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Fe (III) complexes of a bis-benzimidazolyl diamide ligand: Spectral and Catalytic studies

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ABSTRACT

A new tetradentate bis benzimidaozlyl diamide ligand N,N′-Bis (benzimidazol-2-yl-methyl)-hexane-1,6-dicarboxamide (GBSA) has been synthesized and utilized to prepare new Fe(III) complexes with exogenous anionic ligand $X = Cl^-$ and NO_3^-. Isomer shift values are in the range found for Iron in the +3 oxidation state while Quadrupole Splitting indicates large distortion from a six coordinate geometry, a finding supported by low temperature EPR work. The $E_{1/2}$ values are found to be quite cathodic indicating stability of the Iron (III) complexes. The oxidation of alcohols was investigated using $[Fe(GBSA)Cl_3]$ as the catalyst with TBHP as an alternate source of oxygen. The respective carbonyl products have been isolated and characterized by ^{1}H NMR, electronic spectroscopy, mass and IR spectral studies.

1. Introduction

The formation of ketones or aldehydes from the catalytic oxidation of primary and secondary alcohols is an important reaction in organic synthesis [1,2]. Transition metal ion catalyzed oxidation of alcohols is of current interest, and various transition metal compounds and oxidant systems have been reported [3]. Copper (I), copper (II) salts [4,6] and Co (III) complexes [5] have been utilized to catalyze the oxidation of alcohols with molecular oxygen and H_2O_2. Oxidation of alcohols using H_2O_2 and catalytic amounts of Fe (III) complexes has also been described [7–9]. In the present work we report the oxidation of cinnamyl alcohol, 1-phenyl ethanol, cyclohexanol, and 1,2,3,4-tetrahydro-1-naphthol to their respective carbonyl products utilizing tertiary butyl hydroperoxide (TBHP) as an alternative source of oxygen. The oxidation of alcohols was investigated using $[Fe(GBSA)Cl_3]$ as the catalyst. The respective carbonyl products have been isolated and characterized by ^{1}HNMR, electronic spectroscopy, mass and IR spectral studies.

2. Experimental

2.1. Materials and physical measurements

Glycine benzimidazole dihydrochloride was prepared following the procedure reported by Cescon and Day [10]. Spectroscopic grade solvents were used for the spectral and electrochemical studies and the rest were freshly distilled off before use. All other chemicals were obtained from commercial sources and were used as such. Anhydrous Iron (III) chloride and Iron (III) nitrate were purchased from Sigma–Aldrich. Carbon, Hydrogen and Nitrogen were estimated by using Elemental Analyzer at USIC, University of Delhi, Delhi. IR spectra were recorded in solid state as KBr pellets on a Perkin-Elmer FTIR-2000 spectrometer (IR stretching frequencies measured to an accuracy of $\pm 1\ cm^{-1}$). The electronic spectra were recorded in HPLC grade DMF on a Shimadzu 1601 spectrophotometer in the region of 200–1100 nm (Errors in UV–vis wavelength maxima are ±1 and ±4 nm). The ^{1}H NMR and ^{13}CNMR spectra of ligand were recorded in d^6-DMSO on a 400 MHz JEOL instrument at the Department of Chemistry, University of Delhi, Delhi. ESI mass spectra were recorded on a Waters Micromass -LCT mass spectrometer in chloroform. Cyclic voltammogram of the complexes was studied on BAS CV 50 W electrochemical analyzing system in dimethyl sulfoxide:Acetonitrile (8:3) solution at Department of chemistry, University of Delhi, Delhi. ^{57}Fe Mossbauer spectra were obtained using a ^{57}Co in Rh source, mounted on a constant acceleration spectrometer, Wissel MB-550, GNDU, Amritsar. The X-band EPR spectra were recorded on a Bruker-spectrospin with a variable

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temperature liquid nitrogen cryostat at 120 K at IIT Kanpur, India (error in g-values is ±0.01). Magnetic susceptibilities of the complexes were recorded on vibrating Sample Magnetometer at 298 K in solid state at the Department of Chemistry, University of Delhi, Delhi (error bar: ±0.1 BM).

