



Research Article

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Synthesis, spectral and cyclic voltammetric studies of iron (III) complexes with N, N', N''-tris-(benzimidazolyl)-methane ligand

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ABSTRACT

The tripodal ligand N, N', N''-tris-(Benzimidazolyl)-methane (TBM) containing benzimidazole as pendant groups has been synthesized and utilized to prepare Fe (III) complexes of general composition $[Fe (TBM) X_3] \cdot n H_2O$. Where X is an exogenous anionic ligand ($X=Cl, NO_3^-, CH_3COO^-$ & $HCOO^-$). Complexes of 1:1 stoichiometry form with the ligands in methanol and were characterized by elemental analysis, IR, UV-VIS spectroscopic and other analytical techniques. The cyclic voltammograms of the complexes were taken in DMSO. Cyclic Voltammetric measurement of the complexes display quasi reversible redox wave. The $-ve$ reduction potential values reveal the strong binding of anionic donors stabilizing the Fe (II) oxidation state. The magnetic moment data reveal the monomeric nature. The IR spectral data reveal unidentate mode of binding of the benzimidazole and anionic donors to the iron site. The UV spectra reveal that the UV bands are all blue shifted upon coordination and in general in enhance in intensity. The large molar extinction coefficients reveal that the iron site in the complexes is of low symmetry. The complexes have been screened for their antibacterial and antifungal activity. The result of this study shows that the Fe (III) complexes are effective against the bacterial pathogens.

Keywords:-TBM[N, N', N''-tri-(Benzimidazolyl) methane], Tridentate, Benzimidazolyl, Exogenous, ligand, E. coli.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust. 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. These results show that Fe^{3+} will act as an electron acceptor ($E^0=0.77V$) and iron (III) salts are known to be readily hydrolyzed. Ligands containing pendant nitrogen donor heterocyclic linked to bridging carbon atom have been extensively used in coordination and organometallic chemistry (1). Such type of ligand have been potentially useful for stabilizing metal in both high and low oxidation states (2). Iron (III) complexes have been synthesized earlier with a bidentate ligand BPBM (3)/ O-GBBA (4) and also Schiff bases (5, 6). A variety of studies indicate that the active site of Iron remains in the ferric oxidation state throughout the course of mechanism (7-14). Schiff bases and benzimidazole heterocyclic complexes play Important role in various biological activities (15-18). Enzymes that catalyze the incorporation of oxygen atom derived from dioxygen into organic substrate usually contain either Iron and copper (19-22).

EXPERIMENTAL SECTION

All the solvents were dried over molecular sieves. IR spectra were taken on a Shimadzu IR-435 spectrophotometer, 1H NMR spectra on 90 MHz Perkin – Elmer at USIC at University of Delhi, Delhi-7 and University of Rajasthan, Jaipur. Magnetic Susceptibility was determined by the use of a CAHN - 2000 balance in the solid state. Cyclic voltammetry studies were taken from Dayalbagh Deemed University, Agra and UV-VISIBLE spectra from St. John's College, Agra. Biological study was performed at Dungan College, Bikaner, Rajasthan.

Preparation of the Ligand:

The ligand was synthesized as described before (23). A mixture of 24 mmoles of benzimidazole, 120 mill moles of anhydrous K_2CO_3 and 1.2 mmoles of tetra butyl ammonium hydrogen sulphate were vigorously stirred and refluxed in dry chloroform (25 ml) overnight. Then the mixture was filtered and the residue washed with hot chloroform (2 x 25 ml). The organic solution was evaporated and the crude product purified by crystallization ($\text{EtOH-H}_2\text{O}$), while crystals were obtained with good yield (60%). The common formula of the ligand is $\text{C}_{22}\text{H}_{16}\text{N}_6$. The ligand was characterized by C, H, N; IR, ^1H NMR and ^{13}C NMR. TBM: ^1H NMR ($\text{DMSO-}d_6$) (rel. intensity in ppm) : 7.0 (m, 9H) ; 7.76 (s, 3H) ; 7.8-8.0 (m, 3H) ; 8.76 (s, H) : ^{13}C NMR ($\text{DMSO-}d_6$) (rel. intensity in ppm) : 142.1(s) ; 138.2(s) ; 121.95(s) ; 115.4 (s).

