Isolation and spectral characterization of novel complexes [FeL\textsubscript{1}ClH\textsubscript{2}O] and [FeL\textsubscript{2}ClH\textsubscript{2}O](H\textsubscript{2}L\textsubscript{1}=N-(3-hydroxy-propyl)-2-[[3-hydroxy-propylcarbamoyl]-methyl]-amino}-acetamide and H\textsubscript{2}L\textsubscript{2}=N-(2-hydroxy-ethyl)-2-[[2-hydroxy-ethylcarbamoyl]-methyl]-amino}-acetamide):\textsuperscript{57}Fe-Mössbauer, cyclicvoltammetric and SOD mimic studies
INTRODUCTION

The coordination chemistry of dicarboxylic acid ligands and their complexes is a centre stage of research to inorganic and bioinorganic chemists [1-4]. Although some structural informations for this class of complexes are reported [5], but they are still relatively scarce. The main reason for this is the fact that dicarboxylic acid ligands generally tend to react with metal salts to yield insoluble polymeric materials which are often difficult to characterize and almost impossible to crystallize. Furthermore, reactions of polymeric copper(II), manganese(II) and cobalt(II) dicarboxylic acid complexes with bidentate donor ligands like 1,10-phenanthroline and 2,2′-bipyridine may lead to the synthesis of crystalline compounds. Some of these compounds could grow single crystals which were easily structurally characterized by X-ray methods [6-8]. The transition metal coordination polymers constructed by multicarboxylate ligands exhibit potential applications as zeolite-like materials for molecular selection, catalysis, ion exchange, non-linear optics and microelectronics, as well as in the variety of architectures and topologies [9]. Fortunately, multi functional carboxylate ligands have proved good candidates because they can be regarded not only as hydrogen bonding acceptors but also as hydrogen bonding donors, depending upon the number of deprotonated carboxylic groups [10]. The ligands derived from dicarboxylic acids and aminoalcohols [propanolamine (PA) or ethanolamine (EA)] have also attracted attention in last decades. Reaction of picolinic acid (pyridine-2-carboxylic acid) and 3-amino-1-propanol under reflux condition follows a condensation path involving –COOH and NH₂ functions [11]. The chemical properties of aminoalcohols because of their basic nitrogen atom and the hydroxyl group,
resemble those of both amines and alcohols i.e. aminoalcohols (e.g. ethanol and propanol amines). These aminoalcohols are the versatile ligands that readily form coordination compounds with almost all metal ions and behave as N and O- donor ligands [12]. The –NH proton of the amide group (-CONH) as well as the hydroxyl proton of the resulting substrate is polar in basic medium and the ligand behaves as a dianion. The synthesis of transition metal complexes is a continuously developing area of investigation in inorganic and bioinorganic chemistry [13] in view of their uses to study the redox function of many metalloenzymes [14]. Iron is one of the most abundant transition metal on earth. Virtually every form of life, with exception of a couple of specialized bacteria, has requirement for iron an essential element for nearly all the organisms [15]. The uptake storage and transport of iron in biological system has been thoroughly studied [16]. Spectroscopic transitions of iron clusters with calf-thymas DNA have also been used to evaluate the binding to the DNA helix [17, 18].

The basic unit of peptide linkage i.e. (CO-NH) group is a part of primary structure of proteins and is of the crucial importance in the biological system [19]. Ligand moieties containing oxamide function show anti-inflammatory, anti pyretic and analgesic activities [20, 21]. Fe⁺³-peptide complex is a potential compound for use as an iron source in biological situations [22]. Ligands with amide coordination sites like that in oligopeptides, oxamide and oxamates [23, 24-26] etc. usually bind metal ions through nitrogen atoms after disproportion of amide groups and stabilize metal ions in their higher (+3 and above) oxidation states. This versatility of iron complexes and amide ligands derived from condensation of dicarboxylic acid and PA or EA contemplated to carry out studies on such iron complexes. To our knowledge the condensation
reactions of a functionalized dicarboxylic acid, such as iminodiacetic acid and amino propanol or ethanol reagent are not reported in the literature. In this chapter, the investigations on the condensation reaction of iminodiacetic acid with 3-amino-1-propanol and 2-amino-1-ethanol under reflux condition have been described. The spectral characterization has indicated that the carboxylic acid function of the iminodiacetic acid condenses with the –NH₂ group of the 3-amino-1-propanol and 2-amino-1-ethanol. This process produces an oily mass, which is quite reactive towards metal salts even in neutral medium resulting in stable solid products. We report the isolation of ligands H₂L₁ and H₂L₂ and their iron complexes (1) and (2). The detailed spectral investigations specially the ⁵⁷Fe Mössbauer data of mononuclear Fe³⁺ complexes and SOD mimic activities have also been discussed.
EXPERIMENTAL

Materials

Iminodiacetic acid (S.d.fine), 3-amino-1-propanol (E.Merck), 2-amino-1-ethanol (E.Merck) and anhydrous ferric chloride (Aldrich) were used as received. The solvents were purified by standard procedures before use.