2.2. *Synthesis*

2.2.1. *Preparation of the ligand N,N′-Bis (benzimidazol-2-yl-methyl)-hexane-1,6-dicarboxamide (GBSA)*

The condensation was similar to that reported earlier by Bakshi and Mathur [11] and Vagg and co-workers [12]. Suberic acid (1.97 g, 0.1136 mmol) and 2-(amino methyl) benzimidazole dihydrochloride (5 g, 0.0227 mmol) were taken in pyridine (20 ml). The mixture was stirred gently for 10 min, during which a white precipitate appeared. The reaction mixture was then heated slowly on a water bath at a temperature of 40 °C. A solution of triphenyl phosphite (TPP) (7.07 ml, 22.8 mmol) was added drop wise over a period of 15 min. The mixture was stirred simultaneously. After addition of $P(OPh_3)_3$ was complete and the initially formed precipitate had dissolved, the temperature of the reaction was slowly raised to 70 °C. The clear solution thus obtained was stirred for about 9–10 h at a temperature of 70–75 °C on a water-bath. The resulting brown colored solution was then washed with sodium bicarbonate till all effervescence ceased and then washed twice with distilled water. A yellowish white solid appeared which was washed first with water and then acetone (Scheme 1). This was then recrystallized with methanol and precipitated by water. The product was filtered off, and dried and analyzed for the composition $C_{24}H_{28}N_6O_2{\cdot}0.5H_2O$, Yield: 3 g (50.1%), m.p. 233 °C.

The spectroscopic analysis of the ligand is as shown below:

Analytical data: Found (cal): C: 65.0 (65.3), H: 7.3(6.5), N: 17.8(19.0).
UV–vis [λ_{max} (nm), log ε in DMF] = 277[4.54], 271 [4.59].

2.2.2. *Preparation of the complexes*

2.2.2.1. [Fe(GBSA)Cl$_3$] (1). $FeCl_3$ (1 mmol) was dissolved in methanol (5 ml) and added to a methanolic solution of the ligand GBSA (1 mmol) (15 ml). The resulting brown colored solution was stirred for 4–5 h, after which the volume was reduced to about 60% on a water bath. The concentrated solution was kept for cooling in a refrigerator for 1–2 h. The product obtained was washed with small amount of acetonitrile (4–5 ml) and air dried. The product analyzed for the composition $[Fe(C_{24}H_{28}N_6O_2)Cl_3]{\cdot}2.5H_2O$

Yield: 80 mg (53%).
Analytical data: Found (cal): C: 44.7(45.0), H: 5.9(5.1), N: 12.6(13.1), Fe: Found (calc): 9.1 (9.2).
UV–vis [λ_{max} (nm), log ε in DMF] = 271[4.3], 277 [4.3], 349 [3.4].

2.2.2.2. [Fe(GBSA)(NO$_3$)$_3$] (2). $Fe(NO_3)_3{\cdot}9H_2O$ (1 mmol) (5 ml) was dissolved in methanol (5 ml) and added to a methanolic solution of the ligand GBSA (1 mmol) (15 ml). The resulting brown colored solution was stirred for 4–5 h, after which the volume was reduced to about 60% on a water bath. The concentrated solution was kept for cooling in a refrigerator for 1–2 h. The product obtained was washed with small amount of cold methanol (4–5 ml) and dried over P_2O_5. The product analyzed for the composition $[Fe(C_{24}H_{28}N_6O_2)(NO_3)_3]{\cdot}2.5H_2O$.

Yield: 90 mg (75%).
Analytical data: Found (cal): C:39.6(40.0), H:5.0(4.5), N:16.6(17.5), Fe: Found (calc): 7.0 (6.6).
UV–vis [λ_{max} (nm), log ε in DMF] = 271[4.1], 277 [4.1], 349 [3.0].

Table 1
IR spectral data of ligand for Fe (III) complexes of the ligand GBSA.

Assignments	GBSA	[Fe(GBSA)Cl$_3$]	[Fe(GBSA)(NO$_3$)$_3$]
ν_{OH} stretching	3440	3420	3405
ν_{NH} amide	3317	3326	3341
ν_{NH} benzimida.	3058	3037	3037
ν_{CH} stretching	2923	2918	2926
$\nu_{C=O}$ amide I	1645	1684	1669
ν_{C-N} amide II	1546	1524	1524
$\nu_{-C=C-N=C-}$	1457	1460	1463
ν_{anions}	–	–	1384(s), 820(a)
$\nu_{benzene\ ring}$	735	744	747

