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# Synthesis, Spectral, Cyclic Voltammetric and Antimicrobial Studies of Iron (III) Complexes with Tetradentate Bis-benzimidazole Based Diamide Ligand

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**ABSTRACT**

A new tetradentate Bis-benzimidazole based ligand, N-Octyl-N,N'-Bis-(2-Methyl-Benzimidazoly)-benzene-1, 3-dicarboxamide(O-GBBA) has been synthesized and utilized to prepare Iron (III) complexes of general composition $[Fe(O\text{-}GBBA)X_2].X.nH_2O$ where X is an exogenous anionic ligand ($X=Cl^-$, $NO_3^-$). These complexes were prepared in the molar ratios of metal: ligand (1:1) and characterized by elemental analysis, IR, UV spectroscopic and other analytical techniques. Cyclic voltammetric measurements of the complexes display quasi reversible redox wave due to the Iron (III)/Iron (II) process. The distorted octahedral geometry with monomeric composition was proposed for both theses complexes on the basis of these studies. These complexes have been screened for their antimicrobial activities against bacteria, Lactobacillus and fungi, A.Niger, Rhizopus & Mucer. These complexes were found to exhibit considerable antimicrobial activity.

**Key words:** Benzimidazole, Diamide, Ligand, Exogenous, Lactobacillus and *A.niger.*

## INTRODUCTION

Iron is the second most abundant element after aluminum. Oxidation states (+2) and (+3) are very common for Iron since $E^0$for $(Fe^{+2}/Fe^0)$ is -0.44 volts and for $(Fe^{+3}/Fe^{+2})$ is 0.77 volts have tremendous complex forming tendency[5-6]. Enzymes that catalyze the incorporation of oxygen atom derived from dioxygen into organic substrate usually contain either Iron or Copper[1-4]. A variety of studies indicate that the active site of Iron remain in the ferric oxidation state throughout the course of mechanism[7-14]. Ligands containing pendant nitrogen donor heterocyclic linked to a bridging carbon atom have been extensively used in coordination and organometallic chemistry[15]. Such types of ligands have been potentially useful for stabilizing metal in both high and low oxidation states[16]. Ribonucleotide reductase converts ribonucleotide into deoxyribonucleotide in the first committed step in DNA biosynthesis[17].

## EXPERIMENTAL

### Materials & Methods

All the chemicals used were of analytical

grade and solvents used for spectral studies were of spectroscopic grade. The IR spectra of ligand & its complexes were recorded on a Bruker spectrophotometer in 4000-400 $cm^{-1}$ region. Electronic absorption spectra were obtained on a UV-VIS spectrometer, UV 570433 using a prepared methanol solution in the 200-1000 nm. The $^1H$ NMR spectral analyses were performed on a Bruker-Advance 400 $MH_Z$ spectrophotometer using $CDCl_3$ as solvent. Cyclic voltammetric measurements were carried out using a BAS CV 50W electrochemical analyzing system ($E_{1/2}$ measured to an accuracy of +1.0mv). Magnetic susceptibility measurements were taken in CAHN 2000 magnetic balance. The structures of the compounds have been drawn using Chem draw software.

**Synthesis of ligand, O-GBBA**

A solution of GBBA (500mg,1.179mmol) was suspended in 20 mL of dry DMF and stirred for 4-5 h with dry $K_2CO_3$ (325.4mg, 2.358mmol) on a 72 h on a water bath at 70-75$^0$C. Subsequently the solvent was stripped off on a rotary evaporator and the residue was extracted with chloroform (insoluble part was rejected). Upon adding hexane to this filtrate, a white precipitate was deposited, which was washed with hexane, dried and recrystallized using (8:2) methanol: water solution. It was then analyzed for the composition $C_{40}H_{52}N_6O_2.CH_3OH.2H_2O$. Yield: 40% C: 66.3(65.7); H: 8.2(8.4); N: 11.8(11.0); $\lambda_{max.}$ (nm):280,274,242.

**Synthesis of metal complexes**

A solution of metal salts with $Cl^-$, $NO_3^-$ as anion in 10 ml of methanol were added to ligand solution in 1:1 stochiometry with stirring of the above reaction mixture for 25-30 minutes at room temperature yielded brownish colored complexes respectively. The compounds obtained were filtered off, washed with methanol and dried over $P_4O_{10}$. These complexes were further characterized by analytical and spectral techniques.

[$FeCl_2$ (O-GBBA)].Cl.$3H_2O$: Yield, 76.5% Anal. Found (Calcd.): C, 55.52(56%); H, 6.70 (7%); N, 9.71(10%); Fe, 6.47(6%).$\lambda_{max}$ (nm): 284, 278,348,490.

