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Synthetic and Electrochemical Studies of Dipyrido 1,5,8,12 Teteraaza [14] Tetradecatetraene-N_4 Macrocyclic Complexes of Mn (III) and Fe (III)

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ABSTRACT

Tetraazamacrocyclic complex has been synthesized by the condensation of Dipyrido 1,5,8,12 Teteraaza [14] Tetradecatetraene-N_4, metal, salt of Mn (III) and Fe (III). These synthesized complexes were characterized by elemental analysis, Molar conductivity measurement UV/Vis, IR and cyclic voltammetric technique. These complexes were also screened against antimicrobial activity agents. The complexes were found to be destroyed octahedral geometry on the basis of electronic spectra. Electrochemical behavior of these complexes suggested that metal centers were distinguished by their intrinsic redox system.

Keywords: Macrocyclic complexes, Synthesis, Characterization, cyclic voltammetry

I. INTRODUCTION

Now- a- days macrocyclic chemistry is a growing area of research in inorganic and bioinorganic chemistry in view of its biological significance. The studies of macrocycles have undergone tremendous growth in recent years and their complexation chemistry with a wide variety of metal ions has been extensively studied. Macrocyclic complexes are considered to mimic the synthetic models of metalloporphyrins and metallocorrins due to their intrinsic structural properties [1-10].

Macrocyclic complexes acting as a variety of macrocyclic catalysts have stimulated the studies of a large number of new macrocycles of different cavity size and rigidity are known to the co-ordination chemists, but most of these compounds still suffer from the absence of ionizable functions, a deficiency which is not presented by more classical ligands. However, a macrocyclic featuring ionizable function should combine with two advantages; selectivity gained from the steric requirements of the internal cavity and a pH sensitive complexation. Macrocycles have also played a pivotal role to serve synthetic models from a naturally occurring macrocyclic system like porphyrin and corrin rings, which are found in Heam protein, chlorophyll and metalloenzymes. Consequently a large number of derivative of various metals, containing transition and post transition metals have been synthesized with hopes that some would mimic biological functions. Indeed, several complexes have been effective as catalyst in the solid state. In particular, Cobalt trtraaza Annulene has been explored as dioxygen reduction catalyst at cathode in fuel cells. Macrocyclic complexes of Manganese and Iron are used as Antimicrobial, Antifertility, Anti-inflammatory, Anti-HIV activity and analgesic agents.

Manganese chloride cause causes loss of testicular germ cells in rats and rabbits and decreased libido and importance were noted in men occupationally exposed to manganese. Keeping the importance of synthetic macrocycles in view a detailed account of the studies of coordination behaviour of Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 macrocycles have been taken into consideration [11-21].

III. EXPERIMENTAL

A. Materials

All the regents used in the preparation of macrocyclic ligands and their metal complexes were of regent AnalaR grade. The solvent used for the synthesis of macrocyclic ligand and metal complexes were distilled before use. All other chemicals were of AnalaR grade and used without further purification. 2,3-diaminopyridine and 1 phenyl 1,3-butanedione were procured from Acros, New Jersey USA, The metal salts were purchased from S.D-fine, Mumbai. India, Ranbaxy, India, and were used as received.

Infrared spectra in the 400-4000 cm^{-1} range were recorded on a FTIR Shimardzu spectrophotometer at room temperature with KBr disks. Ultraviolet and visible spectra covering the 14000-37000 cm^{-1} region were obtained on a Shimardzu UV-7000 double beam spectrophotometer with chloroform solutions at room temperature.

Cyclic voltammetry was carried out on potentiostate model 362 EG and G parc instrument PAR coupled with Graphtec x-y recorder WX 4000 made in Japan and platinum electrode was used as working electrode. A saturated calomel electrode was taken as a reference electrode which was separated from a bulk electrolyte solution by a Salt Bridge prepared with agar and saturated aqueous KCl and a DMF solution containing a complex (4.0×10^{-4} Mol) and tetra n-butylaluminium perchlorate (TBAP) (4.0×10^{-2} Mol) was used as base electrolyte and deaerated prior to each measurement with N_2. In the cell a blanket of inert gas was maintained during the measurement. All the measurements were performed at the room temperature [22-35].