3. Results and discussion

3.1. *Electronic spectroscopy*

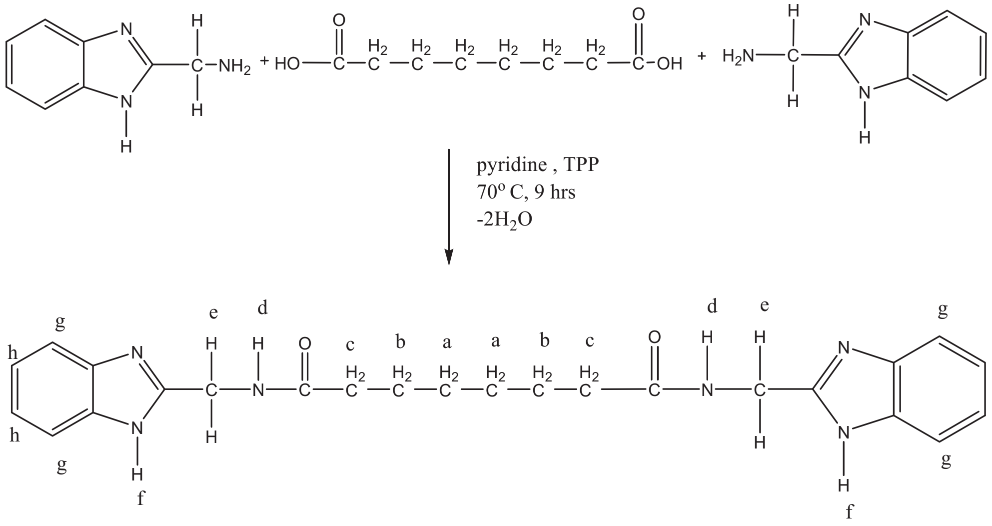
The UV Spectral data for the ligand and the complexes were taken in DMF and methanol depending on their solubility. The ligand and complexes show bands in the region 271–277 nm. These bands are characteristics of the benzimidazole group and arise from π to π^* transitions. They show enhanced absorption as indicated by their extinction coefficients. The UV bands are in general shifted upon coordination suggesting binding of Iron (III) to the ligand donor atom [13]. Both the complexes exhibit a broad shoulder at 349 nm. The band at 349 nm in the above complexes are predominantly assigned to charge transfer transition from pπ orbital of chloride or oxygen of nitrate to half filled dπ^* orbital of the Fe^{III} metal centre, i.e. $Cl^- \rightarrow Fe^{III}/NO_3{}^- \rightarrow Fe^{III}$. [14]. Such a charge transfer has been observed for other benzimidazole Fe (III) complexes.

3.2. *IR spectra*

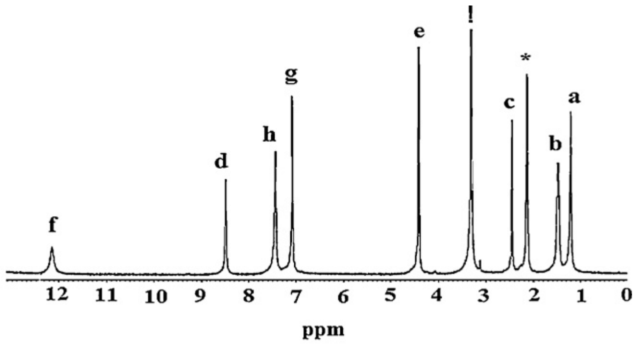
IR stretching bands for ligand and the complexes showing coordination of anions are listed in Table 1. The ligand L and its Iron (III) complexes have characteristic IR bands in the range 1645–1669 cm^{-1}, 1524–1546 cm^{-1}, 1457–1463 cm^{-1} which are assigned to amide I ($\nu_{C=O}$ stretching), amide II (ν_{C-N} stretching) and benzimidazole ring ($\nu_{C=C-N=C}$ stretching) respectively. The benzene ring gives a peak in the range 735–747 cm^{-1}. In the complexes, shift in amide I band, due to C=O group and increase/decrease in amide II band due to C—N group [15] is indicative of the coordination of the ligand through carbonyl oxygen in the complexes [16–18]. IR bands due to benzimidazole NH and amide NH are shifted indicating the involvement of these groups in hydrogen bonding either with the solvent molecules or with the exogenous anionic ligand in the complexes. A broad band in the region 3405–3440 cm^{-1} in the complexes indicates presence of water molecule or O—H stretching due to H-bonding with the solvent. Characteristic stretching frequencies for the coordinated anion are also observed: bands at 1384 cm^{-1} and 820 cm^{-1} are observed for the symmetric and anti symmetric stretching vibration of the nitrate group in the nitrate complexes respectively.

3.3. *^{1}H-NMR and ^{13}CNMR*

The ^{1}H NMR of the ligand GBSA in d^6-DMSO shows signals for both aliphatic and aromatic protons (Fig. 1) [19]. A singlet arises at 12.5 ppm due to benzimidazole NH(f), The amide NH(d) proton gives rise to a triplet at 8.86–8.84 ppm (coupled with adjacent CH_2 proton (e). A symmetrical multiplet in the range of 7.46–7.43 ppm arises due to benzimidazole ring protons (g and h). The CH_2 protons (e) give rise to a doublet at 4.79–4.77 ppm due to the coupling with adjacent amide NH proton. The CH_2 proton (c) gives a broad peak at 2.81 ppm. The CH_2 proton (b) gives a multiplet at 1.84 ppm while



Scheme 1. N,N′-Bis (benzimidazol-2-yl-methyl)-hexane-1,6-dicarboxamide (GBSA).



