</sub>                 | White           | 73 | 269 <sup>0</sup> C | 14.31<br>(14.58) | 53.39<br>(53.12) | 4.38<br>(4.68) | 10.79<br>(10.93) | 15 | Diamagnetic |
| CdL <sub>2</sub> ( $\alpha$ -Picolin) <sub>2</sub> | White           | 73 | 270 <sup>0</sup> C | 13.90<br>(14.07) | 54.56<br>(54.27) | 4.91<br>(5.02) | 10.39<br>(10.55) | 14 | Diamagnetic |

### 3.2 Conductivity

The Low Molar Conductance Values, (11-15 Ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) Of 10<sup>-3</sup> M Solution Of Complexes In DMSO At Room Temperature Suggest Their Non-Electrolytic Nature<sup>(21)</sup>. The Analytical Data Suggest The Formulation Of Complexes As ML<sub>2</sub>X<sub>2</sub> Where M Stands For Ni(II), Co(II), Zn(II) And Cd(II), L Stands For Ligand VBH And X Stands For H<sub>2</sub>O, Pyridine And  $\alpha$ -Picolin.

### 3.3 I.R. Spectra

The Ligand Absorbs At 3450 Cm<sup>-1</sup> Due To  $\nu_{O-H}$  Stretching Vibration Of Phenolic Group Of The Ligand<sup>(22-23)</sup>. The Band Remains Intact In Complexes That Shows Its Non Co-Ordination To The Metal Ion In The Complexes. Above 3000 Cm<sup>-1</sup> The Spectra Of The Ligand Exhibits More Two Bands i.e. At 3345cm<sup>-1</sup> Due To  $\nu_{N-H}$ <sup>(24)</sup> And At 3090 Cm<sup>-1</sup> Due To  $\nu_{C-H}$ <sup>(25)</sup> Stretching Of Aromatic Moiety. The Band At 3345 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<sup>-1</sup> Is Assigned To  $\nu_{C-H}$  Of OCH<sub>3</sub> Group Of The Ligand. The Strong Band At 1680 Cm<sup>-1</sup> Is Assigned To  $\nu_{C=O}$  Of  $\alpha$ ,  $\beta$  Unsaturated Keto Group. It Is Further Substantiated By The Appearance Of Two Strong Band At 1215 And 1170 Cm<sup>-1</sup> Due To Rocking Mode Of Vibration Of Ketonic Group And Methyl Group Respectively Attached To It<sup>(27)</sup>. The Free Ligand Doesn't Display Band At 1650 Cm<sup>-1</sup> Due To Amide Band i.e.,  $\nu_{NH-C=O}$  Rather A Broad Bands Appears At 3200 Cm<sup>-1</sup> Due To  $\nu_{O-H}$  (Aliphatic) H- Bonded With Other  $\nu_{C=O}$  Group<sup>(28)</sup>. The Above Supposition Is Further Supported By The Appearance Of Bands At 3040, 1590, 1440 And 1240 Cm<sup>-1</sup> Due To  $\nu_{C-H}$ ,  $\nu_{CH=N-N-C}$ ,  $\nu_{C=C}$  And  $\nu_{C-O}$  (Enolic) Of The Free Ligand Which Clearly Indicates The Existence Of The Ligand In Enolic Form<sup>(29)</sup>. In All The Complexes The Band At 3200 Cm<sup>-1</sup> Due To Hydrogen Bonded  $\nu_{O-H}$  Of Enolic Form Is Found Absent Conforming The Deprotonation And Co-Ordination Through Deprotonated Oxygen To The Metal Ion<sup>(30)</sup>. A Band Of Medium Intensity Is Observed At 1610 Cm<sup>-1</sup> Due To  $\nu_{CH=N}$  (Azomethine) Stretching Vibration<sup>(31)</sup> In The Ligand. This Band Suffers Red Shift And Appears At 1570-1580 Cm<sup>-1</sup> In Complexes Which Is Indicative Of Co-Ordination Through Azomethine Nitrogen<sup>(32)</sup>. The Co-Ordination 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<sup>-1</sup> Is Assigned To  $\nu_{M-O}$  While The Other At 420 Cm<sup>-1</sup> Is Assigned To  $\nu_{M-N}$ <sup>(33)</sup>. Thus The Ligand Acts As Monoanionic Bidentate Forming A Chelate With Metal Ions.