B. Preparation of the Macrocycles and their Complexes

Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 macrocycle (A) and Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 macrocycle (B) and their complexes were obtained although with low yields according to the literature procedure with slight modification. We have followed template method for the preparation of following macrocyclic complexes [35-40].

Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (A) Cl] macrocyclic complex.

A mixture of ligand (A) (4.0×10^{-4} Mol), and manganese (II) chloride (8.0×10^{-3} Mol), N, N-dimethylformamide ~15 mL was refluxed for 6 h with stirring. The solvent was removed on rotary evaporator the residue was washed several times with ether and extracted with chloroform. The product, which was recovered by evaporating the extract to dryness and than recrystallized from benzene to give a brownish coloured compound; yield ~50.0% IR (KBr Disk): ν C=N 1595, ν C=C 1420 cm^{-1}.

Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (B) Cl] macrocyclic complex.

The reaction of ligand (B) (2.0×10^{-4} Mol) and manganese (II) chloride (5.0×10^{-3} Mol), in N-N-dimethylformamide~15 mL, followed by the above procedure, gave coloured compound. IR (KBr disk): ν C=N 1590, ν C=C 1472, 1425 cm^{-1}.

Isothiocyanato Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (A)NCS].

A mixture of ligand (A) (5.0×10^{-4} Mol), manganese (II) acetate tetrahydrate (7.0×10^{-3} Mol), in N,N-dimethylformamide ~60.0 mL was refluxed and then KSCN (1.0×10^{-2} Mol), was added until the colloidal precipitate was deposited. After being stored overnight in a refrigerator, the crystalline solid was separated by filtration. The dichloromethane solution of the crude product was chromatographed on activated alumina column (200 mesh). A deeply coloured band on the top of the column was eluted with dichloromethane, and then chloroform. The second effluent was collected and evaporated to dryness in vacuum to give coloured compound IR (KBr disk): ν C≡N 2047, ν C=N 1590, ν C=C 1475, 1412cm^{-1}.

Isothiocyanato Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (B)NCS].

The reaction of ligand (B) (5.0×10^{-4} Mol), and manganese (II) acetate tetrahydrate (5.0×10^{-3} Mol), and KSCN (1.0×10^{-2} Mol), in N,N-dimethylformamide ~10 mL, and water ~60 mL, followed by the above procedure, gave blue-violet compound. IR (KBr disk): ν C≡N 2047, ν C=N 1475, 1412cm^{-1}.

Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 iron (III) complex [Fe (A) Cl]

A mixture of ligand (A) (4.0×10^{-4} Mol), iron (II) chloride tetrahydrate (2.0×10^{-3} Mol), and acetonitrile ~20 mL, was refluxed for 6h with stirring while nitrogen gas was continuously bubbled through it. On cooling the reaction mixture with ice-water, the crystalline product was recovered by filtration and was thoroughly washed with methanol to give dark green compound. IR (KBr disk): ν C=N 1595, ν C=C 1485, 1412cm^{-1}.

Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 iron (III) complex [Fe (B) Cl]

The complex was prepared from ligand (B) (4.0 × 10^{-4} Mol), and iron chloride tetrahydrate (2.0 × 10^{-4} Mol), in acetonitrile ~ 15 mL, following the above procedure, and was thoroughly washed with methanol to give dark green compound. IR (KBr disk): ν C=N 1590, ν C=C 1485, 1425cm^{-1}. A mixture of 2,3-diaminopyridine and 1 phenyl 1,3-butanedione in N,N-dimethylformamide ~6mL was heated under reflux for 6 h with stirring. Upon cooling the reaction mixture with ice-water, the crystalline solid was recovered by filtration and washed several times with methanol to give dark red needles; yield ~(27%). The dichloromethane solution of this material (0.41g) was applied to the top of a chromatrographic column of silica gel (60-80) mesh, and eluted with dichloromethane. The solid material, which was recovered by evaporating the initial effluent to dryness on rotavap, was recrystallized from carbon tetrachloride to obtain the macrocycle (A) reddish coloured.