Instrumentation

IR Spectra were recorded on a Perkin-Elmer spectrum GX automatic recording spectrophotometer as KBr disc. Electronic spectra and conductivities of an aqueous solution of the complexes were recorded on a cintra-5GBS UV-Visible spectrophotometer and Systronics-305 digital conductivity bridge, respectively, at 298K. The X-Band and EPR spectrum was taken at room temperature (298K) on a Varian E-112 specrophotometer operating at 9.1GHz. FAB- mass spectra were recorded on Jeol SX-102/DA-6000 mass spectrometer using argon (6kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded in m-nitrobenzyl alcohol (NBA) matrix. The elemental C, H, and N analyses were obtained from micro-analytical Laboratory of Central Drug research Institute (CDRI), Lucknow, India. CSChem-3D-MOPAC software has been used to get the minimum energy perspective plots for geometry of the complexes [27]. The Mössbauer measurements were performed at UGC-DAE consortium for scientific research, Kolkata, India. The Mössbauer measurements were made with a standard PC-based system operating in the constant acceleration mode. The velocity drive was calibrated using 57-Co source and a 25 μm thick natural iron foil as an absorber. The sextet of α-
iron was useful in calibrating the centre of gravity of the spectrum and velocity calibration constant, which are essential for the analysis of the spectrum. The experiment was performed at RT when absorber was kept stationary and the source device was moving with a constant velocity (10 mm/s). The spectrum was fitted with NORMOS program 1990 for its solution. Cyclic voltammograms were recorded on a CH-Instrument Electro-Chemical Analyzer using $10^{-3}$M solution of the complexes with tetrabutylammonium perchlorate as supporting electrolyte. A three electrode cell was used which comprised of Pt micro cylinder working electrode, a Pt wire as auxiliary electrode and Ag/AgCl as the reference electrode.

**Preparation of the ligands**

**Synthesis of ligand (H$_2$L$_1$)**

Powdered iminodiacetic acid (0.1 mol, 13 g) was mixed thoroughly with 3-amino-1-propanol (0.2 mol, 15 mL) in excess in neat condition followed by refluxing the mixture for 12 h. A thick yellow coloured oil was obtained which could not be further purified. However, the analytical and the spectroscopic data has characterized the product as the ligand H$_2$L$_1$.

[Yield 95%], Anal.Cal. (%) for C$_{10}$N$_3$H$_{21}$O$_4$: C, 48.56; H, 8.56; N, 16.99,

Found (%), C, 48.32; H, 8.54; N, 16.53. FT-IR (as KBr disc, cm$^{-1}$): $\nu$(C-H), 2873, 2948 cm$^{-1}$; $\nu$(O-H), 3459 cm$^{-1}$; (amide I,II,III), 1643s, 1549,1253 cm$^{-1}$; $\nu$(N-H), 3361 cm$^{-1}$.

$^1$H NMR (300 MHz, D$_2$O) $\delta$, ppm: 2.1, (CH$_2$-NH-CH$_2$); 2.2, (-OH); 8.1, (NH-C=O); 3.24, 3.47, 3.58, 1.76, (-CH$_2$). $^{13}$C NMR ($\delta$ ppm, D$_2$O) (75 MHz): 53, [-CH$_2$-NH]; 171, (NH-C=O); 39, 35, 61, (-CH$_2$).
Synthesis of ligand (H$_2$L$_2$)

The ligand (H$_2$L$_2$) was prepared adopting similar procedure as for (H$_2$L$_1$) except using 2-amino-1-ethanol (0.1 mol, 6.1 mL) which also could not be further purified. However, the analytical and the spectroscopic data indicated the yellow coloured oil as ligand H$_2$L$_2$.

