



## Template Synthesis of Macrocyclic Complexes of Bivalent Co<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> Ions with Cyclic Glyoxal Carbohydrazone (1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraene-3,10-dione)

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### ABSTRACT

Cyclic glyoxalcarbohydrazone[(1,2,4,5,8,9,11,12-octaazacyclotetradeca-5,7,12,14-tetraene-3,10-dione) = (glyoxalcarbzh)<sub>2</sub>] complexes of Ni<sup>II</sup>, Pd<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> of composition M (glyoxalcarbzh)<sub>2</sub>X<sub>2</sub>nH<sub>2</sub>O (M = Ni<sup>II</sup>, Pd<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup> or Cd<sup>II</sup> and X = Cl<sup>-</sup>, 1/2 SO<sub>4</sub><sup>-2</sup> and n = 0, 1 or 4) have been isolated by refluxing appropriate metal salts with glyoxal and carbohydrazone in requisite proportion for 8 to 10 hours in aqueous ethanol on steam bath. The refluxate on concentration and cooling in ice gave crystalline precipitate of appropriate complexes. The complex salts are soluble in hot aqueous ethanol and conduct electricity showing 1:2 ionic natures. Except Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup> the complexes of Co<sup>II</sup> and Ni<sup>II</sup> are paramagnetic and their magnetic moment value suggested octahedral geometry. The UV and IR spectral results supported octahedral structure for Co<sup>II</sup> and Ni<sup>II</sup> while planar for Pd<sup>II</sup> complexes.

**Key word:** Cyclic glyoxalcarbohydrazone, bivalent metal complexes.

### INTRODUCTION

The concept of macrocyclic compound and their metal complex grew rapidly after synthesis of crown ether by Pederson in 1966<sup>1</sup>. The growing application of macrocyclic complexes in transport of alkali metal nutrient to plant kingdom enhanced the interest of Chemist and Biologist to synthesize and characterize the metal complexes with macrocyclic crown ether<sup>2-7</sup>. In present paper we describe the preparation and characterization of complexes of macrocyclic ligand bis (glyoxalcarbohydrazone) with bivalent metal ions.

### EXPERIMENTAL

The metal salts, glyoxal dihydrate, hydrazine hydrate, diethyl carbonate and organic solvents were extra pure reagent of E. Merck and Anal R grade chemicals of BDH. Palladium (II) Chloride was obtained from Johnson Matthey London. Carbohydrazone was prepared by refluxing diethyl carbonate {O=C(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>} with 98% hydrazine hydrate on steam bath as reported in literature<sup>8</sup>. The magnetic susceptibility of complexes were determined by Gouy method at room temperature using [Hg{Co(NCS)<sub>4</sub>}] as standard ( $\chi_g =$

16.24×10<sup>-6</sup> CGS.unit at 20°C). The metal content, halogens and sulphate were determined by standard process<sup>9</sup>. The results of C,H and N were obtained from BIT Mesra. Ranchi.The IR spectra were recorded as KBr disc in the range 450–4000cm<sup>-1</sup> onShemadzu Spectrophotometer and Electronic spectra on UV-Vis 2500PC series spectrophotometerat IIT Patna.

### Preparation of complex salts

M{bis (glyoxalcarbohydrazone)}X<sub>2</sub>nH<sub>2</sub>O (M = Co<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup>, n = 0, 1 or 4, X = Cl<sup>-</sup> or 1/2 SO<sub>4</sub><sup>-2</sup>). About 0.01 mol of carbohydrazide, 0.01molglyoxaldihydrate, and 0.005 mol metal chlorides were mixed in 100 ml water and 50 ml ethanol. The mixed reaction mixtures were refluxed on steam bath with constant stirring for 8–10 hours. The resulting solution was filtered and concentrated to 20-25 ml and pH was adjusted to 4-5 by adding a few drop of appropriate dilute acid. On cooling and standing the refluxateovernightin cold,microfine crystalline precipitate separated. The product were collected on Buckner funnel and washed with cold ethanol. The products were dried over CaCl<sub>2</sub>desiccators and analyzed.The complexsulphates were obtained when metal salt was taken as sulphate. The analytical results and molar electrical conductance value of products are mention in Table 1 and 2.