IV. RESULTS AND DISCUSSION

synthesized manganese (III) and iron (III) complexes of macrocyclic ligand (A) and macrocyclic ligand (B); Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (A) Cl], Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (B) Cl], isothiocyanato Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (A)NCS], isothiocyanato Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 manganese (III) complex [Mn (B)NCS], Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 iron (III) complex [Fe (A) Cl] and Chloro Me_2 Ph_2 dipydrido [b, i] [1,5,8,12] tetraaza [14] tetradecatetraene-N_4 iron (III) complex [Fe (B) Cl]. These macrocyclic complexes of manganese (III) and iron (III) complexes were characterized by CHN analysis, UV-VIS and IR spectroscopy as well as electrochemical measurements.

The corresponding manganese (III) complexes of a 1:1 molar ratio of macrocyclic ligand (A or B) to metal with an anion in the axial position were prepared. In macrocyclic manganese chelate system, the Mn (III) state seems to be electronically more stable than the Mn (II) complex due to ligand-field stabilization effect. The iron (III) complexes were also prepared by reaction of the macrocyclic ligand (A or B) with iron (III) salt in acetonitrile. The analytical data in and melting points of the complexes are given in Table 1. Elemental analysis of crystalline sample these macrocyclic complexes are in accordance with the compounds of these compositions. The characteristic IR bands of the manganese (III)complexes showed an intense absorption band at ~2045cm^{-1} which is correlated with a C≡N stretching mode of the SCN^- anion. These complexes seem to be N-bonded as the frequencies appeared ~2052 cm^{-1}. Ultraviolet and visible spectra covering the 14000-37000 cm^{-1} range were recorded for macrocycle [Mn (B) Cl] and [Fe (B) Cl]. The general features of the spectra for [Mn (A) Cl] ad [Mn (B) Cl], [Mn (A) NCS], [Mn (B) NCS], [Fe (A)Cl] and [Fe(B) Cl] respectively, are almost similar to one another.

The bands observed about the 16000 cm^{-1} region are assigned to CT transition from metal to ligand and $\pi \rightarrow \pi *$ transition within ligand molecules because the molar extinction coefficient of these band are higher than those usually assigned to d→d* star transition [41-46].

A. Electrochemical Studies

A typical cyclic voltammogram shown in figure 1 for [Fe(B)Cl] and electrochemical data of the macrocyclic manganese (III) iron (III) complexes are presented in Table 2. [Fe(B)Cl] showed two one electron reduction processes at –0.15 and -1.25 V vs SCE. As the free ligand B is not reduced in this region, the reduction of the complex is considered with iron ion. The product seems to be [Fe^{II}(B)Cl] and [Fe^{II}(B)], respectively, and not anion and radicals. These studies showed that the redox behaviour of iron. The cyclic voltammogram of complex [Fe(B)Cl] and complex [Fe (A)Cl] are almost similar to each other. Thus the delocalization of a conjugated system in [Fe (B)Cl] and [Fe (A)Cl] macrocyclic complexes is approximately analogous to each other. These results are consistent with the electronic spectral behavior [Mn(B)Cl], [Mn(A)Cl], [Mn(B)NCS] and [Mn(A)NCS] which showed one-electron reversible reduction in the potential range -0.50 to -0.55 V vs SCE.

It is also noteworthy that reductions of these complexes are metal centered, and the product are [Mn^{II} (B)] in [Mn^{II} (A)]. The cyclic voltammogram for macrocyclic complex [Mn(B)Cl] is also similar to that macrocyclic complex [Mn(A)Cl].

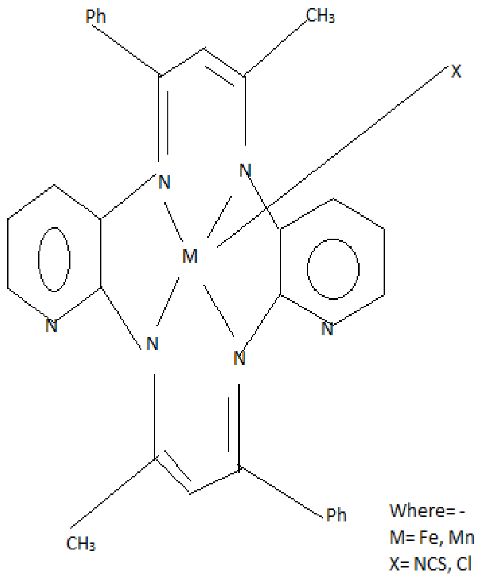
It has been observed that electrochemical potential for complex [Mn(B)Cl] is different from that for Complex [Mn(B)NCS]. These studies show that the effect of axial ligation on the macrocyclic complexes may differ upto some extent.