*-DMSO

!- Moisture

Fig. 1. ^{1}H NMR of the ligand GBSA.

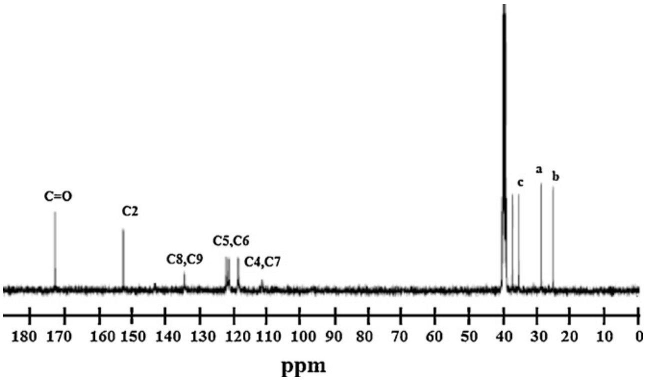


Fig. 2. ^{13}C NMR of the ligand GBSA.

the central CH_2 protons (a) of the central chain arise as a multiplet at 1.54 ppm (coupled with adjacent CH_2 protons) (b).

^{13}C spectra: Peak values, δ ppm: C atoms of the benzimidazole ring (C7, C4): 118; C atoms of the benzimidazole ring (C5, C6): 121; C atoms of the benzimidazole ring (C8, C9): 134; C atom of the benzimidazole ring (C2): 152; (C1) atom of the methylene group of benzimidazole ring: 37; C atom of the C=O group: 172; C atom of the methylene group attached to C=O: 35; C atom of the methylene group of the central chain: 25; C atom of the innermost methylene group of the central chain: 28 (Fig. 2) [20].

3.4. Cyclic voltammetry

The cyclic voltammetric data of complexes are listed in (Table 2, Figs. 3 and 4). The cyclic voltammograms were recorded in 8:3 (DMSO:Acetonitrile), containing 0.10 M TBAP as supporting electrolyte at a platinum working electrode. A three-electrode configuration composed of Pt-disk working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode was used for measurements. The reversible one electron Fc^+/Fc couple has an $E_{1/2}$ of +75 mV versus $Ag/AgNO_3$. The complexes display a reversible redox wave assigned to Fe (III)/Fe (II) redox couple. $E_{1/2}$ values for $[Fe(GBSA)Cl_3]$ and $[Fe(GBSA)(NO_3)_3]$) are found to be −324 mV and

Table 2
Electrochemical data of Fe(III) complexes of GBSA.

Complex	E_c (mV)	E_a (mV)	$E_{1/2}$ (mV)
$[Fe(GBSA)Cl_3]$	−380.0	−268.0	−324.0
$[Fe(GBSA)(NO_3)_3]$	−292.0	−178.0	−235.0

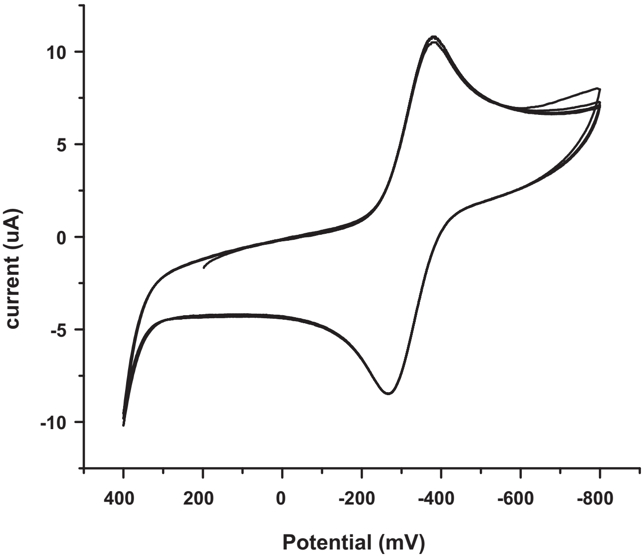


Fig. 3. Cyclic voltammogram of $[Fe(GBSA)Cl_3]$ in DMSO:acetonitrile (8:3) at a scan rate of 200 mV/s.