[Yield 95%], Anal. Cal. (%) for C$_8$N$_3$H$_{17}$O$_4$: C, 43.83; H, 7.82; N, 19.17, Found (%), C, 43.32; H, 7.54; N, 18.93. FT-IR (as KBr disc, cm$^{-1}$): $\nu$(C-H), 2879 cm$^{-1}$; $\nu$(O-H), 3496 cm$^{-1}$; (amide I,II,III), 1677, 1531, 1250 cm$^{-1}$; $\nu$(N-H), 3255,3053 cm$^{-1}$. $^1$H NMR (300 MHz, D$_2$O) $\delta$, ppm: 2.2, (CH$_2$-NH-CH$_2$); 2.0, (-OH); 8.5, (NH-C=O); 3.5, 3.4, 3.8, (-CH$_2$). $^{13}$C NMR ($\delta$ ppm, D$_2$O) (75 MHz): 54, [-CH$_2$-NH]; 172, (NH-C=O); 46, 65 (-CH$_2$).

Synthesis of the complex [FeL$_1$ClH$_2$O] (1)

The yellow coloured oil H$_2$L$_1$ (N-(3-hydroxy-propyl)-2-[(3-hydroxy-propylcarbamoyl)-methyl]-amino]acetamide) (5 mmol, 1.235 mL) was dissolved in 6 ml ethanol. After this process triethyl amine (1 mL) was added with slow stirring for 1 h then the solution mixture was reacted with equimolar ethanolic solution of anhydrous FeCl$_3$ (5 mmol, 0.81g) yielding orange coloured precipitate. The Precipitate was further washed with ethanol and air dried in desiccator.

[Yield 90%; m.p. 220 °C (dec)]. Anal. Calc. (%) for C$_{10}$N$_3$H$_{21}$O$_5$FeCl: C, 33.87; H, 5.97; N, 11.85, Found (%), C, 33.51; H, 5.90; N, 12.32. FT-IR (as KBr disc, cm$^{-1}$): $\nu$(C-H), 2943cm$^{-1}$; $\nu$(O-H), 3410 cm$^{-1}$; $\nu$(N-H), 3271 and 3101cm$^{-1}$; (amide
I,II,III), 1641s, 1586,1297 cm\(^{-1}\). FAB mass spectrum: [FeL\(_1\)ClH\(_2\)O\(^+\)]\(^+\) (m/z = 354; 60%), [FeL\(_1\)Cl\(^+\)] (m/z = 336; 35%), [FeL\(_1\)+H\(^+\)] (m/z = 301; 30%), [Fe(L\(_1\)/2)]\(^+\) (m/z = 178; 18%), [L\(_1\)+H\(^+\)] (m/z = 246; 45%).

**Synthesis of the complex [FeL\(_2\)ClH\(_2\)O\]** (2)

The yellow coloured oil H\(_2\)L\(_2\) (N-(2-hydroxy-ethyl)-2-[(2-hydroxy-ethylcarbamoyl)-methyl]-amino]-acetamide) (5 mmol, 1.095 mL) was dissolved in 6 ml ethanol giving yellow solution. Then triethyl amine (1 mL) was added with slow stirring for 1 h followed by addition of equimolar ethanolic solution of anhydrous FeCl\(_3\) (5 mmol, 0.81g) yielding orange coloured precipitate. The Precipitate was further washed with ethanol and air dried in desiccator.

[Yield 90%, m.p. 162 °C (dec)]. Anal. Calc. (%) for C\(_8\)N\(_3\)H\(_{17}\)O\(_5\)FeCl: C, 29.43; H, 5.25; N, 12.87, Found (%), C, 28.90; H, 5.12; N, 12.52. FT-IR (as KBr disc, cm\(^{-1}\)): v(C-H), 2943cm\(^{-1}\); v(O-H), 3374 cm\(^{-1}\); v(N-H), 3259 and 3108cm\(^{-1}\); (amide I,II,III), 1643s, 1511,1283 cm\(^{-1}\). FAB mass spectrum: [FeL\(_2\)ClH\(_2\)O\(^+\)]\(^+\) (m/z = 326; 68%), [FeL\(_2\)Cl\(^+\)] (m/z = 308; 40%), [FeL\(_2\)+H\(^+\)] (m/z = 274; 20%), [Fe(L\(_2\)/2)+ 2H\(^+\)] \(^+\) (m/z = 167; 18%), [L\(_2\)+H\(^+\)] (m/z = 218; <10%).
RESULTS & DISCUSSION