[Fe $(NO_3)_2$(O-GBBA)].$NO_3$.$4H_2O$: Yield, 73.4% Anal. Found (Calcd.): C, 49.89(50%); H, 6.23 (6%); N, 13.09(13%); Fe, 5.82(6%).$\lambda_{max.}$ (nm): 284, 276,360,495.

## RESULTS AND DISCUSSION

**UV-Visible and 1H NMR studies**

The electronic spectra of the complexes were taken in methanol. The free ligand show two strong bands in the UV region at 274 and 280 nm. These bands are assigned to the π-π* transitions characteristic of benzimidazole group. The spectra of complexes also two strong bands at 284-285, 276-277 nm corresponding to π-π* transition. The

**Table 1: The 1HNMR data (in ppm) of ligand, O-GBBA**

| Chemical shift (δ in ppm) | a | b | c | d | e | f | g | h | i | j |
|---|---|---|---|---|---|---|---|---|---|---|
| O-GBBA | 4.9 | 7.4-7.5 | 7.6 | 7.8 | 8.1 | 8.3 | 8.5 | 4.2 | 1.1-1.4 | 0.8 |

**Table 2: IR spectral bands for the ligand (L) and their metal complexes ($cm^{-1}$)**

| Ligand/Complex | $\upsilon_{NH}$ amide | $\upsilon_{NH}$ benzimidazole | $\upsilon_{CO}$ amide | $\upsilon_{CN}$ amide | $\upsilon_{C=N-C=C-}$ benzimidazole | Special peaks |
|---|---|---|---|---|---|---|
| [O-GBBA (L)] | 3256 | - | 1643 | 1544 | 1461 | |
| [$FeCl_2$ (L)]Cl.$3H_2O$ | 3212 | - | 1614 | 1555 | 1447 | |
| [Fe $(NO_3)_2$(L)]. .$NO_3$.$4H_2O$ | 3221 | - | 1616 | 1550 | 1449 | $\upsilon_{-O-N-O}$ 1378 |

bands are slightly blue shifted with lowered extinction coefficients. The UV bands are all blue shifted upon coordination suggesting the binding of Fe (III) to the ligand donor atom. We observed bands in the region between 485-495 nm and 345-360 nm. These bands can be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ transitions respectively similar to the related complexes[18]. The 345-360 nm bands may arise due to contribution from low energy L→M charge transfer transition. On the basis of electronic spectra distorted octahedral geometry around Fe (III) ion is suggested.

The $^1$HNMR spectra of ligand, O-GBBA in $CDCl_3$[19] show signal for both aliphatic and aromatic protons with theoretically predicted splitting. A signal is observed between 9.43 and 8.05 ppm corresponding to N-H amide proton and multiplets in the range 7.1-7.8 ppm arise due to the benzimidazole ring protons characteristic of an AA'BB' pattern. The linker benzene ring protons are found at 7.5, 8.1 and 8.4 ppm for the ligand. The -$CH_2$ group attached to the benzimidazole ring gives rise to a doublet between 4.2 and 4.9 ppm to coupling with the amide NH protons. The N-Octyl chain in our ligand is found at 0.8, 1.1-1.4 and 4.2 ppm respectively. The 1H NMR data (chemical shift in ppm) are shown in the Table 1 below.

**IR spectroscopy and Cyclic voltammetry**

The free ligand, O-GBBA has characteristic IR Bands at 1640, 1544 & 1461cm $^{-1}$.

**Table 3: Cyclic voltammetric data**

| Complex | Scan rate (mV/Sec.) | Supporting Electrolyte | Solvent | Oxidation Potential(V) | Reduction Potential(V) |
|---|---|---|---|---|---|
| $[FeCl_2 (L)].Cl.3H_2O$ | 100 | $Ag/AgNO_3$ | DMSO | +1.25 | -0.34 |
| $[Fe (NO_3)_2(L)]. .NO_3.4H_2O$ | 100 | -do- | -do- | +1.28 | -0.45 |

Where L=O-GBBA ligand

**Table 4: Magnetic susceptibility data at room temperature (300K)**

| S. No. | Complex | $\mu_{eff.}$ /atom (B.M.) |
|---|---|---|
| 1. | $[FeCl_2 (L)].Cl.3H_2O$ | 5.81 |
| 2. | $[Fe (NO_3)_2(L)].NO_3.4H_2O$ | 5.78 |

