

## Synthesis of a Macrocyclic Ligand, Ph<sub>4</sub>-[14]-Tetraene-N<sub>4</sub> and its Metal Complexes with Chromium-, Iron-, Cobalt- and Nickel(II)

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A series of metal complexes of chromium-, iron-, cobalt- and nickel(II) with a macrocyclic ligand 6,7,13,14-Ph<sub>4</sub>-[14]-6,7,12,14-tetraene-1,5,8,12-N<sub>4</sub> has been prepared and characterized on the basis of infrared, electronic, NMR spectral studies as well as conductivity and magnetic moment studies. The ligand reacts with metal(II) salts under conditions of non-aqueous chelation to give macrocyclic complex M(Ph<sub>4</sub>-[14]-tetraene-N<sub>4</sub>)X<sub>2</sub> [M = Co(II), Ni(II), Fe(II), Cr(II); X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup>].

### INTRODUCTION

There has been spectacular growth in the interests of metal complexes with tetra-aza macrocyclic ligands followed by extensive works on the metal controlled template and metal-free non-template synthesis of macrocyclic species<sup>1-7</sup>. In continuation of our work in the field<sup>8-11</sup>, we report here a series of metal complexes with the macrocyclic title ligand Ph<sub>4</sub>-[14]-tetraene-N<sub>4</sub>.

### EXPERIMENTAL

The metal salts used were of BDH make. 1,3-Diaminopropane and benzil (E. Merck) were used as such. For the preparation of the ligand procedure as reported in the literature was followed<sup>12</sup>. 1,3-Diaminopropane was dissolved in dry and cold methanol and allowed to react with methanolic solution of benzil in equimolar proportion under reflux on a water bath for several hours at room temperature. The solution thus obtained on crystallisation gave the cream coloured solid which was filtered, washed and dried. The complexes were prepared by refluxing metal salts and ligand in equimolar proportion in methanolic medium. On chemical analysis, the stoichiometries of the complexes were found to be of the type M(Ph<sub>4</sub>-[14]-tetraene-N<sub>4</sub>)-X<sub>2</sub>. Metal ion catalysed *in situ* method, in which 1,3-diaminopropane and benzil were allowed to organise themselves around a central metal cation, gave similar results.

The infrared spectra of the ligand as well as its complexes were recorded on a Beckmann IR-20 spectrophotometer. The conductivity measurements were made on a Systronics conductometer model 303 using dimethylsulfoxide as a solvent. Magnetic moments were measured by the Gouy method using Hg[Co(NCS)<sub>4</sub>] as a calibrant. The absorption spectra of dimethylsulfoxide solutions of these complexes were recorded on a Cary-2390 spectrophotometer using a pair of 1 cm quartz cuvettes. <sup>1</sup>H-NMR spectra were recorded (in CDCl<sub>3</sub>)

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on a Varian F-16 spectrometer. Analytical, infrared and electronic spectra alongwith magnetic moment and conductivity data of the complexes have been recorded in Table-1. Chromium(II) complex is green whereas the remaining three complexes are brown.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF THE METAL-COMPLEXES

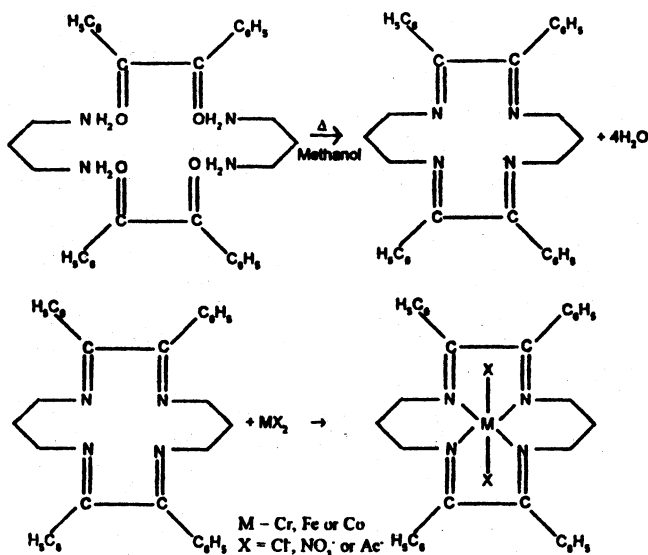
Compound (Colour)	$\mu_{\text{eff}}$ (B.M.)	$\Lambda_{\text{max}}$ $\Omega^{-1} \text{ cm}^2$ $\text{mol}^{-1}$	IR spectral data ( $\text{cm}^{-1}$ )		Electronic spectral data ( $\text{cm}^{-1}$ )	Analysis %, found (calcd.)	
			$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$		M	N
$\text{Cr}(\text{C}_{34}\text{H}_{32}\text{N}_4)\text{Cl}_2$ (Green)	5.20	40	1620	450	11,000	8.40 (8.42)	9.42 (9.40)
$\text{Fe}(\text{C}_{34}\text{H}_{32}\text{N}_4)\text{Cl}_2$ (Brown)	4.62	35	1618	455	12,000	9.02 (9.04)	9.00 (9.02)
$\text{Co}(\text{C}_{34}\text{H}_{32}\text{N}_4)(\text{NO}_3)_2$ (Brown)	1.80	35	1620	445	14,000	8.70 (8.72)	12.46 (12.42)
$\text{Ni}(\text{C}_{34}\text{H}_{32}\text{N}_4)(\text{OAc})_2$ (Brown)	Diam.	240	1622	455	15,500 20,000	8.74 (8.72)	8.32 (8.36)

