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Research Article

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Isolation and Spectral Characterization of Complexes $[FeL_1ClH_2O]$ and $[FeL_2ClH_2O]$ (H_2L_1=N-(3-hydroxy-propyl)-2-{[(3-hydroxy-propylcarbamoyl)-methyl]-amino}-acetamide and H_2L_2=N-(2-hydroxy-ethyl)-2-{[2-hydroxy-ethylcarbamoyl)-methyl]-amino}-acetamide): ^{57}Fe Mössbauer and Cyclic Voltammetric Investigations

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Abstract: Two ligands H_2L_1 & H_2L_2 were synthesized employing a condensation reaction of iminodiacetic acid with propanolamine (PA) and ethanolamine (EA), respectively. The ligands behave as strong chelating agents towards $FeCl_3$ affording the title complexes, which were further characterized employing analytical and spectral (IR, ^{1}H and ^{13}C NMR, FAB Mass, EPR & Mössbauer) techniques. The ^{57}Fe Mössbauer spectra for the complexes exhibit a quadrupole splitting confirming the presence of iron nuclei in the asymmetric environment. The relevant parameters δ and ΔQ and the line width are in excellent agreement with high spin state of Fe(III) centre with the presence of Kramer's double degeneracy in a distorted octahedral environment. The cyclic voltammetric (CV) results confirm the presence of quasi reversible redox couples (Fe^{III}/Fe^{II}) in aqueous solutions.

Keywords: Iminodiacetic acid, propanolamine, ethanolamine, ^{57}Fe Mössbauer, cyclic voltammetry

1. INTRODUCTION

The coordination chemistry based on dicarboxylic acid ligands has been an emerging area of research for inorganic and bioinorganic chemists [1-4]. The scientific attentions are still needed to unfold the structural conundrum of the complexes as they remained unexplored [5]. The main reasons could be the complexation reactions leads to insoluble polymeric materials which are often difficult to characterize.

Furthermore, reactions of copper(II), manganese(II) and cobalt(II) with dicarboxylic acid ligands in presence of ancillary nitrogen based ligands like 1,10-phenanthroline and 2,2'-bipyridine may lead to the synthesis of crystalline compounds [6-8].

Coordination polymers constructed by multicarboxylate ligands exhibit potential applications as zeolite-like properties for molecular selection, catalysis, ion exchange as well as exhibits variety of pleasing topological [9] features. Fortunately, depending upon the exploitation of deprotonated carboxylate, they could represent excellent hydrogen bonding acceptors as well as donors materials [10]. The ligands derived from dicarboxylic acids and aminoalcohols such as propanolamine (PA) or ethanolamine (EA) have also attracted attention in last decades [11]. These aminoalcohols are versatile N and O- donor ligands as they readily form coordination compounds with the most of the transition metal ions [12].

The synthesis of transition metal complexes is a rapidly growing research area in inorganic and bioinorganic chemistry [13] in view of their uses to study the redox function of many metalloenzymes [14]. Virtually every form of life, with exception of a couple of specialized bacteria, has requirement for iron an essential element [15]. The uptake, storage and transport of iron in biological system have 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. -CONH is a part of primary structure of proteins and is of the crucial importance in the biological system [19]. Ligand moities containing oxamide functionality 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 implication [22]. Ligands with amide functionality such as oligopeptides, oxamide and oxamates [23-26] shows strong complexation affinity after deproportion of amide groups and thus, stabilize metal ions in their higher 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 (Scheme 1). 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 paper, the investigations on the condensation reactions 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 group of the iminodiactic acid condenses with the $-NH_2$ group of the 3-amino-1-propanol and 2-amino-1-ethanol. We report the isolation of ligands H_2L_1 and H_2L_2 and their iron complexes **1** and **2**. The detailed spectral investigations specially the ^{57}Fe Mössbauer data of mononuclear Fe^{3+} complexes have also been discussed.

2. 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.