Table 1: Analytical Data for Tetraaza [14] tetradecatetraene-N$_4$ Macrocyclic Complex.

Complex	Empirical Formula	Elemental Analyses Calculated / Found (%)		
		C	H	N
[Mn(A)Cl]	$C_{30}H_{24}N_6MnCl$	64.46 (63.90)	4.29 (4.15)	15.04 (15.70)
[Mn(B)Cl]	$C_{30}H_{24}N_6MnCl$	64.46 (63.90)	4.29 (4.15)	15.04 (15.70)
[Mn(A)NCS]	$C_{31}H_{24}N_7SMn$	64.03 (63.85	4.13 (4.00)	16.86 (16.58)
[Mn(B)NCS]	$C_{31}H_{24}N_7SMn$	64.03 (63.85	4.13 (4.00)	16.86 (16.58)
[Fe(A)Cl]	$C_{30}H_{24}N_6FeCl$	64.35 (63.88)	4.29 (4.15)	15.01 (14.80)
[Fe(B)Cl]	$C_{30}H_{24}N_6FeCl$	64.35 (63.88)	4.29 (4.15)	15.01 (16.80)

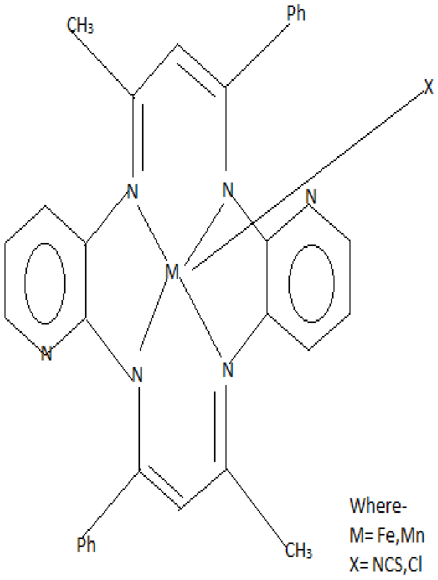
Table 2: Electrochemical data for the Manganese (III) and iron (III) Complexes using DMF TBAP (4.0×10^{-4} Mol) as base electrolyte.

Complex	$E_{1/2}$[M(III/II)], V	$E_{1/2}$[M(II/I)], V
[Mn(A)Cl]	-0.52	-
[Mn(B)Cl]	-0.52	-
[Mn(A)NCS]	-0.55	-
[Mn(B)NCS]	-0.55	-
[Fe(A)Cl]	-0.15	-1.25
[Fe(B)Cl]	-0.15	-1.25



Where= -
M= Fe, Mn
X= NCS, Cl

Macrocycle - A



Where-
M= Fe,Mn
X= NCS,Cl

Macrocycle-B

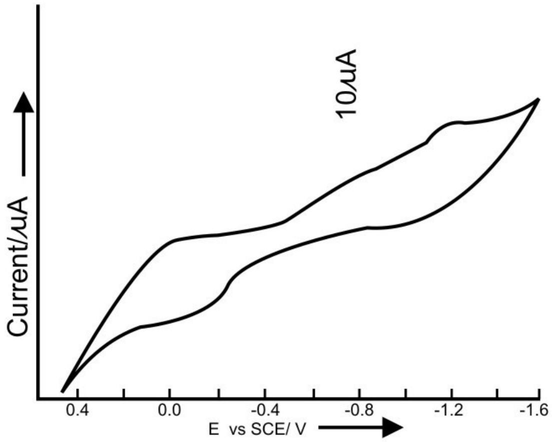


Fig. 1. Cyclic voltammogram of Fe(A) Cl (5.0×10^{-4}M) in CH_3 CN containing 0.1M TEAP at room temperature (Scan rate 100mVS^{-1}).

CONCLUSIONS

On the bases of above, such as elemental analyses, conductance measurements and magnetic susceptibilities, as well as IR, NMR and electronic spectral studies, a five co-ordinate, square pyramidal geometry as shown in figure may be proposed for all the synthesized complexes. It has been suggested that chelation/coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor group within the whole chelate ring system. Many other factors, such as solubility, dipole moment, conductivity influenced by the metal ion, may possibly explain these complexes.

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