## RESULTS AND DISCUSSION

The analytical results of macrocyclic complexes formed on condensation of glyoxal and carbohydrazide with Co<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> salts corresponds to composition M (glyoxalcarbohydrazone)<sub>2</sub>X<sub>2</sub>nH<sub>2</sub>O (M = Co<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup>, n = 0 forPd<sup>II</sup>,Zn<sup>II</sup>and Cd<sup>II</sup>while 4 for Co<sup>II</sup> or Ni<sup>II</sup>and X = Cl<sup>-</sup> or 1/2 SO<sub>4</sub><sup>-2</sup>). The complex salts are soluble in hot water or hot aqueous ethanol. The neutral complexes M(glyoxalcarbohydrazone)<sub>2</sub>X<sub>2</sub>nH<sub>2</sub>O dissolved in DMF and pyridine base on warming. The complexes are stable in air and aqueous medium. The electrical conductance value of complex salts in DMF occur in the range E<sub>∞</sub> = 102–138 ohm<sup>-1</sup>mol<sup>-1</sup>cm<sup>2</sup> indicating ionic nature of complexes<sup>7</sup>. As expected Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup> complexes are diamagnetic and Co<sup>II</sup> orNi<sup>II</sup> complexes are paramagnetic. The magnetic moment at room temperature of Co<sup>II</sup> complexes

were found 4.92 and 5.01 for Co (glyoxalhydrazone)<sub>2</sub>X<sub>2</sub>nH<sub>2</sub>O (X = Cl<sup>-</sup> and 1/2 SO<sub>4</sub><sup>-2</sup>). Which is similar to most of the spin free octahedral Co<sup>II</sup> complexes<sup>6-7</sup>. The magnetic moment value of Ni<sup>II</sup> complexes (Table-B) occur in the range of octahedral environment of Ni<sup>II</sup>atom<sup>10</sup>.

The electronic absorption spectra of Ni<sup>II</sup>complexes displayed three distinct absorption band at 9680-9700, 16240-16360 and 24600-24840 cm<sup>-1</sup> assignable to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>, <sup>3</sup>T<sub>1g</sub> → <sup>3</sup>T<sub>1g</sub>(P) transitions. The electronic absorptionspectra of aqueous ethanolic solution of Co<sup>II</sup>complex salts displayed electronic transitions near 19250-19300 and 23400-23500 cm<sup>-1</sup> as weak and broad bands due to d-d transitions. The electronic bands are assigned as <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> and <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(P) transition as observed for octahedral Co<sup>II</sup>atom<sup>7-8</sup>. The Pd<sup>II</sup> complexes displayed a medium band at 425nm (23570 cm<sup>-1</sup>) attributed from <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>A<sub>2g</sub> transition in square planer field<sup>8-9</sup>. (Table 1)

The spectral parameters 10Dq, B and β for Ni<sup>II</sup>complexsalts [Ni(glyoxalcarbohydrazone)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]X<sub>2</sub>nH<sub>2</sub>O (X = Cl<sup>-</sup> or 1/2 SO<sub>4</sub><sup>-2</sup> and n = 2)were calculated using diagonal sum rule<sup>12</sup>and found to be 10Dq = 9680 cm<sup>-1</sup>, B = 786 cm<sup>-1</sup> and β = 0.75 forcomplex chlorides and 10Dq = 9700cm<sup>-1</sup>, B = 806cm<sup>-1</sup> and β = 0.77forcomplexsulphates. The 20 – 25% reduction of β value indicated appreciable covalent character in complex<sup>12-13</sup> [Ni (glyoxalcarbohydrazone)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]X<sub>2</sub>nH<sub>2</sub>O. The infrared spectra of complexes in KBr disc exhibit broad band at 3050-3400cm<sup>-1</sup> attributed from ν(N-H),ν(C-H) and hydrogen bonded H<sub>2</sub>O and coordinated H<sub>2</sub>O of complexes molecule. The complexes shows a broad strong band at 1665-1652 cm<sup>-1</sup> attributed from ν(C=O) of carbohydrazone (-NH-CO-NH-) group of cyclic ring<sup>14-15</sup>. The medium band at 1592 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>are assigned to ν(C=N) and δ(N-H) of cyclic ring. The IR bands at 1430, 1332, 1256 and 1105 cm<sup>-1</sup> are due to ν(N-H), ν(C-C), ν(N-N) and ν(C-N) of cyclic ring system of the complex<sup>13</sup>. The complex sulphates display a strong a broad band at 1100-1120 cm<sup>-1</sup>and second weak band of 618 cm<sup>-1</sup>attributed from ionic sulphate group present in complex sulphates. A medium band at 836 and 735 cm<sup>-1</sup> and weak bands at 635 and 506 cm<sup>-1</sup>areattributed to ν(N-H), δ(C-H) and deformation vibrations of ring system.A medium

broad band located near 675-685  $\text{cm}^{-1}$  is attributed to rocking vibration of coordinated water molecule<sup>14-15</sup>. Thus on the basis of above observations macrocyclic structure is proposed to complex  $\text{M}(\text{glyoxalcbhzH})_2\text{X}_2\text{nH}_2\text{O}$ . The complexes of  $\text{Ni}^{\text{II}}$  and  $\text{Co}^{\text{II}}$  possess octahedral structure with two coordinated  $\text{H}_2\text{O}$  molecule while  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$

complexes are four coordinated tetrahedral but  $\text{Pd}^{\text{II}}$  complex  $[\text{Pd}(\text{glyoxalcbhzH})_2]\text{Cl}_2$  is square planer.