Preparation of the Complexes:-

[Fe (L) X_3]:

($\text{X}=\text{Cl}^-$ and NO_3^-)

$\text{FeX}_3 \cdot y\text{H}_2\text{O}$ (1 mmol) and the appropriate ligand were dissolved in 10 ml of methanol respectively. Both the solutions were mixed. The solution was stirred for about three hours and then solvent was stripped off on a rotatory evaporator ($\text{Ca.}45^\circ\text{C}$). The residue was treated with dry ethanol and filtered. To the filtrate, ether was added (1:7). Upon standing a parrot green the precipitate was obtained. The precipitate was then centrifuged and recrystallized with Ethanol-ether (1:5) mixture.

[Fe (L) X_3]:

($\text{X}=\text{HCOO}^-$ and CH_3COO^-)

1 mmol of iron (III) chloride in 10 ml of methanol was treated with a solution of sodium hydroxide in methanol. The iron (II) hydroxide precipitate was filtered off. This was then resuspended in methanol (10 ml) and Acetic acid/Formic Acid solution added to it dropwise directly reacted with ligand (1mmol) in MeOH. The reaction mixture was stirred for about four to five hours. Then the solution was reduced to a small volume on a rotatory evaporator. The solution was created with excess of diethyl-ether. The greenish- blue precipitate formed was filtered off. It was then washed with Methanol-ether mixture (1:5) and was dried over P_2O_5 in vacuum.

Table 1: Elemental Analysis: Found (Calculated):

Complex	% C (cal)	%H(cal)	%N (cal)	% Fe (cal)
[Fe(TBM)Cl ₃].3H ₂ O	49.9(49.4)	3.1(3.7)	15.2(15.7)	11.1(11.9)
[Fe(TBM)(NO ₃) ₃].3H ₂ O	47.1(46.4)	2.8(3.2)	19.0(19.7)	10.7(11.2)
[Fe(TBM)(HCOO) ₃].3H ₂ O	49.2(49.26)	4.2(4.1)	13.9(13.7)	9.2(9.19)
[Fe(TBM) (OAc) ₃].3H ₂ O	51.7(51.6)	4.8(4.7)	12.8(12.9)	8.5(8.6)

RESULTS AND DISCUSSION**i) ELECTRONIC SPECTROSCOPY:**

Electronic spectra of Iron complexes were recorded in MeOH/DMF solutions. Their absorption bands and respective extinction coefficients are reported in Table 2.

Because of larger charge to Fe (III) relative to Mn (II) ligand \rightarrow Metal charge transfer bands often obscure the very low intensity d-d bands. In general where the d-d bands are observed, they have intensities that are larger than those for the relative Mn (II) due to increased M \rightarrow L bond covalency.

Octahedral high spin Fe (III) complexes possess a $^6\text{A}_1$ ground state and generally exhibit a series of four ligand field transitions in the visible and near infrared spectral region. These are assigned as $^6\text{A}_1 \rightarrow ^4\text{E}$, $^6\text{A}_1 \rightarrow ^4\text{A}_1$, $^6\text{A}_1 \rightarrow ^4\text{T}_2$, $^6\text{A}_1 \rightarrow ^4\text{T}_1$ in order of decreasing energies (24). Because of a orbital singlet in the high spin Fe (III), there are no excited states of the same spin multiplicity and all d-d transitions are therefore, spin-forbidden as well as laporte forbidden the singlet quartet transitions depicted above are both spin and parity forbidden with intensity seldom exceeding $1\text{LM}^{-1}\text{cm}^{-1}$. However, these ligand field bands may ligand fields around the Iron atom. In general, the transitions to the $^4\text{T}_1$ and $^4\text{T}_2$ states occur between 600-1200 nm spectral regions and reflect the strength of the ligand field at the iron. Thus, giving information on the effects of ligand bonding to the iron center. The $^4\text{A}_1$, ^4E transitions are ligand field independent consisting only of a spin flip in the e_g orbitals giving to an absorbance band near 400-500 nm (25, 26). Due to the moderately oxidizing property of Fe (III), many iron complexes also exhibit $\text{L} \rightarrow ^2t_{eg}$ LMCT band (27).

It has been noted earlier that a dominant feature around 300 nm in the electronic spectra of some of the Fe(III) complexes containing chloride iron as a terminal ligand can be assigned to a predominantly $Cl^- \rightarrow Fe(III)$. Charge transfer transitions involving primarily the nitrogen donor atom of the benzimidazole nucleus (28).