L=Ligand

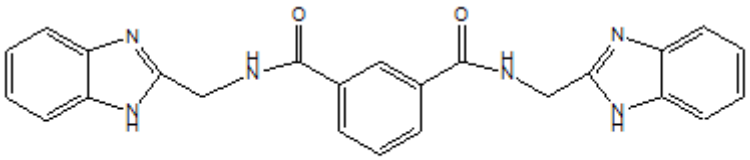
These are assigned to amide I (mainly $\upsilon_{C=N}$ amide stretch), amide II (mainly $\upsilon_{C=O}$ amide stretch) and benzimidazole ($\upsilon_{C=N-C=C}$) stretching frequency respectively[19]. The benzene ring bands appear at 736 cm$^{-1}$(due to benzimidazole ring) and at 691 cm$^{-1}$(linker benzene). $\upsilon_{N-H}$ stretching bands arise at 3296 and 3185 cm$^{-1}$ due to the amide NH and benzimidazole NH respectively. On complexation, a decrease in the amide I stretching frequency and increase in amide II stretching frequency has been

**Table 5: Antimicrobial studies**

| S. No. | Compound | Concentration of complexes | Antifungal activity | | | Antibacterial activity |
|---|---|---|---|---|---|---|
| | | | *A. niger* | Mucor | Rhizopus | Lactobacillus |
| 1 | $[FeCl_2(L)].Cl.3H_2O$ | 40 µg/ml | + | - | + | + |
| 2 | $[Fe (NO_3)_2(L)]. NO_3.4H_2O$ | 40 µg/ml | + | - | + | + |

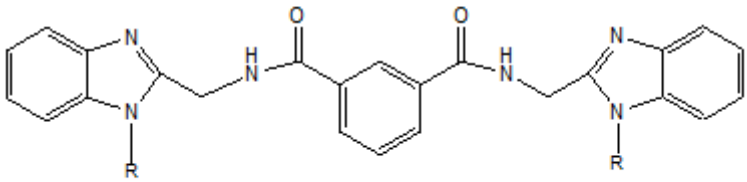
L=Ligand

observed, which is in accordance with the coordination of the ligand through amide carbonyl oxygen. Shifts in N-H stretching frequencies are due to the hydrogen bonding. A broad band in the range 3250-3400 $cm^{-1}$($\upsilon_{O-H}$ stretch) indicates the presence of coordinated/lattice water molecules.



**GBBA**

**Dry DMF ,4-5h,Dry $K_2CO_3$ | Octylation with n-Octyl bromide, heat**



**Where R= -$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$**

**Fig. 1: O-GBRA**

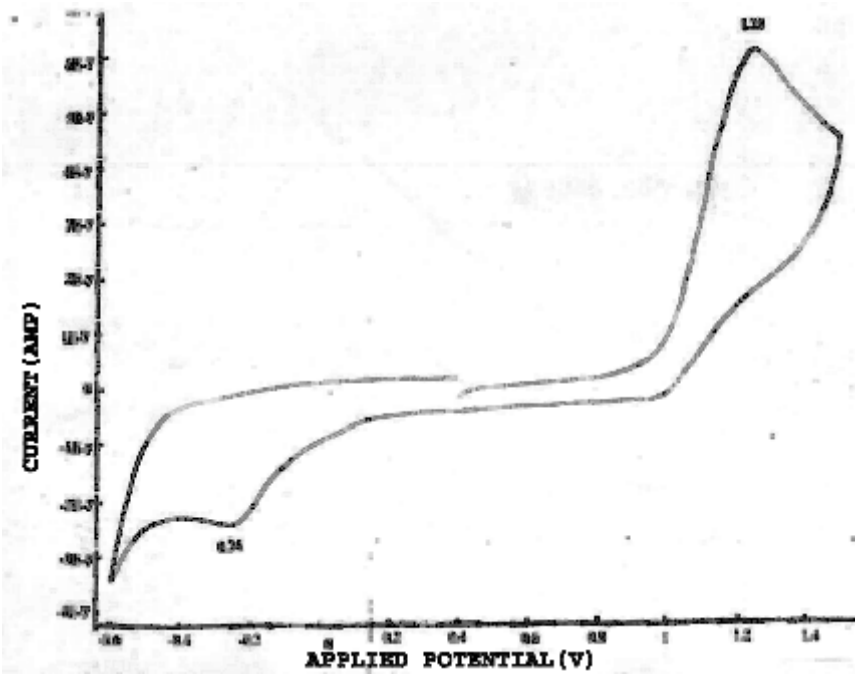



**Fig.2a: Cyclic voltammogram of [Fe $Cl_2$ (L)].Cl.3$H_2O$ in DMSO. Scan rate 100 mV /Sec.**

Characteristic stretching frequencies for coordinated anions are also observed. The nitrate complex shows bands at 1378-1385 and 820-825 $cm^{-1}$ due configuration composed of Pt-disk working electrode, a Pt-wire counter electrode and Ag/ $AgNO_3$ reference electrode was used for measurements. The cyclic voltammograms of the complexes are shown in Fig. 2a and 2b respectively.