Preparation of the ligands

Synthesis of H_2L_1

Iminodiacetic acid (0.1 mol, 13g) was mixed thoroughly with 3-amino-1-propanol (0.2 mol, 15 mL) in excess followed by refluxing the mixture for 12 h. Thick yellow colored oily product was obtained

which could not be further purified. Yield = ~63%. Anal.Cal. for $C_{10}N_3H_{21}O_4$: C, 48.56; H, 8.56; N, 16.99, Anal. Cal. Found, C, 48.32; H, 8.54; N, 16.53. FT-IR (KBr, cm^{-1}): ν(C-H), 2873, 2948cm^{-1}; ν(O-H), 3459 cm^{-1}; (amide I,II,III), 1643s, 1549,1253 cm^{-1}, ν(N-H), 3361 cm^{-1}. ^{1}H NMR (300 MHz, D_2O) δ, ppm: 2.1, (CH_2-N<u>H</u>-CH_2); 2.2, (-O<u>H</u>); 8.1, (N<u>H</u>-C=O); 3.24, 3.47, 3.58, 1.76, (-C<u>H</u>$_2$). ^{13}C NMR (δ ppm, D_2O) (75 MHz): 53, [-<u>C</u> (O)-N]; 171, (NH-<u>C</u>=O); 39, 35, 61, (-<u>C</u>H_2).

Synthesis of H_2L_2

The ligand H_2L_2 was prepared adopting similar procedure as for H_2L_1 except using 2-amino-1-ethanol (0.1mol, 6.1 mL) which also could not be further purified. Yield=95%, Anal.Cal. (%) for $C_8N_3H_{17}O_4$: C, 43.83; H, 7.82; N, 19.17, Found (%), C, 43.32; H, 7.54; N, 18.93. FT-IR (KBr, cm^{-1}): ν(C-H), 2879 cm^{-1}; ν(O-H), 3496 cm^{-1}; (amide I,II,III), 1677, 1531, 1250 cm^{-1}; ν(N-H), 3255,3053 cm^{-1}. ^{1}H NMR (300 MHz, D_2O) δ, ppm: 2.2, (CH_2-N<u>H</u>-CH_2); 2.0, (-O<u>H</u>); 8.5, (N<u>H</u>-C=O); 3.5, 3.4, 3.8, (-C<u>H</u>$_2$). ^{13}C NMR (δ ppm, D_2O) (75 MHz): 54, [-<u>C</u>H_2-NH]; 172, (NH-<u>C</u>=O); 46, 65 (-<u>C</u>H_2).

*Synthesis of the complex $[FeL_1ClH_2O]$ (**1**)*

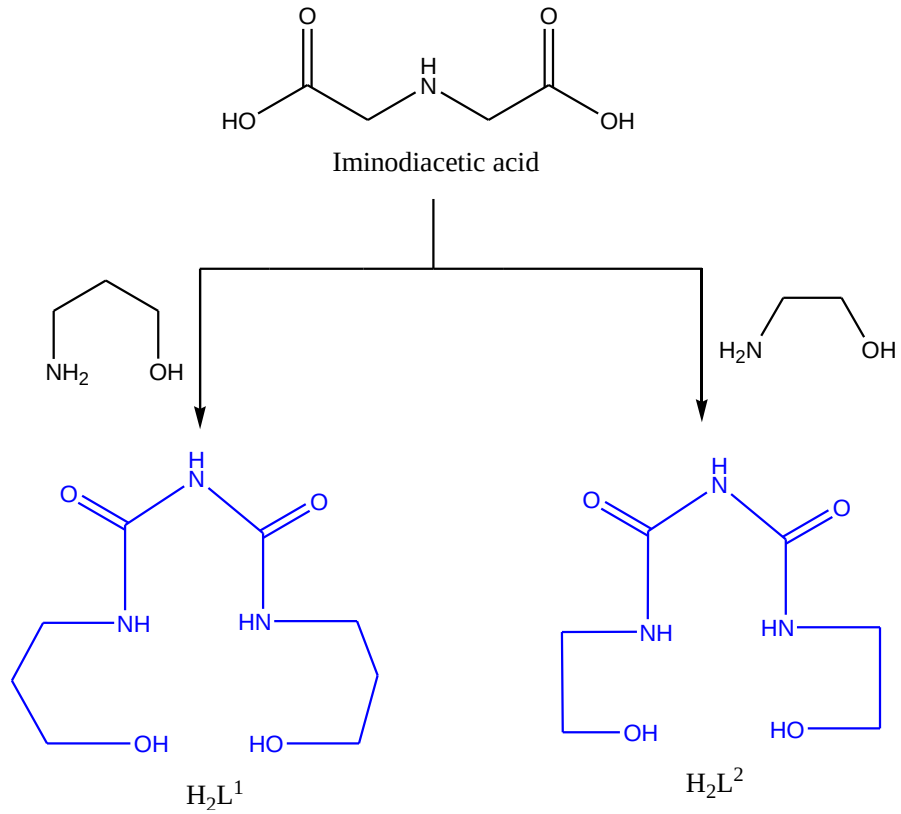
The yellow colored H_2L_1 ligand (5 mmol, 1.235 mL) was dissolved in 6 mL ethanol followed by drop-wise addition of triethyl amine (1 mL) with slow stirring for 1 h. The obtained solution was then reacted with equimolar ethanolic solution of anhydrous $FeCl_3$ (5 mmol, 0.81g) yielding orange colored precipitate. The Precipitate was repeatedly washed with ethanol and dried in desiccator. Yield = ~70%; m.p.= 220 ^{o}C. Anal. Calc. (%) for $C_{10}N_3H_{21}O_5FeCl$: C, 33.87; H, 5.97; N, 11.85, Found (%), C, 33.51; H, 5.90; N, 12.32. FT-IR (KBr, cm^{-1}): ν(C-H), 2943cm^{-1}; ν(O-H), 3410 cm^{-1}; ν(N-H), 3271 and 3101cm^{-1}; (amide I,II,III), 1641s, 1586,1297 cm^{-1}. FAB mass spectrum: $[FeL_1ClH_2O]^+$ (*m/z* = 354; 60%), $[FeL_1Cl]^+$ (*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 $[FeL_2ClH_2O]$ (**2**)*