The present series of Fe (III) complexes show UV spectra, characteristic of the benzimidazolyl group. The U.V. bands are in general blue shifted upon coordination suggesting the binding of Fe (III) to the ligand donor atom. We observe bands in the region of 350-360 nm and 480-490 nm. The 350-360 nm bands may arise due to contribution from low energy $L \rightarrow M$ charge transfer transition in our present complexes. The feature at 480-490 nm is assigned to the ${}^6A_1 \rightarrow {}^4A_1, {}^4E$, d-d transition. The extinction coefficient observed is in keeping with other distorted 5/6 coordinatic high spin Fe (III) complexes in Table No. 2.

Table 2: Observed optical bands (nm) for Fe (III) Complexes and their Extinction coefficients:

Complex	Solvent	λ_{max}	Log ϵ
[Fe (TBM) Cl ₃].3H ₂ O	MeOH	241,265, 272, 480	4.36,5.00,4.99,2.14
[Fe(TBM) (NO ₃) ₃].3H ₂ O	DMF	266, 279, 490	4.90,4.75,2.56
[Fe(TBM)(HCOO) ₃].3H ₂ O	DMSO	241,272, 279, 363	4.36,4.99,4.75,2.99
[Fe (TBM) (OAc) ₃].3H ₂ O	DMSO	248,265, 347, 488	4.37,5.00,2.44,1.96

ii) CYCLIC VOLTAMMETRY:

Fig. 1-A to 1-D depict the cyclic voltammograms to [Fe (III) (TBM) Cl₃], [Fe (III) (Me-TBM) Cl₃] and [Fe (III) (BPBM) Cl₃] complexes in DMSO respectively. The redox potential data are with respect to standard calomel electrode, while the supporting electrolyte used was 0.1, molar Lithium Perchlorate.

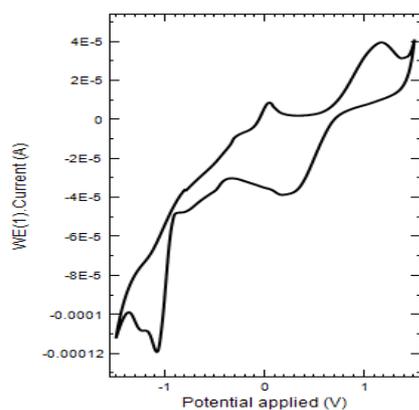


Fig: 1-A: Cyclic voltammogram of [Fe (TBM) Cl₃] 3H₂O in DMSO Scan rate 100 mV/ Sec.

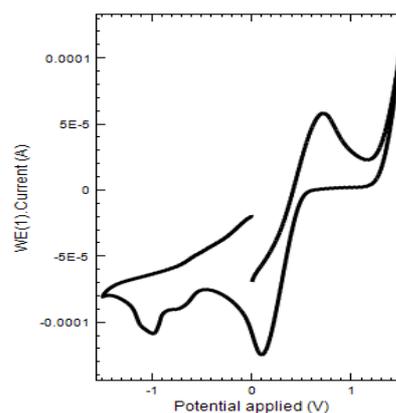


Fig: 1-B: Cyclic voltammogram of [Fe (TBM) (NO₃)₃] 3H₂O in DMSO Scan rate 100 mV/ Sec.

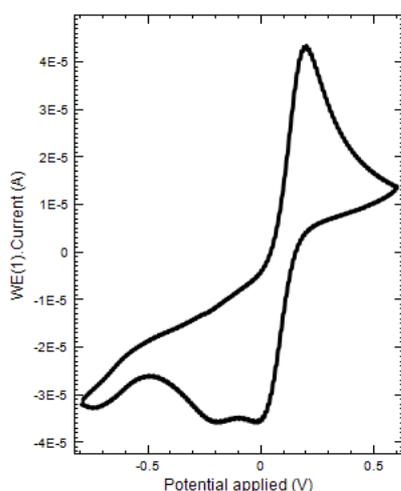


Fig: 1-C: Cyclic voltammogram of [Fe (TBM) (HCOO)₃] 3H₂O in DMSO Scan rate 100 mV/ Sec.

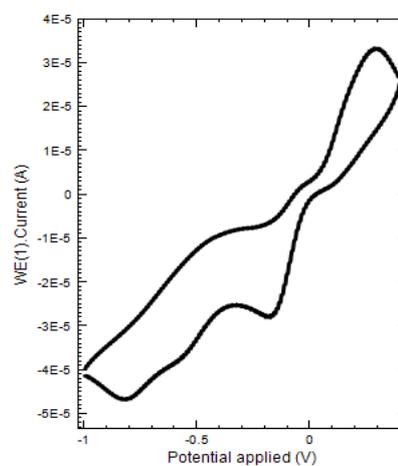


Fig: 1-D: Cyclic voltammogram of [Fe (TBM) (OAc)₃]. 3H₂O in DMSO Scan rate 100 mV/ Sec.

