

## STUDIES ON MIXED LIGAND COMPLEXES OF IRON (III), CHROMIUM (III) AND NICKEL (II) CONTAINING DICARBOXYLIC ACID AND 5, 7, 7, 12, 14, 14 HEXAMETHYL 1, 4, 8, 11 TETRAAZACYCLOTETRADECA 4, 11 DIENE

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Mixed ligand complexes of Fe(III), Cr(III) and Ni(II) with dicarboxylic acid and 14 membered tetraazamacrocycles have been synthesized. The general composition of the complexes are  $\text{trans-[M(DAL)]}^{n+}$  where  $n=0, 1$  and DA = dibasic acids e.g. Homophthalic acid (Hm), Diphenic acid (Dp) and L = 5,7,7,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. These complexes were characterized on the basis of elemental analyses, conductometric, magnetic, infrared, column and thin layer chromatography and electronic spectral studies. The present complexes are high spin species consistent with essentially octahedral stereochemistry with trans configuration.

**Key words:** Mixed ligand, Cyclic complexes, High spin species.

### Introduction

Studies on macrocycles and their metal complexes have received a considerable attention in recent years in respect to their pharmacological (Hollinshead and Smith 1960), industrial (Samant and Kulkarani 1979) and analytical (Elden *et al* 1980) applications. Malik *et al*, 1983 have prepared and characterized some mixed ligand complexes of Cu(II), Co(II) with tetraazamacrocycles and distinguished their geometry as distorted octahedral. Tetraaza ligands generally form transcomplexes of the type  $[\text{MA}_2\text{L}]^{n+}$  (A=monodentate ligands) and only in the presence of chelating agent cis geometry has been established (Sadanivan *et al* in 1967; Hay and Lawrance 1973). Mixed ligand complexes of imides and amines with tetraazacyclopentadecane alongwith their geometry have been reported (Islam and uddin 1993).

We extended our study in the field of mixed ligand complexes containing Fe(III), Cr(III) and Ni(II) as a central metal atoms. Dicarboxylic acids and tetradentate tetraazamacrocyclic dienes are used as ligands in the present study. The synthesis and characterization of some new mixed ligand complexes of Fe(III), Cr(III) and Ni(II) with homophthalic acid or diphenic acid and 5,7,7,12,14, 14 hexamethyl-1,4,8, 11 tetraazacyclotetradeca 4, 11 diene have been reported.

### Experimental

**Physical Measurements.** The instruments used were the same as reported earlier by Islam and Uddin in 1993.

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magnetic moments were measured on a Johnson Matthey magnetic susceptibility balance. Conductivities of  $1.0 \times 10^{-3}$  solutions of the complexes in acetonitrile were measured at 27°C using a WPA CM35 conductivity meter and dip-type cell with platinized electrodes. Decomposition or melting points were recorded with an electrothermal melting point apparatus.

**Reagents and Chemicals.** All the chemical used were of reagent grade Fe(III), Cr(III), Ni(II) chloride, homophthalic acid, diphenic acid and acetonitrile were obtained from E-Merck (Germany). The macrocyclic ligand 5, 7, 12, 14, 14-hexamethyl 1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene was synthesized by the reported procedure (Martin *et al* 1977).

**Preparation of the Complexes.**  $\text{Trans-[M(DA)L]}^+ \text{Cl}^-$ : Where, M=Fe(III) and DA=Dibasic acid e.g, diphenic acid (Dp) and Homophthalic acid (Hm), L = tetraazacyclic diene.

Ethanolic solutions of both Fe(III) chloride  $2 \times 10^{-3}$  mole and homophthalic or diphenic acid  $2 \times 10^{-3}$  mole were mixed together. The mixture was stirred for about 10 min but no precipitate appeared. The mixture was further stirred for about 20 min after the addition of the second ligand (tetraazacyclic dienes). At this stage a yellow or reddish brown precipitate appeared. Using column chromatography followed by TLC, pure compound was obtained. The compounds were dried in a vacuum desiccator over silica gel. Composition, colour, molar conductances, melting points, yields and magnetic data obtained are summarised in Table-1.