The ligands H$_2$L$_1$ (N-(3-hydroxy-propyl)-2-[(3-hydroxy-propylcarbamoyl)-methyl]-amino]-acetamide) and H$_2$L$_2$ (N-(2-hydroxy-ethyl)-2-[(2-hydroxy-ethylcarbamoyl)-methyl]-amino]-acetamide) were prepared employing condensation reaction between iminodiacetic acid, NH(CH$_2$COOH)$_2$ and 3-amino-1-propanol, [NH$_2$(CH$_2$)$_3$OH] or 2-amino-1-ethanol, [NH$_2$(CH$_2$)$_2$OH] under refluxed conditions. The complexes (1) and (2) were obtained by the reaction of Fe$^{3+}$ with ligand H$_2$L$_1$ or H$_2$L$_2$ in the presence of triethylamine, (C$_2$H$_5$)$_3$N, giving the corresponding products. It is apparent that the complexes are formed in two step process in which first step is the condensation step followed by the complexation step as indicated in Fig. 1.
Fig. 1: Synthetic procedure for the ligand (H₂L₁) and (H₂L₂).
Analytical and FAB- mass spectral studies

Analytical data of the complexes agreed with the molecular formulae [FeL₁ClH₂O] (1) and [FeL₂ClH₂O] (2), which are consistent with mononuclear stoichiometries for (1) and (2). FAB-mass spectral studies of the complexes exhibited peaks from weak (10-20 %) to strong (~ 70%) abundance (intensities). The positions (m/z values) of the peaks are assignable to the molecular ion fragmentation species formed due to a step wise cleavage of the species generated from the fragmented ions of the ligand moiety. The spectrum of [FeL₁ClH₂O] (1) exhibited the molecular ion peak of [FeL₁ClH₂O]^+ at m/z = 354 along with various important stepwise fragmentation species such as [FeL₁Cl]^+, [FeL₁+H]^+, [Fe (L₁/2)]^+ and [L₁+H]^+ at m/z = 336, 301, 178 and 246, respectively. The fragmentation process of the mononuclear complex (2) contained a weak intensity peak due to the molecular ion [FeL₂ClH₂O]^+ at m/z = 326 and that of corresponding step-wise formation of the species i.e. [FeL₂Cl]^+, [FeL₂+H]^+, [Fe(L₂/2)+2H]^+, [L₂+H]^+ at m/z = 308, 274, 167, 218, respectively. Peaks assignable to the free ligand i.e. [L₁+H]^+ at m/z = 246 and [L₂]^+ at m/z = 219 were also observed. The present FAB mass data indicate that the ligand moiety [L₁] or [L₂] are chelated to the metal ion and correspond to the proposed structural formulae of (1) and (2).

FT-IR Spectral studies

The FT-IR spectra of the complexes are slightly different from that of the parent ligands as the characteristic ν(C-O-H) stretching vibrations appearing at around 3460-3500 cm⁻¹ in the uncoordinated ligand moiety is absent in the complexes and a
new band in the low frequency region (~470) cm\(^{-1}\) assignable to M-O bond stretching frequency of the coordinated ligand was indicated. This indicate that the ligand H\(_2\)L\(_1\) and H\(_2\)L\(_2\) bind the metal Fe\(^{3+}\) ion as a anionic (L\(_1^2-/L_2^2-\)) chelating ligand. The spectra exhibited a broad band in 3100-3200 cm\(^{-1}\) region due to (N-H) bond stretching vibration as well as bands in the region 1619-1651, 1539-1589 and 1250-1291 cm\(^{-1}\) characterized as (amide I), (amide II) and (amide III) stretching frequencies, respectively [28]. It is apparent from the IR data that during coordination, the amide group does not undergo deprotonation process such that amide (CO-NH) function is retained. The nature and the position of the absorption bands at 3410 cm\(^{-1}\) in (1) and at 3374 cm\(^{-1}\) in (2) are characteristic of H\(_2\)O coordinated to the metal ions [29,30]. The appearance of medium intensity bands at ~430 ≈ 420 and ~245 in the Far IR region cm\(^{-1}\) region are due to the coordinated Fe-N, Fe-Cl and M-N frequencies [31,28].

\(^1\)H NMR and \(^{13}\)C NMR spectral studies

\(^1\)H NMR spectra of the complexes recorded in D\(_2\)O exhibited multiplets in the region 3.4-3.9 ppm arising from protons associated with the various aliphatic groups (as skeletal –CH\(_2\)- protons) as well as a relatively broad peak in 10.1-10.4 ppm range characteristic iminic (-NH-) proton resonance of the coordinated imda\(^2-\). However, spectra did not show resonance signals characteristic of the amide (CO-NH) present in the molecular unit. The (inter-molecular and or intra-molecular) proton exchange coupled with the nuclear quadrupole relaxation of the nitrogen nucleus (I = 1) are often responsible for this observation [32] with the matrix/solvent.
$^{13}$C NMR spectra of the present complexes (1) and (2) contained a number of medium to strong intensity multiplets in the highfield i.e. 34-41 and low field 170-176 ppm ranges, which may be assigned to the carbon resonances characteristic of the –CH$_2$-, CO-NH-, CH$_2$-NH and >C=O functions [33-35]. However, for the complexes the observed broad undefined feature for the resonance peaks is due to paramagnetic effect of Fe$^{3+}$ [36].