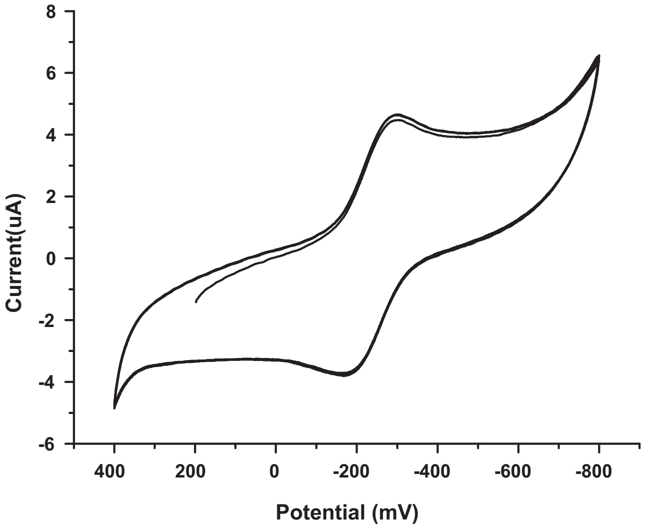


Fig. 4. Cyclic voltammogram of [Fe(GBSA)$(NO_3)_3$] in DMSO:acetonitrile (8:3) at a scan rate of 200 mV/s.

Table 3
Magnetic moment values for the Iron (III) complexes of GBSA.

Complexes	Magnetic moment (BM)[a]
[Fe(GBSA)Cl_3]	5.7
[Fe(GBSA)$(NO_3)_3$]	5.4

[a] Error bar = ±0.1 BM.

−235 mV respectively against reference Ag/$AgNO_3$ electrode. Chloride complex shows cathodic potential in comparison to the nitrate complex. Therefore the binding of chloride anion stabilizes the Fe (III) centre whereas nitrate anion destabilizes the Fe (III) centre. The variation in $E_{1/2}$ observed supports that the anionic ligands remain bound to Fe (III) centre in solution, an assumption which has been confirmed from other spectral studies. The chloride complex has a cathodic redox potential, this suggest that the Cl^- anion is more effective in reducing the Lewis acidity of the Iron (III) centre as compared to the $NO_3{}^-$ anion.

3.5. Magnetic susceptibility

Magnetic susceptibility of both the Fe (III) complexes was determined by using Vibrating Sample Magnetometer at room temperature (298 K) in solid state and is reported in (Table 3). The data incorporates diamagnetic correction for the ligand in each complex and has been estimated using Pascal constants. It is found that the values obtained are in the range of 5.4–5.7 BM. These are slightly lower than the spin only value of 5.9 BM/Fe^{3+} ion and may be attributed to a weak-intermolecular magnetic interaction in the solid state cannot be ruled out.

3.6. EPR spectroscopy

(Table 4, Figs. 5 and 6) shows X-EPR spectra of Iron (III) complexes at liquid nitrogen temperature in DMSO. The present series of Fe (III) complexes bound with chloride ion show signals at $g = 4.4$, with transitions at low field ($g \sim 5.3$ and $g \sim 7.2$) while in the case of nitrate bound complex, an additional signal at $g = 3.0$ was also observed. Dowsing and Gibson [21] have shown that the absorptions at 1500 G and 700 G are expected if λ is almost equal to 1/3 and D is greater than 0.23 cm^{-1}. The line at 1500 G is known to broaden or split as λ departs from 1/3. Thus, the departure of the absorption away from $g_{eff} = 4.3$ is a signal for distortion from purely rhombic to axial geometry. Since, the present series of Iron (III) complexes show multiple signals. This is interpreted in terms of six coordinate Fe (III) complexes undergoing departure from a purely rhombic symmetry towards axial symmetry [22,23].

Table 4
X-Band EPR data for Iron (III) complexes of GBSA.

Complexes	Observed EPR[a] g-values
[Fe(GBSA)Cl_3]	4.4, 5.3, 7.2
[Fe(GBSA)$(NO_3)_3$]	3.0, 4.4, 7.2

[a] Effective g-values.

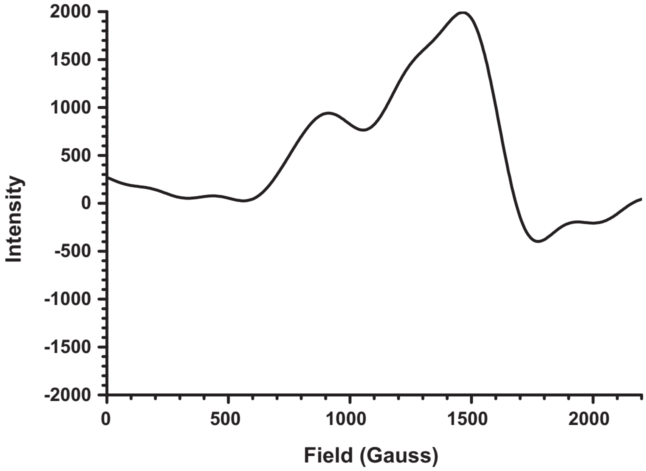


Fig. 5. X-band EPR spectrum of [Fe(GBSA)Cl_3] in DMSO at liquid nitrogen temperature.