Trans-[M(DA)L]<sup>n+</sup>: Where, M=Cr(III) or Ni(II), DA= Dicarboxylic acid, L= tetraazacyclic diene and n=0, 1.

Ethanollic solutions of both the metal chloride  $2 \times 10^{-3}$  mole and dicarboxylic acid  $2 \times 10^{-3}$  mole were mixed and stirred for 15 min. The ethanollic solution of  $2 \times 10^{-3}$  mole of the tetraazacyclic diene was added dropwise to the previous solution and refluxed for about 4 h. Precipitation was completed and the products were recovered by the above mentioned method. Pure products were dried in a vacuum desiccator over silica gel.

## Results and Discussion

**Elemental Analyses and Conductivity.** The analytical and physical data of the complexes are accumulated in Table 1. All of these complexes are soluble in water, DMF, DMSO, nitrobenzene and acetonitrile. The molar conductance values (Table-1) indicate that Fe(III) and Cr(III) complexes are 1:1 electrolytes in acetonitrile and it was also confirmed elsewhere (Geary 1971).

For the Ni(II) complexes the molar conductance values in DMSO indicate the nonelectrolytic behaviour which was also confirmed by Islam and Uddin in 1993.

**Magnetic Moments.** The effective magnetic moment of Fe(III) complexes are 5.93-5.97 B.M. (Table-1) which indicate that the complexes are paramagnetic with five unpaired electrons and thus suggesting high spin octahedral complexes. On the other hand chromium (III)

complexes yielded effective magnetic moments 3.87-4.22 B.M. (Table-1) corresponding to three unpaired electron hence suggesting high spin octahedral complexes. The effective magnetic moments of the Ni(II) complexes are in the range 3.00-3.36 B.M. indicating the octahedral symmetry and this observation is confirmed by the work of Bailar *et al* 1975

**Electronic Spectra.** The electronic spectral data of Fe(III) complexes gave four bands in the regions (23097-23201), (28500-28932), (31954-32055) and (43290-43668)  $\text{cm}^{-1}$  corresponding to the transitions  ${}^6A_{1g} \rightarrow {}^4E_{1g}$  (G),  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (D),  ${}^6A_{1g} \rightarrow {}^4E_g$  (D), and a charge transfer band respectively. Three bands in the regions (17987-18000), (25230-25502) and (38319-39979)  $\text{cm}^{-1}$  corresponding to the transitions  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  (F),  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (F), and a charge

**Table 2**  
IR spectral data for the complexes (Band Maxima in  $\text{cm}^{-1}$ ).

Types of complexes	$\nu\text{N-H}$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{N-H})$	$\nu(\text{M-O})$
1	3150	1660	1340	435	320
2	3165	1600	1347	425	340
3	3155	1595	1335	420	345
4	3155	1625	1350	450	335
5	3150	1691	1343	430	332
6	3160	1620	1356	445	325

**Table 1**  
Analytical data and physico-chemical properties of the complexes

Complex No with Composition*	Colour	Yield %	Metal %	Carbon %	Hydrogen %	Nitrogen %	Melting or Decomposition points $^{\circ}\text{C}$	Molar conductance $\text{ohm}^{-1}\text{cm}^2 \text{mole}^{-1}$	$\mu_{\text{eff}}$ B.M
1.[Fe.(Hm)L]Cl	Reddish brown	78	10.32 (10.16)	54.42 (54.61)	6.60 (6.91)	10.39 (10.19)	240	160.12	5.97
2.[Fe(Dp)L]Cl	Yellow	80	9.88 (10.20)	65.91 (65.77)	7.21 (7.30)	10.00 (10.19)	242	160.12	5.93
3.[Cr(Hm)L]Cl	Green	57	9.20 (9.53)	54.84 (54.61)	6.67(6.91)	10.91 (10.19)	280-284(D)	103.02	3.87
4.[Cr(Dp)L]Cl	Green	67	9.76 (9.56)	65.47 (65.77)	7.11 (7.30)	10.45 (10.23)	294 (D)	134.64	4.22
5.[Ni(Hm)L]Cl	Green	61	10.05 (10.35)	58.22 (58.06)	7.10 (7.35)	11.00 (19.83)	280	6.9	3.36
6.[Ni(Dp)L]Cl	Green	63	16.62 (16.49)	69.65 (69.94)	7.79 (7.77)	10.65 (10.87)	280-283(D)	14.76	3.00

