



# Complexes of Manganese (II), Cobalt (II), Nickel (II) and Copper (II) with a 16 Membered Macrocyclic Schiff Base Octaaza Tetradentate Ligand

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**Abstract:** A 16- membered macrocyclic complexes are formed by the reaction of malonodihydrazide with manganese (II), cobalt (II), nickel (II) and copper (II) acetates in presence of benzaldehyde. The template condensation produces a 16 membered macrocyclic ligand 1,2,4,5,9,10,12, 13 - Octaaza – 3, 11 – diphenylcyclohexadeca – 6,8,14,16 - tetra-one ligand ( $L = C_{20}H_{24}N_8O_4$ ). The complexes are characterized by elemental analysis, magnetic moment and conductance measurements, infrared, UV- visible and mass spectroscopic studies. The complexes of the type  $[M(L)Cl_2]$  ( $M = Mn, Co, Ni, Cu$ ) are all octahedral in nature.

**Keywords:** Manganese (II), Cobalt (II), Nickel (II) and Copper (II).

## 1.0 INTRODUCTION

Macrocyclic complexes formed by the template condensation reactions are well established [1-6]. Macrocyclic complexes of transition metals having both oxo and aza groups in a ligand are well known for the ligand having dioxotetraaza [7,8], tetraoxotetraaza [9], tetraoxooctaaza [10,11] moieties. Macrocyclic complexes of transition metal (II) ions having oxo and aza groups shows some interesting properties and biological functions, such as being models of metalloproteins and oxygen carrier systems [7]. 16-membered macrocyclic complexes of Mn (II), Co (II), Ni (II) and Cu (II) having the ligand 1,2,4,5,9,10,12, 13 - Octaaza – 3, 11 – diphenylcyclohexadeca – 6,8,14,16 - tetra-one are not yet reported.

Therefore, in the present programme ,synthesis and characterization of some macrocyclic complexes of, manganese (II), cobalt (II), nickel (II) and copper (II) having the ligand 1,2,4,5,9,10,12, 13 - Octaaza – 3, 11 – diphenylcyclohexadeca – 6,8,14,16 - tetra-one formed by the template condensation of malonodihydrazide and benzaldehyde (2:2) in the presence of corresponding metal chlorides have been reported.

## 2.0 EXPERIMENTAL

All the reagents were of AR grade and used as received from BDH England and Aldrich chemical company. The ligand precursor malonodihydrazide was prepared by the literature procedure. Elemental analyses for carbon, hydrogen and nitrogen were obtained using a Perkin Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded using a Perkin Elmer-883 IR spectrophotometer in 4000-200  $cm^{-1}$  region in KBr discs. Mass spectra were recorded by using a micromass ZAB SE mass spectrometer, UV-visible spectra were recorded in DMSO on a Shimadzu UV-160 spectrophotometer. Conductances were determined by a Systronics 300 model conductivity meters in DMSO with a dip type cell having platinum electrodes. Magnetic moment measurements were made on a Sherwood scientific magnetic susceptibility balance. The metal contents were determined gravimetrically.

## 2.1 Preparation of complexes [M(L)Cl<sub>2</sub>], (M=Mn (II), Co (II), Ni (II), Cu (II))

To a solution of malonodihydrazide C<sub>3</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (0.53g, 4 mmol in 25 ml water), benzaldehyde (0.17 g, 4 mmol) and a solution of metal acetates, 2 mmol in 25 ml water were added. The resultant mixture was refluxed for 3h with constant stirring and then cooled. A light violet precipitate was formed immediately. The precipitate was filtered, washed with water and dried in vacuum desiccators over fused CaCl<sub>2</sub>. Analytical data, color, magnetic moment and molar conductances are presented in table I

**TABLE I :Characterization data of complexes**

Compounds Color	% Yield	M.P °C	Percentage Found (Calculated)				$\mu_{\text{eff}}$ (BM)	Molar Conductance Ohm <sup>-1</sup> cm <sup>2</sup> Mol <sup>-1</sup> (DMSO)
			M	C	H	N		
[Mn(L)Cl <sub>2</sub> ] (off white)	62	110(d)	8.88 (8.97)	46.32 (46.98)	4.88 (4.89)	17.98 (18.27)	5.68	3.21
[Co(L)Cl <sub>2</sub> ] (Pink)	69	122(d)	9.52 (9.56)	46.38 (46.77)	4.85 (4.86)	18.02 (18.15)	4.62	3.80
[Ni(L)Cl <sub>2</sub> ] (Yellowish brown)	70	118(d)	9.52 (9.56)	46.35 (46.77)	4.81 (4.86)	17.98 (18.15)	3.12	1.52
[Cu(L)Cl <sub>2</sub> ] (Yellowish green)	66	117(d)	10.20 (10.22)	45.96 (46.33)	4.80 (4.82)	17.96 (18.82)	2.05	1.28

## 3.0 RESULT AND DISCUSSION

The macrocyclic complexes were formed by the template condensation of malonodihydrazide and benzaldehyde in the molar ratio 2:2 in the presence of the corresponding metal acetate. In the complexes, four N atoms of the 16-membered macrocyclic ligand is coordinated to the metal ions. Complexes are non electrolytic in nature. Elemental analyses of the complexes and mass spectra are consistent with the proposed formula. The suggested structures of the complexes are octahedral in nature.