**Electronic (ligand field) and EPR spectral studies**

The electronic spectra of complexes (1) and (2) exhibited weak intensity band characteristic of the d-d transitions in addition to strong intensity metal← ligand (M←L) charge transfer transitions. A spectral behaviour characteristic of the high spin d$^5$ i.e. Fe(III) system in an octahedral environment arises due to closely spaced d-d transition bands [37]. The positions of the important bands observed are 26,954, 23,640, 21,505 and 16,051 cm$^{-1}$ in complex (1) and 27,397, 23,809, 21,186 and 16,129 in complex (2) which are well known [38] and arise due to the spin forbidden transitions involving $^6$A$_{1g}$ ground electronic state to the various high energy states with different spin multiplicities i.e. $^4$E$_g$, $^4$T$_{2g}$, $^4$T$_{1g}$ and $^4$A$_{1g}$. The resulting electronic transitions in the octahedral geometry around Fe$^{3+}$ ion are $[^4$A$_{1g}$, $^4$E$_g]$ ←$^6$A$_{1g}$, $[^4$T$_{2g}]$ ←$^6$A$_{1g}$ and $[^4$T$_{2g}$, $^4$T$_{1g}$] ←$^6$A$_{1g}$. The Electronic transitions with their assignments for the complexes (1) and (2) are shown in Table 1.

The X-band EPR spectra of complexes (1) and (2) recorded at room temperature were nearly identical but exhibited anisotropic nature with $g_{II} = 2.013$ and $g_{\perp} = 1.83$ for (1) and $g_{II} = 2.07$ and $g_{\perp} = 1.831$ for (2) of the resonance signals.
This anisotropic nature is well known to arise from the presence of distortion either electronic or structural. $G < 4$ in both complexes exhibited that there is no interaction between neighbouring nuclei or negligible interaction [39].

**Table 1.** Electronic transitions with their assignments for the complexes (1) and (2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bond positions ($\text{cm}^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$/atom (mol cm$^{-1}$ L$^{1-}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[FeL$_1$ClH$_2$O] (1)</td>
<td>26,954</td>
<td>371</td>
<td>1652</td>
<td>CT+ $\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td></td>
<td>23,640</td>
<td>423</td>
<td>657</td>
<td>$[^{4}A_{1g},^{4}E_{g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
<tr>
<td></td>
<td>21,505</td>
<td>465</td>
<td>330</td>
<td>$[^{3}T_{2g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
<tr>
<td></td>
<td>16,051</td>
<td>623</td>
<td>218</td>
<td>$[^{4}T_{2g},^{4}T_{1g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
<tr>
<td>[FeL$_2$ClH$_2$O] (2)</td>
<td>27,397</td>
<td>365</td>
<td>1572</td>
<td>CT+ $\pi \rightarrow \pi^*$</td>
</tr>
<tr>
<td></td>
<td>23,809</td>
<td>420</td>
<td>732</td>
<td>$[^{4}A_{1g},^{4}E_{g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
<tr>
<td></td>
<td>21,186</td>
<td>472</td>
<td>312</td>
<td>$[^{3}T_{2g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
<tr>
<td></td>
<td>16,129</td>
<td>620</td>
<td>198</td>
<td>$[^{4}T_{2g},^{4}T_{1g}] \leftarrow ^{6}A_{1g}$</td>
</tr>
</tbody>
</table>