Composition\*: The experimental values were in agreement with the calculated values where, Hm<sup>2</sup> = C<sub>9</sub>H<sub>6</sub>O<sub>4</sub>; L = C<sub>16</sub>H<sub>12</sub>N<sub>4</sub>; Dp = C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>. Percentages calculated are given in parenthesis.

transfer band respectively are obtained for Cr(III) complexes. All these bands indicate octahedral stereochemistry.

Finally, the complexes of Ni(II) gave three bands at (9000-9065), (15820-15735) and (28321-28726)  $\text{cm}^{-1}$  corresponding to the transitions  ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \longrightarrow {}^3T_{1g}$ , and  ${}^3A_{2g}(\text{F}) \longrightarrow {}^3T_{1g}(\text{P})$ , respectively. These bands indicate octahedral symmetry of the Ni(II) complexes (Islam and Uddin 1993).

**IR Studies.** The IR spectral data are given in Table 2 which indicate the characteristic bands and their assignments of our present complex. The coordinating macrocycles contain two imido nitrogen atoms which show an absorption band in the region  $1660 \text{ cm}^{-1}$  and two (>N-H) groups in a band maxima in the region  $3175 \text{ cm}^{-1}$  respectively (Islam and Uddin 1993). However, due to their coordination to a metal atom, these band maxima are shifted to the range ( $1591\text{-}1625$ )  $\text{cm}^{-1}$  and ( $3150\text{-}3165$ )  $\text{cm}^{-1}$  respectively. This proves the complexation of the metal cations with the macrocycle through its nitrogen atoms. A distinct band observed in the region ( $420\text{-}425$ )  $\text{cm}^{-1}$  also indicates the coordination of nitrogen atoms with the metals.

Another important feature of the spectra of the complexes is that there is no absorption band of the (-OH) group but a new absorption band occurs in the region ( $320\text{-}345$ )  $\text{cm}^{-1}$  indicating M-O bonds. The shift of  $\nu_{\text{C-O}}$  frequency from  $1350 \text{ cm}^{-1}$  in the spectrum the ligand to lower values in the spectra of the complexes further confirms the coordination of metals to the oxygen atoms of the carboxylic groups which is comparable with the work of Islam and Uddin in 1992.

IR Spectra of the cis-complexes (folded geometry) are generally more complicated than those of trans-complexes (planar geometry). Our present complexes display only one  $\nu(\text{NH})$  band and thus confirm the trans geometry of the complexes.

All of these physico chemical evidences and references envisage us to give a general structure of the type shown in Fig 1.

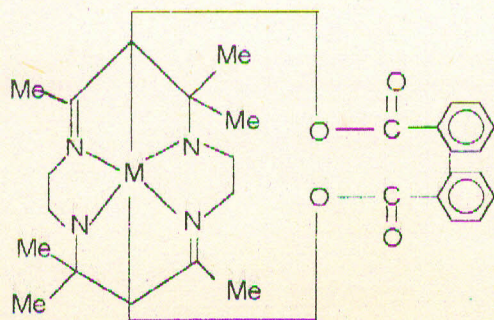


Fig 1. Structure of the complex  $[M(\text{Dp})(\text{L})]$  where,  $M = \text{Ni}^{++}$ .

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