

**Complexes of Chromium (III) and Iron (III) with 16 Membered Macrocyclic Schiff Base  
Octaaza, Tetradentate Ligand**

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**Abstract**

16- membered macrocyclic complexes are formed by the reaction of malonodihydrazide with chromium (III) and iron (III) chlorides in presence of acetates. The template condensation products, containing a 1,2,4,5,9,10,12, 13 - Octaaza – 3, 11 – diphenylcyclohexadeca – 6,8,14,16 - tetra-one ligand (L= C<sub>20</sub> H<sub>24</sub>N<sub>8</sub>O<sub>4</sub>). 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<sub>2</sub>] Cl (M=Cr(III),Fe(III)) are all octahedral in nature.

**Key Words:** Macrocyclic, Chromium, Iron, Chlorides, Magnetic Moment

**1.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 Cr(III) and Fe(III) 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 chromium (III) and iron (III)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 acetates have been reported.

**2.EXPERIMENTAL**

All the reagents were of AR grade and used as received from BHD England and Aldrich chemical company. The ligand precursor malonodihydrazide was prepared by the literature procedure. Element 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<sup>-1</sup> 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. Conductance were determined by a systronics 300 model conductivity meter 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 and chlorine were determined gravimetrically.

## 2.Preparation of complexes [M(L)CL<sub>2</sub>]Cl,[M=Cr(III) and Fe(III)]

To a solution of malonodihydrazide[12] C<sub>3</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (0.53g, 4 mol in 25 ml water), benzaldehyde (0.17 g,4mmol) and a solution of chromium trichloridehexahydrate CrCl<sub>3</sub>.6H<sub>2</sub>O(0.53) gm, 2 mmol in 25 ml

water were added . The resultant mixture was refluxed for 3h with constant string and then cooled. Alight violet precipitate was formed immediately. The precipitate was filtered, washed with water and dried in a vacuum desiccators over fused CaCl<sub>2</sub>. The m.p. was>300<sup>0</sup>C and yield 0.62g (65%). The same procedure, was applied for preparation of Fe (III,) complexes using respective metal source.

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		
[Cr(L)Ac <sub>2</sub> ]Ac (Light Violet)	62	110(d)	7.70 (7.77)	46.12 (46.63)	4.92 (4.93)	16.68 (16.74)	5.68	3.21
[Fe(L)Ac <sub>2</sub> ]Ac (Deep Blue)	69	122(d)	8.30 (8.32)	46.00 (46.36)	4.88 (4.90)	16.48 (16.64)	4.62	3.80

TABLE II

Important Infrared bands of the complexes as KBr disc( in cm<sup>-1</sup>)

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
[Cr(L)Ac <sub>2</sub> ]Ac	3382,3282	1677	555	283
[Fe(L)Ac <sub>2</sub> ]Ac	3335,3275	1675	530	290

## 3.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 chloride. In the complexes, four N atoms of the 16-membered macrocyclic ligand is coordinated to the metal. The Cr (III) and Fe (III) complexes are 1:1 electrolyte. Elemental

analyses of the complexes and mass spectra are consisted with the proposed formula. The suggested structure of the complexes are octahedral in nature.

### 3.1 INFRARED SPECTRA

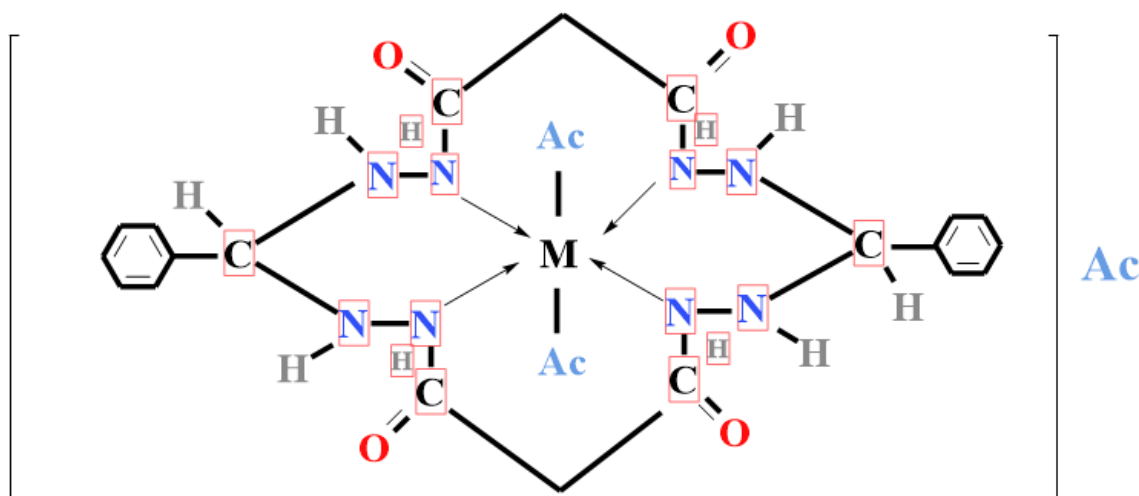
The infrared spectra of the complexes shows a strong band in the region  $1675-1640\text{ cm}^{-1}$ , which is attributed to  $\nu(\text{CO})$  of amide group[14]. Two medium bands in the regions  $3380-3300\text{ cm}^{-1}$  are suggested to  $\nu(\text{N-H})$  modes of  $-\text{NHCO}-$  and  $-\text{CH}_2\text{HN}-$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

### 3.2 MAGNETIC MOMENT AND ELECTRONIC SPECTRA

The magnetic moment of Cr (III) compound is 3.80 B.M corresponding to three unpaired electrons which is observed for nearly all known mononuclear Cr (III) complexes [16] irrespective of the strength of the ligand field. The observed magnetic moments for the compounds of Fe (III) are 5.62 B.M., respectively, suggesting high spin  $d^5$  configuration with octahedral geometry. Magnetically, Fe (III) compounds are high spin in nearly all of their compounds except those with strong ligands.

The Cr (III) complexes exhibit two bands at 570 and 520 nm. The Fe (III) complexes show lone band at 550nm.

The above mentioned bands can be assigned to the transitions



Ac = Acetate ion

M= Cr (III) & Fe (III)

${}^4A_{2g} \leftarrow {}^4T_{1g}(F)$ ,  ${}^4T_{1g} \leftarrow {}^4T_{1g}(f)$  for Co (II)  ${}^4T_{2g} \leftarrow {}^4T_{1g}(f)$ ,  ${}^3T_{2g} \leftarrow {}^3T_{1g}(f)$  for Ni (II) respectively, which was suggested for the octahedral Co (II) and Ni (II) complexes[18]. For octahedral Co (II) and Ni (II)  ${}^4T_{2g} \leftarrow {}^4T_{1g}(f)$  and  ${}^4A_{2g} \leftarrow {}^4T_{1g}(f)$  transitions occur in the near IR region, which is seldom observed because it is in an

inconvenient region of the spectrum(1000-2000). The band in Copper (II) complexes can be assigned to the transition  ${}^2T_{2g} \leftarrow {}^2E_g(f)$  for  $d^9$  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 consisted with the proposed formula.

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