#### Thermal stability

The complexes are quite stable in air. The hydrated complexes  $[\text{M}(\text{glyoxalcbhzH})_2(\text{H}_2\text{O})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$  gradually lose two water molecules on

**Table 1: Analytical Table and physical data**

Complex Compound	Elemental analysis found (calc)			Electronic UV data $\text{cm}^{-1}$
	% of M	% of N	% of anion	
$[\text{Co}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$	13.3 (13.7)	26.5 (26.3)	16.4 (16.9)	19000, 23000 $\text{cm}^{-1}$
$[\text{Ni}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$	13.4 (13.7)	26.1 (26.3)	16.6 (16.9)	9680, 16200, 24600 $\text{cm}^{-1}$ , $10\text{Dq} = 9680$ $\text{cm}^{-1}$ , $B = 680$ $\text{cm}^{-1}$ , $\beta = 0.77$
$[\text{Pd}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{Cl}_2$	26.1 (26.5)	28.2 (27.9)		23570 $\text{cm}^{-1}$
$[\text{Zn}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{Cl}_2$	17.7 (18.1)	30.7 (31.1)	19.6 (19.9)	-
$[\text{Cd}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{Cl}_2$	27.3 (27.6)	27.2 (27.5)	17.1 (17.4)	-
$[\text{Zn}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{SO}_4\cdot \text{H}_2\text{O}$	15.6 (16.0)	27.5 (27.8)	23.6 (23.8)	-
$[\text{Cd}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{SO}_4\cdot \text{H}_2\text{O}$	25.2 (25.6)	24.6 (24.9)	20.8 (21.1)	-
$[\text{Ni}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$	13.2 (12.9)	25.2 (24.8)	13.4 (13.1)	9700, 16360 & 14840 $\text{cm}^{-1}$ , $10\text{Dq} = 9700$ , $B = 806$ $\text{cm}^{-1}$ , $\beta = 0.77$
$[\text{Co}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$	13.4 (12.9)	25.2 (24.9)	13.3 (13.1)	19250 & 23400 $\text{cm}^{-1}$

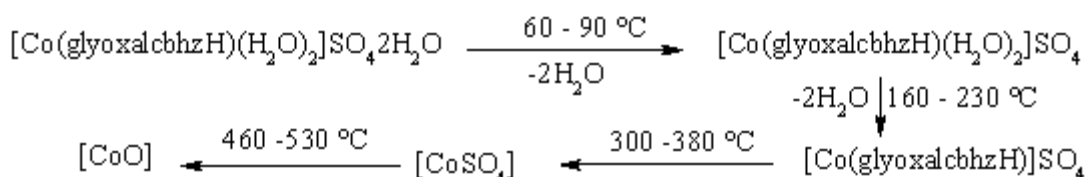
**Table 2:**

Complex Compound	Color	$\mu_{\text{eff}}$ in BM R.T.	$\lambda_a$ $\text{mol}^{-1}\text{ohm}^{-1}\text{cm}^2$
$[\text{Ni}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$	Light green	2.92	128
$[\text{Co}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$	Light pink	4.92	138
$[\text{Zn}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{Cl}_2$	Cream	Dia.	122
$[\text{Cd}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{Cl}_2$	Cream	Dia.	131
$[\text{Ni}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$	Bluish green	3.01	120
$[\text{Co}\{\text{bis}(\text{glyoxalcbhzH})\}(\text{H}_2\text{O})_2]\text{SO}_4\cdot 2\text{H}_2\text{O}$	Pinkish cream	5.01	123
$[\text{Zn}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{SO}_4\cdot \text{H}_2\text{O}$	Cream	Dia.	128
$[\text{Cd}\{\text{bis}(\text{glyoxalcbhzH})\}]\text{SO}_4\cdot \text{H}_2\text{O}$	Cream	Dia.	126

bis(glyoxalcbhzH) = bis (glyoxalcbhydrozone)