The yellow colored H_2L_2 ligand (5.0 mmol, 1.095 mL) was dissolved in 6 ml ethanol followed by drop-wise addition of triethyl amine (1 mL) with slow stirring for 1 h. The above reaction mixture was subjected to addition of equimolar ethanolic solution of anhydrous $FeCl_3$ (5 mmol, 0.81g) yielding orange colored precipitate. The Precipitate was further washed with ethanol and dried in desiccator. Yield = 90%, m.p.= 162 ^{o}C. Anal. Calc. (%) for $C_8N_3H_{17}O_5FeCl$: C, 29.43; H, 5.25; N, 12.87, Found (%), C, 28.90; H, 5.12; N, 12.52. FT-IR (KBr, cm^{-1}): ν(C-H), 2943cm^{-1}; ν(O-H), 3374 cm^{-1}; ν(N-H), 3259 and 3108cm^{-1}; (amide I,II,III), 1643s, 1511,1283 cm^{-1}. FAB mass spectrum: $[FeL_2ClH_2O]^+$ (*m/z* = 326; 68%), $[FeL_2Cl]^+$ (*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%).

Physical measurements

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 9.1 GHz. 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.



Scheme 1. *Synthetic procedure for the ligand H_2L_1 and H_2L_2.*

Minimum energy perspective models

CSChem-3D-MOPAC software has been used to get the minimum energy perspective plots for geometry of the complexes [27]. This provides the most stable (ground state) arrangements of the ligand environment around the metal ions. The structural parameters like relevant bond lengths and bond angles were also computed.

Mössbauer spectral studies

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 voltammetric studies

Cyclic voltammograms were recorded on a CH-Instrument Electro-Chemical Analyzer using 10^{-3}M solution of the complexes with 0.1M 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.

3. RESULTS AND DISCUSSION

The ligands H_2L_1 (N-(3-hydroxy-propyl)-2-{[(3-hydroxy-propylcarbamoyl)-methyl]-amino}-acetamide) and H_2L_2 (N-(2-hydroxy-ethyl)-2-{[2-hydroxy-ethylcarbamoyl)-methyl]-amino}-acetamide) were prepared employing condensation reaction between iminodiacetic acid, $NH(CH_2COOH)_2$ and 3-amino-1-propanol, $[NH_2(CH_2)_3OH]$ or 2-amino-1-ethanol, $[NH_2(CH_2)_2OH]$ under refluxed conditions. Complexes **1** and **2** were obtained in two step reactions by Fe^{3+} with H_2L_1 or H_2L_2 in the presence of triethylamine as indicated in **Scheme 1**.