It is found that all the complexes show a reversible wave between +0.125 to +0.135 volts vs. SCE. This is assigned to the reduction of Fe (III) to Fe (II) in the respective complexes. An irreversible oxidation wave is also observed for all of them in the region of +1.2 volts vs. SCE. This is assigned to the Fe (III)/Fe (II) oxidation. The irreversibility and the high current for this couple indicates that the Fe (IV) state generated is extremely unstable and highly oxidizing possibly reacting with solvent also. Solvent with the electrolyte was run as a blank, and did not show any wave in the region investigated for the present series of Iron (III) complexes in Table No. 3.

Table 3: Cyclic Voltammetric Data:

Complex	Scan rate (mV/Sec.)	Supporting electrolyte	Solvent	Oxidation potential	Reduction potential
[Fe(TBM)Cl ₃].3H ₂ O	100	Ag/AgNO ₃	DMSO	4.63	-2.55
[Fe(TBM)(NO ₃) ₃].3H ₂ O	100	Ag/AgNO ₃	DMSO	9.43	-3.27
[Fe(TBM)(HCOO) ₃].3H ₂ O	100	Ag/AgNO ₃	DMSO	3.37	-2.13
[Fe(TBM)(OAc) ₃].CH ₃ OH	100	Ag/AgNO ₃	DMSO	2.18	-1.12

iii) MAGNETIC SUSCEPTIBILITY STUDIES:

The magnetic moment data obtained for Fe (III) complexes using a CAHN-2000 Magnetic balance are reported in Table 4.4. The data incorporates the diamagnetic correction for the ligand in each complex and has been obtained using Pascal's constant. It is found that these magnetic moments are close to the spin only value of 5.9 B.M./Fe³⁺ atoms. This is exhibited since Fe³⁺ has a ⁶A_{1g} ground term with negligible temperature independent paramagnetism. It also does not show any reduction in magnetic moment below the spin only value due to spin-orbit coupling with higher ligand field terms. These data supports the monomeric nature of the complexes as indicated by analytical studies in Table No. 4.

Table 4: Magnetic Susceptibilities Data:

Complex	μ_{eff} (B.M)
[Fe (TBM) Cl ₃] 3H ₂ O	5.81
[Fe (TBM) (NO ₃) ₃].3H ₂ O	5.75
[Fe (TBM) (HCOO) ₃].3H ₂ O	5.82
[Fe (TBM) (OAc) ₃]. CH ₃ OH	5.91

Table 5: I.R. Spectral Data:

Complex	Assignments
[Fe (TBM) Cl ₃] 3H ₂ O	
1620 (w)	$\nu_{(\text{C}=\text{N})}$
1450 (s)	$\nu_{(\text{C}=\text{N}-\text{C}-\text{C})}$
1370 (m)	L
740 (s)	L
[Fe (TBM) (NO ₃) ₃]. 3H ₂ O	
1620(m)	$\nu_{(\text{C}=\text{N})}$
1450 (sh)	$\nu_{(\text{C}=\text{N}-\text{C}-\text{C})}$
1430 (sh, w)	$\nu_{\text{a}}(\text{NO}_2)$
1300 (s)	$\nu_{\text{s}}(\text{NO}_2)$
1000 (m)	$\nu_{\text{s}}(\text{NO})$
740 (s)	L
[Fe(TBM)(HCOO) ₃]. 3H ₂ O	
1630 (w)	$\nu_{(\text{C}=\text{N})}$ and $\nu_{(\text{C}=\text{O})}$, Stretching of Unidentate formate
1468 (m)	L
1350	$\nu_{\text{s}}\text{NO}_2$
1315	$\nu_{\text{s}}\text{NO}$
730	L
[Fe(TBM) (OAc) ₃]. 3H ₂ O	
1628(w)	$\nu_{(\text{C}=\text{N})}$ stretching
1462(m)	$\nu_{(\text{C}=\text{N}-\text{C}-\text{C})}$ stretching $\nu_{\text{a}}\text{NO}_2$
1364(m)	(L)
1310(m)	$\nu_{\text{s}}\text{NO}_2$
1040(w)	$\nu_{\text{s}}\text{NO}$
730(s)	(L)

iv) IR SPECTROSCOPY:

