

# DIVALENT METAL COMPLEXES WITH LIGAND DERIVED FROM NINHYDRIN AND AROMATIC DIAMINES AND COMPARISONS OF THEIR REACTIVITIES

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## ABSTRACT

*A new series of divalent cobalt, nickel and copper complexes are prepared templately with 2,2-dihydroxyindane-1, 3-dione and aromatic diamines and comparisons between the reactivities of their 1, 2 and 1, 3 isomers was done. The complexes are characterized as distorted octahedral by elemental analyses, molar conductance, electronic spectra and IR spectral data. The origination of  $-C=N$  in the IR spectral data confirms cyclization. Oxidation followed by volumetric analysis confirms the presence of a divalent metal. The low value of molar conductance indicates them to be non-electrolytes.*

**Keywords:** Ninhydrin, magnetic moments, stereo chemical aspects.

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## INTRODUCTION

Macrocycles prepared synthetically are growing class of compounds with carrying chemistry<sup>(1-5)</sup> viz. donating atoms ring size and type of reaction. The chemical properties of macrocyclic complexes can be terminal to force metal ions to adopt unusual co-ordination geometry. Transition metal macrocycle complexes resemble with natural proteins like hemerythrin and enzymes<sup>(6)</sup>, hence have received much attention as an active part of metallo enzymes 'as biomimic'<sup>(7,8)</sup>, Catalysis is one field where these complexes are very useful<sup>(9)</sup>.

Present work is a template synthesis and study of big and activated dicarbonyls' reaction with variety of diamines. The reactivity of diamine varies with changed position of one amino group on benzene ring w.r.t. other. It further includes the comparison of their metal II complexes – Co(II), Cu(II) and Ni(II) .

## EXPERIMENTAL

**Materials:** The Chemicals used were of Anal R grade and purchased from Aldrich fluka, sd-fine and Ranbaxy. The solvent was purified according to standard procedures.

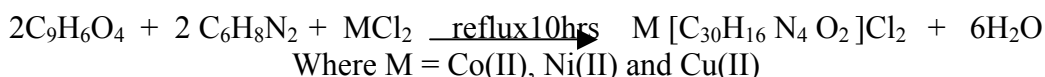
**Isolation of metal Complexes:** The free macrocyclic ligand was separated to observe the condensation of the starting materials but the yield of the ligand was too small as compared to the yield of the templately synthesized complex. Hence all the complexes were obtained by template synthesis.

0.4 M solution of diamino benzene and ninhydrin was made in MeOH in (~100 cm<sup>3</sup>). The metal was dissolved in minimum quality of MeOH. The solution was refluxed at 85°C for 8-10 hr. (Cu/Ni=8 hrs. Co=10 hr). The extra MeOH was distilled out slowly and the mother liquor was subjected to crystallization in a desiccators for 3 days. The complexes were filtered slowly without vacuum to avoid disintegration of the complex due to pressure. The filtered complex was washed with Me<sub>2</sub>CO and cold MeOH and dried; yield 40% - 65%. The complexes are soluble in DMF and DMSO. But are insoluble in common organic solvent and water. They are thermally

stable upto  $\sim 220^{\circ}\text{C}$ , yield of 2,6 isomer was more. The colour of the crystal depend upon the metal taken.

The estimation of cobalt and nickel was done by complexometric titration where as copper was estimated of Iodometrically. For complexometric titration; .1 g of the complex was taken and oxidized with strong acid to release the metal and volume of the solution made to 100 ml. This solution was titrated with .01 molar EDTA solution to have a colour change from yellow to violet (EDTA in burette). For copper,  $\frac{1}{2}$  Test tube of 10% KI was added to the oxidised solution, followed by titration with 0.01M hypo, through freshly prepared starch as indicator. The end point comes out to be blue to colorless with (hypo in the burette).

The scheme of synthesis of the complexes may be shown by the following reaction:



### **Analytical and Physical measurements:**

The microanalysis of C, H, and N were recorded at Perkin Elmer 2400 at SAIF Chandigarh . Melting points were determined using capillaries in electrical melting point apparatus. The metal contents were estimated using standard methods. Electronic spectra of metal complexes were recorded in the region 1100-200 nm on a Hitachi U-2000 spectrophotometer. IR spectra were recorded on Perkin Elmer instrument using nujol mulls at Department of Chemistry, Panjab University, Chandigarh. Magnetic moments studies were carried out at SAIF, IIT, Roorkee, on Vibrating Sample Magnetometer (Model PAR 155). The conductivity was measured on Toshniwal type CL-01/01 Conductivity Bridge.