3.7. Mössbauer spectroscopy

Mössbauer spectra of Fe (III) complexes were obtained using a ^{57}Co in Rh source, mounted on a constant acceleration spectrometer (Table 5, Figs. 7 and 8). The velocity scale was calibrated using a foil of natural α-Fe at room temperature and all isomer shifts are referred to centre of α-Fe spectrum. Experimental spectra were fitted with Lorentzian lines which are allowed to vary independently and were matched into a doublet, using a least square computer program. Isomer shift values (δ) lie in the range of 0.24–0.44 mm/s with respect to natural iron as is typically observed for other high

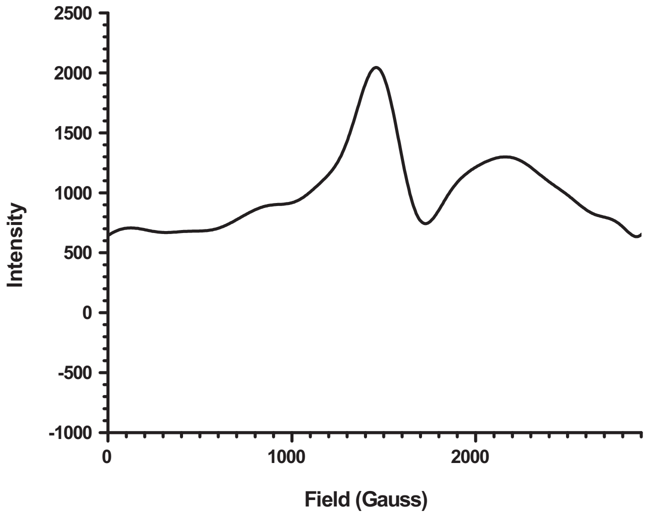


Fig. 6. X-band EPR spectrum of [Fe(GBSA)$(NO_3)_3$] in DMSO at liquid nitrogen temperature.

Table 5
Mössbauer data for Iron (III) complexes of the ligand GBSA.

Complexes	Isomer shift Δ (mm/s)	Quadrupole splitting (ΔE_q)
$[Fe(GBSA)Cl_3]$	0.26	0.35
$[Fe(GBSA)(NO_3)_3]$	0.44	0.82

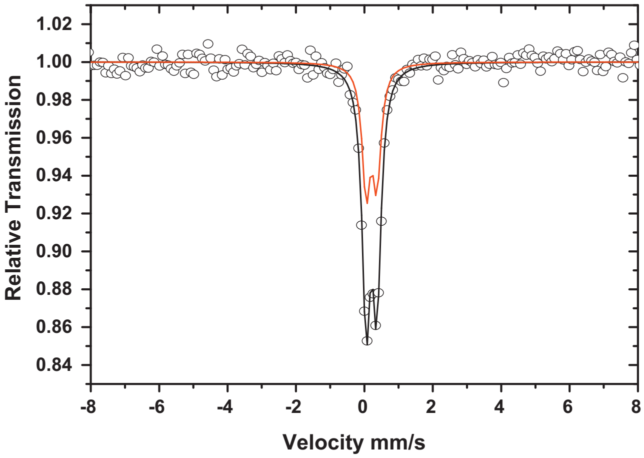


Fig. 7. Mössbauer spectra of $[Fe(GBSA)Cl_3]$.

spin Iron (III) complexes [24]. The isomer shift in the present iron complexes is indicative of iron in (+III) oxidation state. Quadrupole splitting decreases with increase in symmetry of the central ion atom, i.e. larger is the quadrupole splitting; larger is the distortion in geometry of the central Iron atom. In the present case of $[Fe(GBSA)(NO_3)_3]$ has a much larger quadrupole splitting in comparison to $[Fe(GBSA)Cl_3]$ implying a larger distortion for the former complex [25–27].

4. Reactivity of $[Fe(GBSA)Cl_3]$

4.1. Oxidation of alcohols

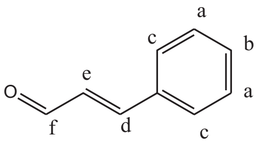
4.1.1. Oxidation of cinnamyl alcohol

The complex $[Fe(GBSA)Cl_3]$ (0.0317 mmol) was taken in 10 ml of methanol. To this cinnamyl alcohol (0.476 mmol) was added along with the oxidant TBHP (0.952 mmol). The ratio of catalyst:substrate:oxidant used was 1:15:30. The reaction mixture was stirred at 50–60 °C on a water bath for approximately 15 h. Periodically, sample was withdrawn and TLC was developed in ethyl acetate (15%):hexane. A spot was visualized with a spray of 2,4-dinitrophenylhydrazine (DNP) suggesting the formation of the corresponding aldehyde during the course of the above oxidation reaction. After about 15 h it was worked up on a column, using hexane and ethyl acetate (5%). The R_f of the product obtained was 0.32. The product obtained was characterized by, ^{1}H NMR, mass spectroscopy and IR spectral studies. The oxidation reaction was also monitored using UV–visible spectroscopy. As the reaction proceeds, it was found that there were no major changes in the charge transfer band of the parent Iron (III) complex. This suggests that the oxidation state of Iron (III) does not change during the course of the reaction. This further supports the mechanism proceeding via a Hydrogen abstraction mechanism [9a].