All the complexes display quasi reversible redox wave due to the Fe (III)/Fe (II) process. The $E_{½}$ values of $[FeCl_2 (L)].Cl.3H_2O$ and $[Fe(NO_3)_2(L)].NO_3.4H_2O$ were found to be -0.34 V and -0.45 V respectively. Anodic shift in $E_{½}$ values indicate the retention of the anion in the coordination sphere of Fe (III). The $E_{½}$ values vary anodically in the order $NO_3^-$ > $Cl^-$. This indicates that bound chloride

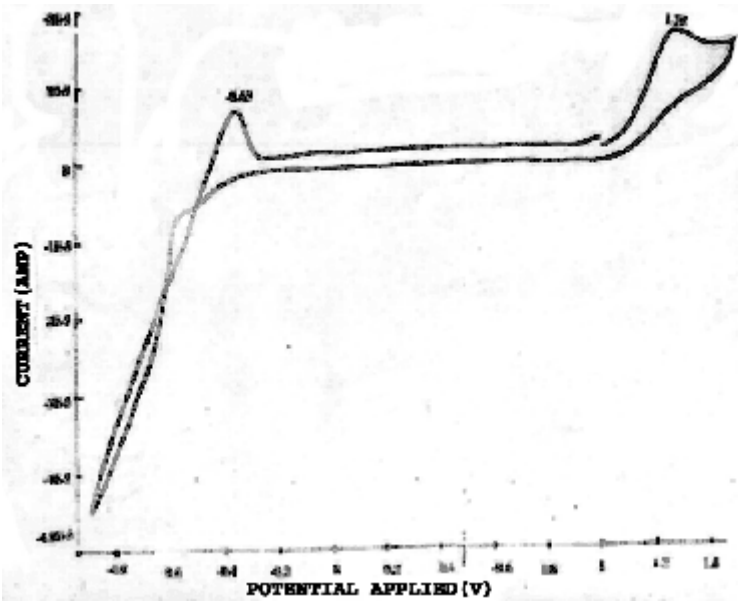



**Fig. 2b: Cyclic voltammogram of $[Fe(NO_3)_2(L)].NO_3.4H_2O$ in DMSO. Scan rate 100 mV /Sec**

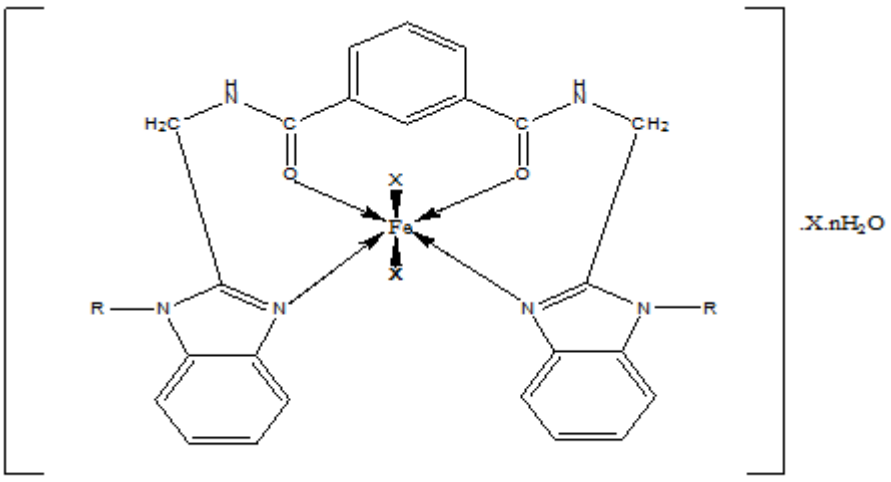



**Fig. 4: Proposed Structures of the metal complexes**

stabilizes the Fe (III) state while bound nitrate destabilizes it.

**Magnetic susceptibility measurements**

The magnetic susceptibilities of the complexes at room temperature were determined by using a CAHN 2000 Magnetic balance and are reported in Table 4.The solid state magnetic moment at room temperature of complex 1 and 2 at room temperature, 5.81 and 5.78 are comparable to the spin-only value of high spin d5 Fe (III), 5.92 B.M., which suggest distorted octahedral & monomeric nature of our complexes.

**Antimicrobial studies**

All the complexes were screened in-vitro for their antimicrobial activity against bacteria and fungi. Iron (III) complexes analyzed for antifungal and antibacterial activities in vitro conditions. All the complexes inhibit the growth of bacteria and fungi. For this study, we used lactobacillus bacteria in curd and A. Niger, Mucer on pickle. To check the inhibition activities, 40 µg/ml in methanol of each complex was used. Only qualitative study of zone of inhibition was performed for each complex and so the zone of inhibition in ppm was not reported. The findings of the above studies are depicted in Table 4.

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