## RESULTS AND DISCUSSION

### Synthesis

The reaction taking place in the preparation of the ligand and of its metal complexes involving 1,3-diaminopropane, benzil and metal(II) salts can be represented as follows:

represented as follows-



All the coloured solid complexes are stable at room temperature. The molar conductances values for the complexes using 10<sup>-3</sup> molar solution in DMF (Table-1) indicate their non-electrolytic and covalent nature except the nickel (II) complex which corresponds to bi-univalent electrolyte. The analytical data show that these macrocyclic complexes can be represented as M(C<sub>34</sub>H<sub>32</sub>N<sub>4</sub>)X<sub>2</sub> [where M = Cr, Fe, Co or Ni; X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or OAc<sup>-</sup>]. Molecular weights of these complexes indicate the monomeric nature of the complexes.

### Infrared spectra

The IR spectrum of the macrocyclic ligand shows a strong band at 2915 cm<sup>-1</sup> which is associated with  $\nu(\text{C—H})$  of phenyl group. The —CH<sub>2</sub>— group present in the ligand is indicated by a band in the range 1435–1425 cm<sup>-1</sup>. These bands remain almost unpearturbed in the spectra of the complexes.

All the complexes show a band around 1620 cm<sup>-1</sup> due to  $\nu(\text{C=N})$ . In the spectrum of the ligand, this band appears at 1650 cm<sup>-1</sup>. Lowering of this band in complexes suggests participation of imine nitrogen atom in coordination<sup>13</sup>. At the same time, no band is observed around 1800–1700 cm<sup>-1</sup> which indicates the condensation of the amine and ketone. The bands appearing around 450 cm<sup>-1</sup> in all the complexes indicate  $\nu(\text{M—N})$  vibration which further confirms the coordination of these groups with the metal ion<sup>13</sup>. Chromium and iron(II) complexes exhibit an intense band at 350 cm<sup>-1</sup> in their spectra which may be attributed to  $\nu(\text{M—Cl})$ .

### Electronic spectra and magnetic moment studies

All the complexes show bands at 34,000–31,500 cm<sup>-1</sup> which may be due to charge transfer transitions. The observed magnetic moment values of 5.0 B.M. for the Fe(II) macrocyclic complex and a weak intensity band at 11,900–11,200 cm<sup>-1</sup> region may be assigned to  ${}^5\text{T}_{2g} \longrightarrow {}^5\text{E}_g$  transition which is consistent with the octahedral geometry around Fe(II) ion. In case of Cr(II) complex, the observed magnetic moment of 4.60 B.M. and electronic spectra showing a weak band at 15,400–14,700 cm<sup>-1</sup> assignable to  ${}^5\text{E}_g \longrightarrow {}^5\text{T}_{2g}$  transition are consistent with the octahedral geometry around Cr(II) ion. The Co(II) complex shows a band at 14,500–13,000 cm<sup>-1</sup> and has magnetic moment of 1.82 B.M. The band may be assigned to the transition  ${}^2\text{E}_g \longrightarrow {}^2\text{T}_{1g}$  and is suggestive of octahedral stereochemistry. In contrast to octahedral geometry for Cr(II), Fe(II) and Co(II) complexes, a square-planar geometry showing two bands at 16,900–15,000 and 20,000–19,500 cm<sup>-1</sup> assignable to transitions  ${}^1\text{A}_{1g} \longrightarrow {}^1\text{B}_{1g}$  and  ${}^1\text{A}_{1g} \longrightarrow {}^1\text{B}_{2g}$  respectively for Ni(II) complexes is proposed. Ni(II) complex is found to be diamagnetic. Magnetic moment and electronic spectral data are in close agreement with earlier reports<sup>14</sup>.

## <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of the ligand shows five kinds of protons, namely —CH<sub>2</sub>— (two kinds) and phenyl protons (three kinds). The twenty phenyl protons appear in three groups in the region 6.90–7.25 ppm and —CH<sub>2</sub>— protons appear in two groups in the region 1.95–2.60 ppm. The signal due to phenyl protons remains almost unperturbed; however, the signal due to —CH<sub>2</sub>— protons shifted downfield indicating coordination of the adjacent N-atoms to the metal ion.

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