^{1}H NMR ($CDCl_3$) (ppm) [Fig. 9(§)]: Signal for benzene ring protons (a, b, c and d) arise in the range of 7.39–7.54. Proton labeled as (e) arises in the range of 6.66–6.72 and (f) proton gives a signal in the range of 9.66–9.68.

IR (cm^{-1}, Neat): 1678 ($\nu_{C=O}$) and 749 ($\nu_{C=C\,benzene}$).
(m/z): 133 (for the pure product). Yield (DNP derivative): 40%.

Thus oxidation of cinnamyl alcohol gave cinnamaldehyde



Cinnamaldehyde

4.1.2. Oxidation of 1-phenyl ethanol

The complex $[Fe(GBSA)Cl_3]$ (0.0317 mmol) was taken in 10 ml of methanol. To this 1-phenyl ethanol (0.476 mmol) was added along with the oxidant TBHP (0.952 mmol). The ratio of catalyst:substrate:oxidant used was 1:15:30. The reaction mixture was stirred at 50–60 °C on a water bath for approximately 12 h. Periodically, sample was withdrawn and TLC was developed in ethyl acetate:hexane (15%). A spot was visualized with a spray of DNP suggesting the formation of the corresponding carbonyl moiety during the course of the above oxidation reaction. After about 12 h it was worked up on a column, using hexane and ethyl acetate (1.5%). The R_f of the product obtained was 0.42. The product obtained was characterized by, ^{1}H NMR, mass spectroscopy and IR spectral studies.

^{1}H NMR ($CDCl_3$) (ppm) [Fig. 10(§)]: The benzene ring protons (a, b, c) gave signals in the range of 7.87–7.89 (t, J = 15 Hz, 2H), 7.36–7.41 (t, J = 15 Hz, 2H) and 7.46–7.51 (t, J = 15 Hz, 1H) while the CH_3 protons (d) appear at 2.52 ppm (s, 3H).

IR (cm^{-1}, Neat): 1686 ($\nu_{C=O}$) and 760 ($\nu_{C=C\,benzene}$).
(m/z): 121 (for the pure product). Yield (DNP derivative): 37%.

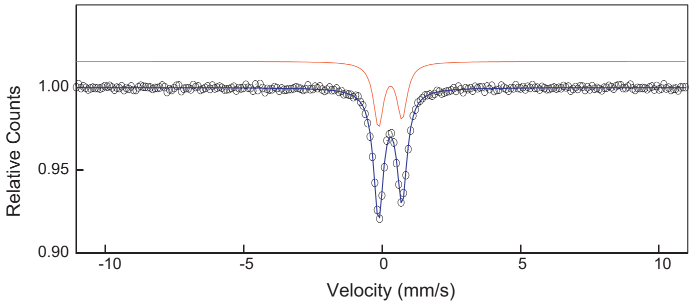
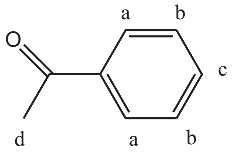


Fig. 8. Mössbauer spectra of $[Fe(GBSA)(NO_3)_3]$.

Thus oxidation of 1-phenyl ethanol gave acetophenone



Acetophenone

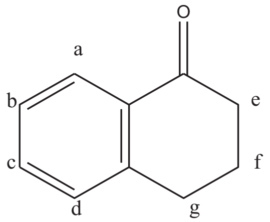
4.1.3. Oxidation of 1,2,3,4-tetrahydro-1-naphthol

The complex [Fe(GBSA)Cl_3] (0.0317 mmol) was taken in 10 ml of methanol. To this 1,2,3,4-tetrahydro-1-naphthol (0.476 mmol) was added along with the oxidant TBHP (0.952 mmol). The ratio of catalyst:substrate:oxidant used was 1:15:30. The reaction mixture was stirred at 50–60 °C on a water bath for approximately 12 h. Periodically, sample was withdrawn and TLC was developed in ethyl acetate (12%):hexane. A spot was visualized with a spray of DNP suggesting the formation of the corresponding carbonyl moiety during the course of the above oxidation reaction. After about 12 h it was worked up on a column, using hexane and ethyl acetate (2%). The R_f of the product obtained was 0.57. The product obtained was characterized by, ^{1}H NMR, mass spectroscopy and IR spectral studies.