**Minimum energy perspective molecular models**

The molecular model computations [40,41] based on the CSChem-3D MOPAC have been employed to solve the minimum energy plots for the molecular structures of the complexes and to determine the important structural parameters like bond lengths and bond angles in the molecules. The plots show that the ligand moieties provide two potential aza (N) sites and two ‘O’ sites to bind metal ions. The mechanical adjustments via augmented mechanical field were used to draw the
optimum minimum energy plots for [FeL\textsubscript{1}ClH\textsubscript{2}O] (1) and [FeL\textsubscript{2}ClH\textsubscript{2}O] (2), which indicate that the metal ions acquire a hexa- coordinate geometry as shown in Fig. 2. The ligand H\textsubscript{2}L\textsubscript{1} and H\textsubscript{2}L\textsubscript{2} both act as tetradentate [N\textsubscript{2}O\textsubscript{2}] donors providing four binding sites [N,N,O,O] to the iron metals. Two other coordination sites of the hexacoordinate geometry are achieved by counter ligands Cl and H\textsubscript{2}O. The overall geometry is distorted octahedral around the Fe\textsuperscript{3+} ions in both the complexes (Fig. 2). Although this is apparent from Fig. 1 that the ligand moiety has seven possible electron rich binding sites to coordinate to metal ions. However, the minimum energy plot [Fig. 2 (a) & (b)] suggests that the optimum energy (i.e. the structure containing the lowest possible energy or least strained structure) can be generated if the ligand moiety H\textsubscript{2}L\textsubscript{1} and H\textsubscript{2}L\textsubscript{2} both act as tetradentate [N\textsubscript{2}O\textsubscript{2}] chelating agent involving the amido nitrogen and the hydroxyl oxo sites that is [N,N,O,O] in binding the Fe\textsuperscript{3+} ion.

The equitorial sites of the octahedron of the six coordinated geometry involve [N,N,O,O] donors and the remaining axial coordination involve Cl and H\textsubscript{2}O as indicated in Fig. 2.
Fig. 2. The perspective view of the complex (a) [FeL$_1$ClH$_2$O] (1) and (b) [FeL$_2$ClH$_2$O] (2).
**Mössbauer spectral studies**

The $^{57}$Fe Mössbauer spectral data provide ample idea about the oxidation state of iron nucleus as well as the possible coordination geometry around the metal ion. The observed representative Mössbauer spectra along with the important computed parameters like isomer shift ($\delta$), quadruple splitting ($\Delta E_Q$), line widths and peak height ratio ($\text{HW}_h/\text{HW}_l$) of (1) and (2) are shown in Figs. 3 and 4, respectively. The least square fit methodology employing Lorentzian line shape was used for the spectral plots, which clearly indicate that the spectra contained only one type of quadrupole splitted doublets. This is consistent with the presence of a non polymeric/non cluster type, preferably a mononuclear stoichiometry i.e. $[\text{Fe}L_1\text{ClH}_2\text{O}]$ (1) and $[\text{Fe}L_2\text{ClH}_2\text{O}]$ (2) of the complexes.

The magnitude of isomer shift ($\delta$) and quadrupole splitting ($\Delta E_Q$) parameters of the present complexes are in the range [42] of the various high- spin state ($S = 5/2$) Fe$^{+3}$ nuclei bearing ($t_{2g}^3e_g^2$) electronic configuration in a hexa-coordinate environment of the ligands [42]. The quadrupole doublet in each case has nearly the same areas and half widths. The peak height ratio ($\text{HW}_h/\text{HW}_l$) is an important parameter [43] to further ascertain whether the complex is a dinuclear (Fe$^{+3}$-Fe$^{+3}$) or mononuclear (Fe$^{+3}$) in nature. It is well known that the magnitude of peak height ratio $\text{HW}_h/\text{HW}_l < 1$ is indicative of a mononuclear species. $\text{HW}_h/\text{HW}_l \geq 1$ is suggesting of a dinuclear/ polynuclear nature of the complexes [43,44]. In the present case the magnitude of $\text{HW}_h/\text{HW}_l < 1$ confirms its mononuclear nature. The spectra did not show any magnetic splitting on application of the external magnetic field. It indicates the effective internal magnetic field at the Mössbauer nuclei is either absent or is too low to show any
significant interaction with the nuclear excitation Fe(±3/2→±1/2) and the spin states remain doubly degenerate (i.e. presence of Kramer’s degeneracy). The quadrupole splitting in high spin Fe(III) complexes with symmetric \((t_{2g}^3e_g^2)\) ground electronic configuration arises mainly due to the presence of structural asymmetry in the ligand field [45]. The nearly asymmetric nature of the quadrupole doublet suggests the presence of a fluctuating electric or magnetic field near the Fe\(^{3+}\) nuclei. Asymmetry in shapes rather than in the areas of quadrupole doublet components may arise from a paramagnetic relaxation effect on the Mössbauer nucleus. For metal ions having \(^6\)S \((^6A_{1g})\) ground term, the fluctuating field is mainly due to the spin- spin relaxations [46,47]. Furthermore, the presence of magnetic exchange i.e. inter molecular anti ferromagnetic interaction between the neighbouring Fe\(^{3+}\) ions in the mononuclear complexes (1) and (2) are expected to enhance the mechanism of the spin-spin relaxation in these molecules [45].