### 3.1 IR SPECTRA

The infrared spectra of the complexes shows a strong band in the region 1675-1640 cm<sup>-1</sup>, which is attributed to  $\nu(\text{CO})$  of amide group [14]. Two medium bands in the regions 3380-3300 cm<sup>-1</sup> are suggested to  $\nu(\text{N-H})$  modes of -NHCO- and -CH<sub>2</sub>NH- moieties respectively [9]. The coordination through N atom of the ligand is supported by the appearance of a band in the region 550-500 cm<sup>-1</sup>, which is tentatively attributed to  $\nu(\text{M-N})$  mode [15]. A medium band in the region is 310-270 cm<sup>-1</sup> is assigned to the  $\nu(\text{M-Cl})$  mode. The absence of  $\nu(\text{NH}_2)$  bands in the complexes, supported the condensation between hydrazide group and benzaldehyde.

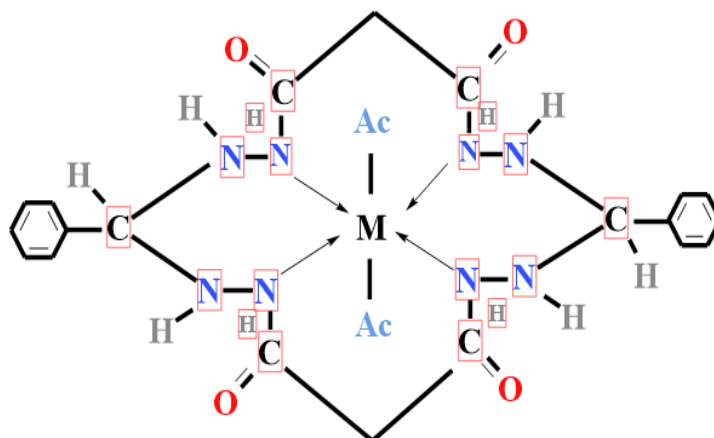
### 3.2 MAGNETIC MOMENT

The magnetic moment of the Mn (II) complex was found to be 5.80 B.M. The magnetic moment of cobalt (II) complexes is 4.90 B.M. corresponding to a Co (II) with high spin octahedral environment of three unpaired electrons. A little higher value than the spin only moment for the three unpaired electrons (3.89 B.M.) may be attributed to the orbital contribution which is generally observed for Co (II) compounds [16]. Nickel (II) complexes shows magnetic moment of 3.20 whereas Copper (II) complex shows 2.15 B.M. corresponding to octahedral geometry.

### 3.3 MOLAR CONDUCTIVITY

Co (II) complex exhibits a pair of bands at 680 and 575 nm whereas Ni (II) shows respective bands at 580 and 475 nm. The single band in the electronic spectrum of Cu (II) complex appears at 600 nm. These features are consistent with the octahedral environment of the mixed ligands around central metal ion [16,17]

The above mentioned bands can be assigned to the transitions  $^4\text{A}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$ ,  $^4\text{T}_{1g} \leftarrow ^4\text{T}_{1g}(\text{F})$  for Co (II)  $^4\text{T}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$ ,  $^3\text{T}_{2g} \leftarrow ^3\text{T}_{1g}(\text{f})$  for Ni (II) respectively, which was suggested for the octahedral Co (II) and Ni (II) complexes [18]. For octahedral Co (II) and Ni (II)  $^4\text{T}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$  and  $^4\text{A}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$  transitions occur in the near IR region, which is seldom observed because it is in an inconspicuous region of the spectrum (10000-20000 cm<sup>-1</sup>). The band in Copper (II) complexes can be assigned to the transition  $^2\text{T}_{2g} \leftarrow ^2\text{E}_g(\text{F})$  for d<sup>9</sup> configuration of Cu (II) in an octahedral geometry [9]. The mass spectra of the complexes showed molecular ion peaks and other fragments and they are consistent with the proposed formula.



Ac = Acetate ion

M= Mn (II), Co (II), Ni (II) & Cu (II)

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