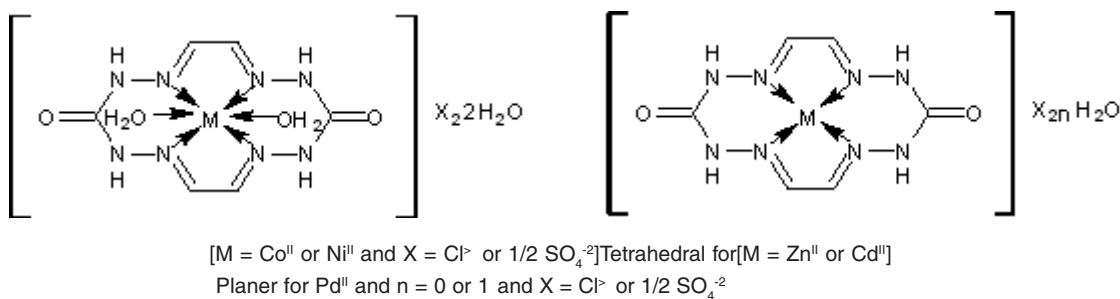
heating above 50°C and Cd<sup>II</sup> or Zn<sup>II</sup> complexes become anhydrous below 90°C while Ni<sup>II</sup> and Co<sup>II</sup> complexes salts retain two H<sub>2</sub>O and these are lost on heating above 160°C. The complexes decompose above 300°C to 380°C either in metal oxide and complex sulphate. In case of sulphate

the final residue of heated product was metal oxide obtained between 460°C to 530°C. The thermal stability was studied at heating rate 10°C per minute in static air. The decomposition of complex sulphate can be shown as follows on the basis of TGA studies.



The probable structure on the basis of analytical results, electrical conductance data and

their physical measurement are suggested for Co<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> complexes as shown below.



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### REFERENCES

- Pederson C.J., *J. Amer. Chem. Soc.*, **89**: 7017 (1967).
- a) Pederson C.J., *Chem. Rev.*, **104**: 2723 (2004).  
b) Prasad R.N. and Sharma Monica., *J. Indian. Chem. Soc.*, **83**: 1260 (2006).  
c) Prasad R.N. and Mathur M., *J. Indian. Chem. Soc.*, **80**: 803 (2003).  
d) Prasad R.N. and Sharma Nisha., *J. Indian. Chem. Soc.*, **89**: 29 (2012).
- Ohira A., Sakata M., Hirayama C. and Kunitake M., *Org. Biomol. Chem.*, **1**: 251 (2003).
- Uemura S., Sakata M., Taniguchi I., Hirayama C. and Kunitake M., *Langmuir*, **17**: 5 (2001).
- Wang D., Xu O.M., Wan L.J., Wang C. and Bai C.L., *Sur. Sci.*, **489L**: 568 (2001).
- Mohammad Tawkir, S.A. Iqbal, Balkrishan and Ishaq Jaffarany, *Orient J. Chem.*, **27**(2): 603-609 (2011).
- H.O. Ogunsuyi, O.O. Ajay, K.O. Pinmoroti and M.O.A. Oladipo, *Orient J. Chem.*, **28**(1): 333-

- 342 (2012).
8. a) Mishra L.K., and Jha Y., *J. Indian. Chem. Soc.*, **76**: 98-99 (1999).  
b) Sinha B.K., Kant R. and Singh R., *J. Indian. Chem. Soc.*, **76**: 65-68 (1999).
  9. Geary W.J., *Coord. Chem. Rev.*, **7**: 81 (1971).
  10. Vogel A.I., "A Text Book of Quantitative Inorganic Analysis", 4<sup>th</sup> Ed., Longmans Green, London. (1978).
  11. Figgis B.N. and Lewis J., *Prog. Inorg. Chem.*, **6**: 37 (1964).
  12. Lever A.B.P., "Inorganic Electronic Spectroscopy" Elsevier Amsterdam., Page 318, 324, 357. (1968).
  13. a) Ballhausen C.J., "Introduction to ligand field theory" Mc.Graw Hill., NewYork. Page 256 (1962).  
b) Jorgensen C.K., *Adv. Chem. Phys.*, **5**: 33 (1963).
  14. a) Bostrup O. and Jorgensen C.K., *Acta. Chem. Scand.*, **11**: 1223 (1957).  
b) Tanabe Y. and Sugano S., *J. Phys. Soc. Japan.*, **9**: 753 (1954).
  15. Belamy L.J., "The Infrared Spectra of Complex Molecule" 2<sup>nd</sup> Ed., Chapman and Hall. London. (1980) .
  16. Feraro J.R., "Low Frequency Vibrations of Inorganic and Coordination Compound" Plenum., NewYork. (1971).