![Mössbauer Spectrum](image)

**Fig. 3.** Representative Mössbauer spectrum of complex \([\text{FeL}_1\text{ClH}_2\text{O}]\) (1) recorded at 298 K.
Thermal studies (TGA)

Thermogravimetric studies (TGA) for the complexes were carried out to examine the stepwise fragmentation pattern as well as to ascertain the nature of water molecules present in the molecular formulae of the complexes. Thermograms of the complexes showed three decomposition steps. In the complex (1) the initial weight loss of 10.083% in the range 100-150 °C temperature indicates the loss of coordinated Cl⁻ ion. In the second step, the observed weight loss of ~ 24.65% for the complex in the temperature range (150–350 °C) corroborates the presence of a coordinated water molecule. Again temperature i.e. in the range (350-540 °C), a weight loss of ~76.50% was observed which corresponds to the probable decomposition of the ligand.

However, the TGA of complex (2) is slightly different from that of (1) in the sense that it exhibited only two decomposition steps. In complex (2) the initial weight
loss of ~ 16.318% in the range of 200-218 °C temperature indicates the release of coordinated water and Cl ion. A gradual change to the temperature range (219-379°C) indicates a weight loss of ~ 29.405% which probably correspond to the decomposition of the ligand. Furthermore, weak endothermic peaks observed in DTA curve in (150–200 °C) (1) and (195–240 °C) in (2) region are also due to the corresponding loss for the coordinated water molecule.

**Cyclic voltammetric studies (CV)**

The electrochemical redox properties of the complexes have been studied using cyclic voltammetry in the potential range from +1.5 to −0.5 V recorded at 0.05 V/s scan rate for (1) and potential range from +1.6 to -0.8 V recorded at 0.05 V/s scan rate for (2) with reference to Ag/AgCl electrode at room temperature in the presence of tetrabutylammonium perchlorate as supporting electrolyte. The cyclic voltammetric parameters i.e. magnitudes of the cathodic potential (Eₚᵋ), anodic potential (Eₚᵃ) and half wave potential (Eᵋₑ₀¹/₂) along with the representative typical scanned cyclic voltammograms have been provided in Figs. 5 & 6.

The observed CV of complex (1) is slightly differ from that of complex (2) in the sense that the former contained an additional irreversible anodic wave at Eₚᵃ = 0.25 V. However, the second anodic peak observed at Eₚⁿᵃ = -0.07 V can be coupled with the cathodic wave Eₚᵋ = -0.3 V to generate a flattened quasi reversible redox couple with Eᵋₑ₀¹/₂ = - 0.185 V (Scheme 1).
For the complex (2) the observed anodic peak at $E_{p}^a = 0.03$ V and cathodic peak at $E_{p}^c = -0.36$ V may be coupled to give a quasi reversible redox couple with $E^{0.1/2} = -0.195$ V.

The half wave potentials $E^{0.1/2}$ for (1) and (2) are in the range reported [48] for monometallic Fe$^{3+}$ complexes. The ratio ($I_{p}^c/I_{p}^a$) of the magnitudes of the cathodic current peak ($I_{p}^c$) to the anodic current peak ($I_{p}^a$) is considerably higher than 1 in the cyclic voltammogram of the present mononuclear complexes (1) and (2) indicating the formation of a flattened quasi reversible redox couple with $E^{0.1/2} = -0.185$ V for (1) and $E^{0.1/2} = -0.195$ V for (2). As indicated by the electrochemical reaction as shown below the additional anodic peak in (1) may be assign to the electrochemical disproportionation reaction. The position and nature of the peak indicates the presence as one electron redox process followed by

(a) $\text{Fe}^{IV}-L_1 \rightleftharpoons \text{Fe}^{III}-L_1 \xrightarrow{E^{0.1/2} = -0.185 \text{ V}} \text{Fe}^{II}-L_1$

(b) $\text{Fe}^{III}-L_2 \rightleftharpoons \text{Fe}^{II}-L_2 \xrightarrow{E^{0.1/2} = -0.195 \text{ V}}$

**Scheme 1.** Electrochemical reactions of (a) (1) & (b) (2).
**Fig. 5.** Cyclic voltammogram of $[\text{FeL}_1\text{ClH}_2\text{O}]$ (1) in $10^{-3}$ M water solution at 0.05 Vs$^{-1}$ scan rate.