^{1}H NMR ($CDCl_3$) (δ ppm) [Fig. 11(§)]: (a) 7.95–7.93(d, 1H, J = 8 Hz), (b, d) 7.23–7.15 (m, 2H, J = 6 Hz), (c) 7.39–7.36 (t, 1H, J = 12 Hz), (e) 2.58–2.55 (t, 2H, J = 6 Hz), (f) 2.08–2.02 (m, 2H, J = 6 Hz), (g) 2.89–2.86 (t, 2H, J = 6 Hz).

IR (cm^{-1}, Neat) 1618 ($\nu_{C=O}$) and 760 ($\nu_{C=C\ benzene}$).
λ_{max} (nm) ($CHCl_3$): 362,260.
(m/z): 147 (of the pure product). Yield (DNP derivative): 45%.

Thus oxidation of 1,2,3,4-Tetrahydro-1-Naphthol gave 3,4-dihydronaphthalen-1(2H)-one.



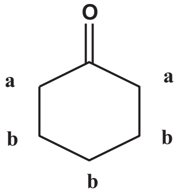
3, 4-dihydronaphthalen-1(2H)-one

4.1.4. Oxidation of cyclohexanol

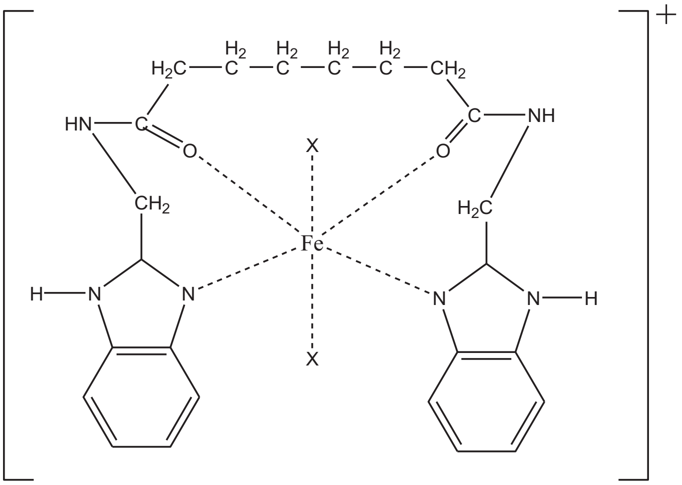
The complex [Fe(GBSA)Cl_3] (0.0317 mmol) was taken in 10 ml of methanol. To this cyclohexanol (0.476 mmol) was added along with the oxidant tertiary butyl hydro peroxide (TBHP) (0.952 mmol). The ratio of catalyst:substrate:oxidant used was 1:15:30. The reaction mixture was stirred at 50–60 °C on a water bath for approximately 12 h. Periodically, sample was withdrawn and TLC was developed in ethyl acetate (12%):hexane. A spot visualized with a spray of DNP suggesting the formation of the corresponding carbonyl moiety during the course of the above oxidation reaction. After about 12 h it was worked up on a column, using hexane and ethyl acetate (1%). The R_f of the product obtained was 0.39. The product obtained was characterized by, ^{1}H NMR, mass spectroscopy and IR spectral studies.

^{1}H NMR ($CDCl_3$) (δ ppm) [Fig. 12 (§)]: (a) 2.13–2.10 (4H, m, J = 11 Hz), (b) 1.66–1.50 (m, 6H, J = 12 Hz).

IR (cm^{-1}, Neat) 1648 ($\nu_{C=O}$). (m/z) = 99 (pure product).
Oxidation of cyclohexanol gave cyclohexanone.



Cyclohexanone



X=Cl$^-$ or NO_3^-

Proposed structure for Iron (III) complexes with the ligand N, N'–Bis (benzimidazol-2-yl-methyl)-hexane-1,6-dicarboxamide

5. Conclusion

A new bizbenzimidazole diamide tetradentate ligand has been synthesized and utilized to prepare Iron (III) complexes. Complexes have been characterized by cyclic voltammetry and Mossbauer analysis. Isomer shift values are in the range found for Iron in the +3 oxidation state while quadrupole splitting indicates large distortion from a six coordinate geometry. The $E_{1/2}$ values are found to be quite cathodic indicating stability of the Iron (III) complexes. The oxidation of alcohols was investigated using [Fe(GBSA)Cl_3] as the catalyst with TBHP as an alternate source of oxygen. The reaction proceeds via hydrogen abstraction mechanism. The catalyst turn over is found to be between six to eight fold.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.08.014.

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