### 3.4 Magnetic Susceptibility And Electronic Spectra

The Magnetic Moment Of Co(II) Complex Have Been Found 4.20-4.21 BM. Which Is Very Close To 3.87 BM Due To The Presence Of 3 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 Degenerated <sup>4</sup>T<sub>1g</sub> Cubic Field Ground Term. Co(II) Complexes Displayed 3 Bands In Their Electronic Spectra Which Are Assigned To  $\nu_1 = ^4T_{1g} \rightarrow ^4T_{2g}$ ,  $\nu_2 = ^4T_{1g} \rightarrow ^4A_{2g}$  And  $\nu_3 = ^4T_{1g} \rightarrow ^4T_{1g}$  (P) Spin Allowed Transitions<sup>(34)</sup>. The  $\nu_2$  And  $\nu_1$  Ratio Has Been Found 2.04 To 2.06 Which Is Indicative Of Octahedral Symmetry Around Co(II) In These Complexes. The Corresponding 10 Dq Values (9072-9250 Cm<sup>-1</sup>), B (616.6-

630  $\text{cm}^{-1}$ ) Are In The Good Agreement With The Reported Values Of Distorted Octahedral Complexes<sup>(35)</sup>. Ni(II) Complexes Record Magnetic Moment In The Range Of 3.14-3.17 BM. The Values Are Greater Than 2.82 BM Corresponding To Two Unpaired Electrons Of Ni(II), A  $D^8$  System. Actually In Ni(II) Complexes Second Order Zeeman Effect Is Operative And Under Its Influence A Magnetic Moment Is Given By

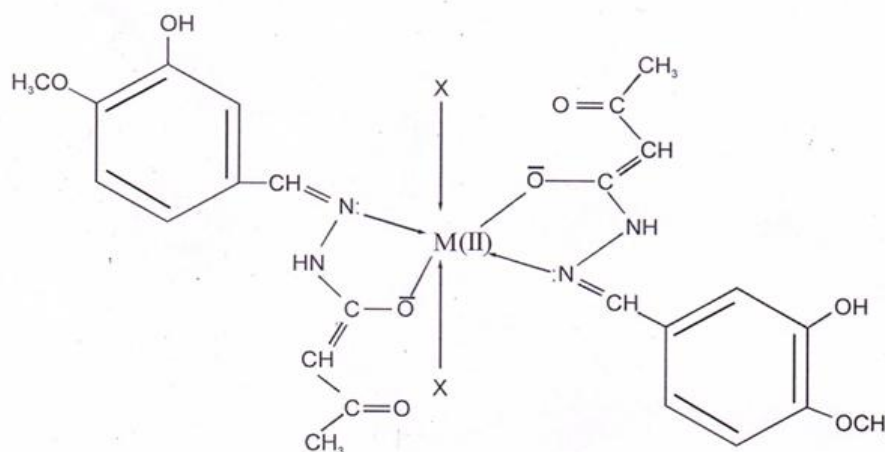
$$\mu_{\text{eff}} = \mu_{s.o} \left( 1 - \frac{4\lambda}{10Dq} \right) BM.$$

Since A  $D^8$  System Is More Than Half Filled, The Spin Orbit Coupling Constant  $\lambda$  Is -Ve ( $-315 \text{ cm}^{-1}$ ) And Hence  $\mu_{\text{eff}}$  Becomes Greater Than  $\mu_{s.o}$  (36-37). Ni(II) Complexes Display Three Bands In Their Electronic Spectra Which Are Assigned To The Following Spin Allowed Transition.  $\nu_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$  And  $\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ .

The  $\nu_2$  To  $\nu_1$  Ratio Is Found 1.59-1.62 And The Corresponding Values Of  $10 Dq$  And  $B$  Come To Be 8385.5 - 8498.5  $\text{cm}^{-1}$  And 645-739  $\text{cm}^{-1}$  Respectively. These Values Are Found In Good Consonance With The Reported Values For Distorted Octahedral Symmetry Of Ni(II) Complexes<sup>(38-39)</sup>. The Zn(II) And Cd(II) Complexes Are Found Diamagnetic Which Is In Accordance With Their  $D^{10}$  Configuration. They Don't Display Any Band In Their Electronic Spectra Due To Lack Of D-D Transition. However Their Elemental Analysis Suggests Six Co-Ordinate Complexes Which Must Have Octahedral Symmetry Around Zn(II) And Cd(II) Metal Ions.

#### IV. Conclusion

The Foregoing Study Of Infrared Spectra Of Complexes In Comparison To That Of The Free Ligand Clearly Reveals That The Ligand 3-Hydroxy-4-Methoxy Benzaldehyde 3-Oxobutanehydrazone Acts As Mono Anionic Bidentate One Co-Ordinating Through Azomethine Nitrogen And Dehydrogenated Hydroxy Oxygen In Its Enolic Form. The Magnetic Moment And Electronic Spectra Of Complexes Lead To Octahedral Symmetry Around The Metal Ions. The Tentative Structure Of Complexes May Be Given As :-



Where  $M = \text{Co, Ni, Zn And Cd}$  And  $X = \text{H}_2\text{O Pyridine And - Picoline}$ .

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