IR spectra of Fe (III) complexes have been obtained in Nujol mull. The band appearing around 1440-1455 cm⁻¹ is assigned to the ν_4 (-C=N-C=C-) stretching. In our Fe (III) complexes the shift is around 10 cm⁻¹ (Table 5). This implies the direct coordination of the ligand to iron (III) (29). It has been reported by Gate House *et. al.* (30) that when nitrate group is bound as a terminal ligand, in the unidentate mode, IR bands appear at 1420 cm⁻¹, 1305cm⁻¹ and 1008 cm⁻¹ respectively. The separation of the two highest frequency bands is less (approx.100 cm⁻¹) for a

unidentate NO_3^- . While it is larger ($1800\text{-}200\text{ cm}^{-1}$) for a chelating bidentate NO_3^- . In our nitrate complexes bands are found in the same region. This suggests that we have a monodentate NO_3^- bound to the iron in the ferric complexes.

The I.R. spectral data of complexes are shown in table 5.

v) **Biological Activities:-**

All the complexes were screened in-vitro for their antimicrobial activity against bacteria and fungi. The antibacterial activities were tested by disc diffusion method at $30\text{ }\mu\text{g/ml}$. concentration and Muller Hinton Agar media (Hi media) used as a reference compound, E.Coli and S.aureus used as the bacterial test organism. The ligand, TBM and the chloro and nitro complexes with Iron (III) were also screened for antibacterial activities against E.coli and S.aureus. As compared to the ligand, the chloro complex has been found to show moderate activity towards only E.coli while the nitro complex has been found to show moderate activity towards both E.coli and S.aureus [Figure 2a and 2b].As compared to chloro complex, nitrate complex is found to show greater antimicrobial activity against E.coli as shown in Table 6.

Table 6: Antibacterial activity of compounds:

S.N.	Compounds	Diameter of zone of inhibition in mm for E.coli		Diameter of zone of inhibition in mm for S.aureus	
		50 ppm	100 ppm	50 ppm	100 ppm
1	TBM	-	01	-	02
2	[Fe (TBM) Cl_3]. $3\text{H}_2\text{O}$	-	02	-	-
3	[Fe (TBM)(NO_3) $_3$]. $3\text{H}_2\text{O}$	-	02	-	02

Fig 2 A: Antibacterial Study of TBM, [Fe (TBM) Cl_3]. $3\text{H}_2\text{O}$ and [Fe (TBM) (NO_3) $_3$]. $3\text{H}_2\text{O}$ against E.coli



Fig 2 B: Antibacterial Study of TBM, [Fe (TBM) Cl_3]. $3\text{H}_2\text{O}$ and [Fe (TBM) (NO_3) $_3$]. $3\text{H}_2\text{O}$ against S.aureus



On the basis of above studies, the proposed structure of Fe (III) Complexes are depicted in figure 3 below:-

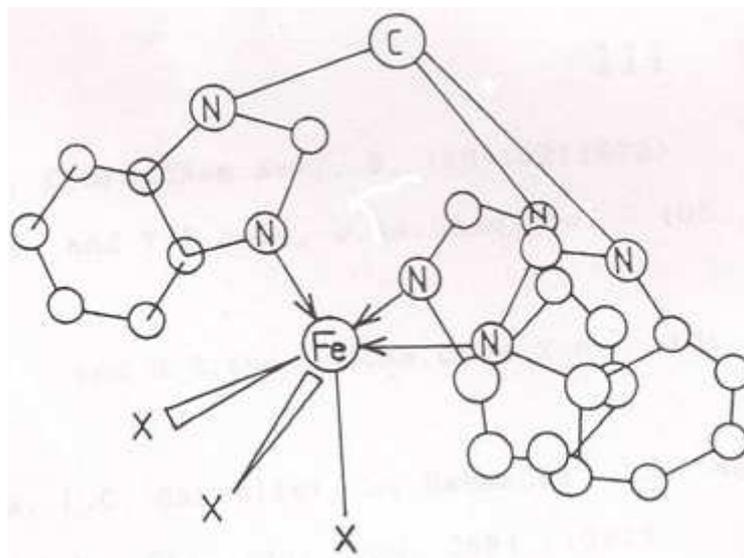


Fig. 3: Proposed Structure of Fe (III) Complexes with TBM Ligand, where X= Cl , NO_3 , HCOO & CH_3COO .

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