$$
\begin{align*}
E_{p}^{a\text{rr}} &= 0.25 \text{ V} \\
E_{p}^{a} &= -0.07 \text{ V} \\
E_{p}^{c} &= -0.3 \text{ V} \\
E_{1/2}^{0} &= -0.185 \text{ V} \\
I_{p}^{c}/I_{p}^{a} &= 1.3 \\
\text{Scan rate} &= 0.05 \text{ Vs}^{-1}
\end{align*}
$$
**Fig. 6.** Cyclic voltammogram of [FeL₂Cl₂H₂O] (2) in 10⁻³ M water solution at 0.05 V s⁻¹ scan rate.

\[ E_p^e = -0.36 \text{ V} \]
\[ E_p^a = 0.03 \text{ V} \]
\[ E_{0\text{1/2}} = -0.195 \text{ V} \]
\[ I_p^c/I_p^a = 3 \]
\[ \text{Scan rate} = 0.05 \text{ V s}^{-1} \]
Superoxide dismutase (SOD) mimic activity

The present complexes (1) and (2) were examined for superoxide dismutase (SOD) mimic activities to investigate whether these compounds are potent to be employed as scavengers for $O_2^-$ radicals. Several complexes containing Cu$^{2+}$ [49,50], Co$^{2+}$ [51], Mn$^{2+}$ [33,52] and Fe$^{3+}$ ions chelated with organic moieties have been successfully used as SOD mimics. The SOD activity depends upon the type of metal ion, coordination number, the ligand environment and the geometry of the overall molecule [49]. The IC$_{50}$ value for the present complexes (1) and (2) comes out to be 23 and 24.5 µmolar dm$^{-3}$, respectively. The SOD mimic activity of both the complexes is comparable exhibiting the similar ligand environment and coordination geometry. The SOD activities of the present complexes have also been compared with some earlier reported complexes [33,49,51,53,54] as well as with that of the native enzyme in Table 2.

**Table 2. IC$_{50}$ values of some ternary complexes and native enzyme.**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>IC$_{50}$ Value (µmol dm$^{-3}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="ClO$_4$">(tren)Cu(E-ImH)</a>$_2$</td>
<td>175</td>
<td>53</td>
</tr>
<tr>
<td>2</td>
<td><a href="ClO$_4$">Cu(PMDT)(phen)</a>$_2$</td>
<td>111</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td><a href="ClO$_4$">Cu(PMDT)(bipy)</a>$_2$</td>
<td>105</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>[Cu(IDA)(phen)(H$_2$O)]·2H$_2$O</td>
<td>62</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>[Cu(dipic)(4-picoline)]$_n$</td>
<td>55</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>[Cu(oda)(Bipy)(H$_2$O)]·4 H$_2$O</td>
<td>18</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>[Cu(ada)(phen)(H$_2$O)]·2H$_2$O</td>
<td>24</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>[Co$_2$(ada)$_2$(phen)$_2$(H$_2$O)$_2$]</td>
<td>180</td>
<td>51</td>
</tr>
<tr>
<td>9</td>
<td>[{Cu(ada)$_3$(bipy)}$_x$·3nH$_2$O]</td>
<td>56</td>
<td>51</td>
</tr>
<tr>
<td>10</td>
<td>[FeL$_1$ClH$_2$O]</td>
<td>23</td>
<td>This Work</td>
</tr>
<tr>
<td>11</td>
<td>[FeL$_2$ClH$_2$O]</td>
<td>24.5</td>
<td>This Work</td>
</tr>
<tr>
<td>12</td>
<td>Native Enzyme (SOD)</td>
<td>0.04</td>
<td>33</td>
</tr>
</tbody>
</table>
CONCLUSION

In this work, two ligands $H_2L_1$ & $H_2L_2$ have been prepared via a condensation reaction of iminodiacetic acid with propanolamine and ethanolamine, respectively. These ligands act as strong chelating moieties towards FeCl$_3$ affording two new complexes (1) and (2). The complexes were characterized employing analytical and spectral (IR, $^1$H and $^{13}$C NMR, FAB Mass, EPR & Mössbauer) techniques. The $^{57}$Fe Mössbauer spectral data for the complexes strongly indicate the presence of an asymmetric environment around the iron nuclei. The relevant Mössbauer parameters $\delta$ and $\Delta Q$ are within the range consistent with high spin state of Fe (III) with the presence of Kramer’s double degeneracy. The cyclic voltammetric studies (CV) confirm the presence of quasi reversible redox couples (Fe$^{III}$/Fe$^{II}$) in aqueous solutions of the complexes.
References