**Abbreviations** B.M. (Bohr Magnetron); DMF-N,N-dimethylformamide; DMSO-Dimethylsulphoxide; nm-nanometer; MeOH-Methanol

## **RESULTS AND DISCUSSION**

The analytical data show the formula for macrocyclic complexes as:  $[\text{M}(\text{C}_{30}\text{H}_{16}\text{N}_4\text{O}_2)\text{Cl}_2]$  where M = Co(II), Ni(II) and Cu(II). The tests for anions are positive only after decomposing the complexes with conc.  $\text{HNO}_3$ , indicating their presence inside the coordination sphere. All macrocyclic complexes are dark coloured solids and are freely soluble in DMF or DMSO. The measurements of molar conductance in DMSO show that these chelates are non-electrolyte (conductance  $\sim 11-13 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , Table-II). All complexes give satisfactory elemental analyses results as shown in the Table-1.

### **IR spectra:**

In the IR spectra of all complexes, appearance of a band at  $\sim 1720 \text{ cm}^{-1}$  may be assigned to carbonyl  $>\text{C}=\text{O}$  group which is formed by dehydration of geminal hydroxyl groups due to heating. It was noted that a pair of peak  $\sim 3200$  and  $3250 \text{ cm}^{-1}$  corresponding to  $-\text{NH}_2$  group present in IR spectra of diaminobenzene is absent in spectra of all complexes. Furthermore, a new peak has appeared in spectra of all complexes at  $\sim 1595-1645$ , which may be assigned to azomethine group ( $-\text{C}=\text{N}$ ), indicating the formation of macrocyclic frame due to condensation of  $-\text{NH}_2$  groups of diaminobenzene and  $>\text{C}=\text{O}$  groups of ninhydrin. The bands present in the range  $\sim 1350-1000 \text{ cm}^{-1}$  in all complexes are assigned to  $\nu(\text{C}-\text{N})$  stretching. The presence of stretching bands at  $1462$  and  $1500 \text{ cm}^{-1}$  may be assigned to  $>\text{C}=\text{C}<$  of benzenoid rings and a

peak at  $721\text{ cm}^{-1}$  is the C-H deformation of meta substitution. In ortho diamino benzenes of value of C-H deformation has changed to  $771\text{ cm}^{-1}$ .<sup>(10)</sup>

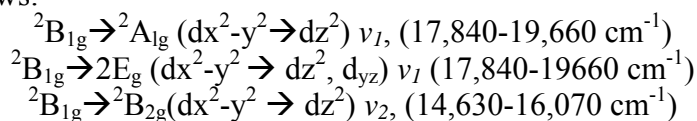
#### **Far IR Spectra:**

The far IR spectra show bands in the region  $\sim 425\text{-}460\text{ cm}^{-1}$  corresponding to  $\nu(\text{M-N})$  vibrations<sup>(16-18)</sup>. The bands present at  $305\text{-}310\text{ cm}^{-1}$  may be assigned as being due to  $(\text{M-Cl})$  vibration<sup>(16-18)</sup>. The absence of  $(\text{M-O})$  vibrations rules out the possibility of coordination through oxygen.<sup>(10, 21)</sup>

#### **Electronic Spectra and Magnetic moment:**

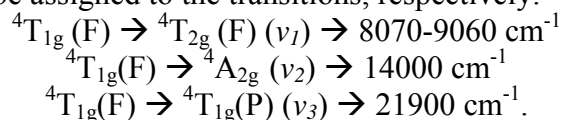
The compounds were also confirmed by the supporting ultra violet –visible spectrum run at the band width of  $2.0\text{ nm}$  with measurement range  $1100 - 200\text{ nm}$  and scanning speed of  $1000\text{ nm/min}$  given in table II. The magnetic moments and electronic transitions are discussed below.

**Copper (II) Complexes:** The value of magnetic moment indicates the presence of one unpaired electron ( $1.99\text{-}2.01\text{ B.M.}$ ). This suggests that the electronic configuration of copper in the complex is  $3d^9, 4s^0$ . The complexes are low spin. Hence electronic spectral bands ( $17,840\text{-}19,660\text{ cm}^{-1}$  a broad band and  $14,630\text{-}16,070\text{ cm}^{-1}$  a shoulder band ) may be assigned to the transitions, respectively, as follows:



This all is indicative of distorted octahedral geometries:<sup>(11-15)</sup>

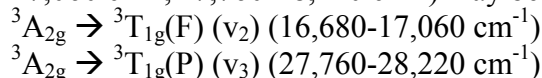
**Cobalt (II) Complexes:** At room temperature the magnetic moments of the cobalt (II) complexes lie in the range  $4.97\text{-}5.01\text{ B.M.}$  indicating  $3d^7 4s^0$  as the electronic configuration. Various spectral bands ( $8070\text{-}9060\text{ cm}^{-1}$ ,  $14000\text{ cm}^{-1}$ ,  $21900\text{ cm}^{-1}$ ) present in electronic spectra of cobalt complexes may be assigned to the transitions, respectively.



This suggests that the environment around the cobalt ion is octahedral<sup>(16)</sup>. The spectra of complexes shows a band in the visible region, which is split due to the presence of low symmetry fields, assuming the effective symmetry to be  $D_{4h}$ <sup>(17-19)</sup>.

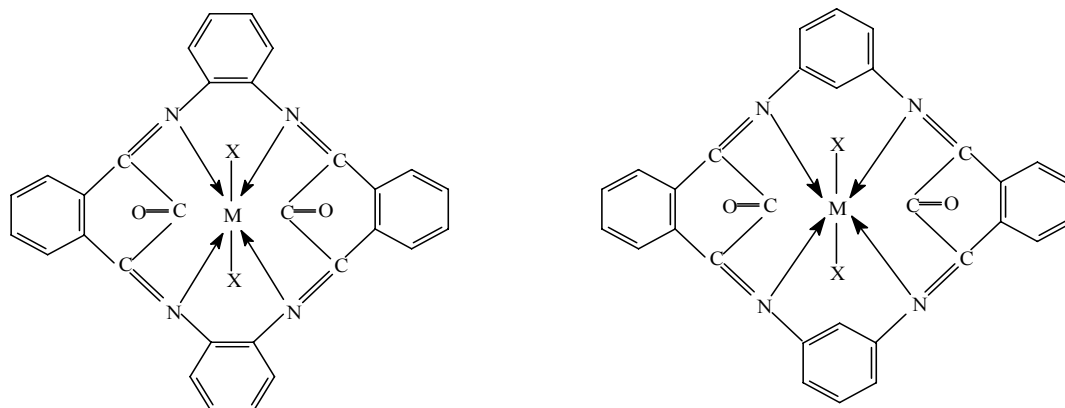
#### **Nickel (II) complexes**

The magnetic moments of nickel complexes lie in the range  $2.96\text{-}2.98\text{ B.M.}$  values indicating the presence of two unpaired electrons with electronic configuration as  $3d^8, 4s^0$ . The configuration of such type is of high spin octahedral complexes. The various electronic spectral bands ( $16,680\text{-}17,060\text{ cm}^{-1}$ ,  $27,760\text{-}28,220\text{ cm}^{-1}$ ) may be assigned to the following transitions as:



The first two bands result from the splitting of one band,  $\nu_1$  and are in the range  $Ca.9730\text{-}10,500$  and  $11,810\text{-}12,340\text{ cm}^{-1}$ , which can be assigned to  $^3B_{1g} \rightarrow ^3E_g$  and  $^3B_{1g} \rightarrow ^3B_{2g}$ , assuming the effective symmetry to be  $D_{4h}$  (component of  $^3T_{2g}$  in  $O_h$  symmetry)<sup>(17)</sup>.

**Proposed Structure:** Therefore based on elemental analyses, conductivity, magnetic, electronic and IR spectral studies the following structures (Fig. 1) may be proposed for these complexes.



**Fig.-1:** Where M = Co(II) Ni(II), Cu (II),X = Cl

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**Table-1: Analytical data of the divalent metal complexes derived from diaminobenzene and ninhydrin**

Percentage Found(Calcd.) %					
Complex	C	H	N	M	Mol. Wt.
Co (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub>	60.6 (60.7)	2.5 (2.7)	9.3 (9.4)	9.7 (9.9)	594
Ni (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub>	60.5 (60.7)	2.4 (2.7)	9.2 (9.4)	9.6 (9.9)	593
Cu (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub>	60.0 (60.1)	2.6 (2.7)	9.2 (9.3)	10.5 (10.7)	598.5

**Table-2: Analytical data of divalent Cu II, Co II, Ni II derived from Ninhydrin and isomeric diamino phenylenes**

S.No.	Complex With Metal	Color	Molar Conductance	Yield	Magnetism	UV-Spectral data in (nm)
1.	Co (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 2 Isomer	Shiny yellow	12.91	47%	5.01	1:381, 1.0752
2.	Co (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 3 Isomer	Black powder	12.91	63%	5.02	1:343.0, 0.4936
3.	Cu (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 2 Isomer	Shiny light green	12.50	45%	2.01	Could not be obtained due to Copper metal
4.	Cu (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 3 Isomer	Black brown powder	12.50	50%	2.01	--do--
5.	Ni (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 2 Isomer	Shiny bottle green	11.20	40%	3.00	1:381. 0.6242
6.	Ni (C <sub>30</sub> H <sub>16</sub> N <sub>4</sub> O <sub>2</sub> )Cl <sub>2</sub> 1, 3 Isomer	Black green powder	11.20	53%	3.01	1:343, 0.8764 2.261, 5.0000