Analytical and FAB- mass spectral studies

Analytical data are in good agreement with the molecular formulae $[FeL_1ClH_2O]$ (**1**) and $[FeL_2ClH_2O]$ (**2**) of the complexes, which are consistent with mononuclear stoichiometries for **1** and **2**. FAB-mass studies of **1** and **2** exhibited peaks from weak (10-20 %) to strong (~ 70%) abundance (intensities). Complex **1** exhibited the molecular ion peak of $[FeL_1ClH_2O]^+$ at *m/z* = 354 along with various important stepwise fragmentation species such as $[FeL_1Cl]^+$, $[FeL_1+H]^+$, $[Fe(L_1/2)]^+$ and $[L_1+H]^+$ at *m/z* = 336, 301, 178 and 246, respectively. Whereas, the fragmentation process of **2** displayed a weak intensity peak corresponding the molecular ion $[FeL_2ClH_2O]^+$ at *m/z* = 326 which is followed by step-wise formation of the fragmented species i.e. $[FeL_2Cl]^+$, $[FeL_2+H]^+$, $[Fe(L_2/2)+2H]^+$, $[L_2+H]^+$ at *m/z* = 308, 274, 167, 218, respectively. Peaks assignable to the free ligand i.e. $[L_1+H^+]$ at m/z = 246 and $[L_2]^+$ at m/z = 219 were also observed. The present FAB mass data indicate that the ligand moiety $[L_1]$ or $[L_2]$ 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 ligands as the characteristic ν(C-O-H) stretching vibrations appearing at around 3460-3500 cm^{-1} in the uncoordinated ligand is absent in the complexes, whereas band in the low frequency region (~ 470) cm^{-1} assignable to M-O bond stretching frequency of the coordinated ligand was observed. This observation support that the ligands H_2L_1 and H_2L_2 bind the metal Fe^{3+} ion as a anionic (L_1^{2-}/L_2^{2-}) chelating mode. 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_2O coordinated to the metal ions [29,30]. The appearance of medium intensity bands at ~430 and ~245 cm^{-1} in the Far IR region are due to the coordinated Fe-N, Fe-Cl and M-N moieties [31,28].

^1H NMR and ^{13}C NMR spectral studies

^1H NMR spectra of the complexes recorded in D_2O 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 ligand L_1^{2-}/L_2^{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 quadruple relaxation of the nitrogen nucleus (I = 1) are often responsible for this observation [32] with the matrix/solvent.

^{13}C NMR spectra of **1** and **2** contained a number of medium to strong intensity multiplets in the high field i.e. 34-41 and low field 170-176 ppm ranges, which may be assigned to the carbon resonances characteristic of the –$\underline{C}H_2$-, $\underline{C}$O-NH-, $\underline{C}H_2$-NH and >$\underline{C}$=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 **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 behavior characteristic of the high spin d^5 i.e. Fe(III) system in an octahedral environment arises due to

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

Complex	Bond position (cm^{-1})	λmax(nm)	ε/atom(mol cm^{-1} L^{-1})	Assignments
$[FeL_1ClH_2O]$ (1)	26,954	371	1652	CT+ π→π*
	23,640	423	657	$[^4A_1g, {}^4E_g]\leftarrow{}^6A_1g$
	21,505	465	330	$[^4T_2g]\leftarrow{}^6A_1g$
	16,051	623	218	$[^4T_2g, {}^4T_1g]\leftarrow{}^6A_1g$
$[FeL_2ClH_2O]$ (2)	27,397	365	1572	CT+ π→π*
	23,809	420	732	$[^4A_1g, {}^4E_g]\leftarrow{}^6A_1g$
	21,186	472	312	$[^4T_2g]\leftarrow{}^6A_1g$
	16,129	620	198	$[^4T_2g, {}^4T_1g]\leftarrow{}^6A_1g$

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 **1** and 27,397, 23,809, 21,186 and 16,129 in **2** which are well known [38] and arise due to the spin forbidden transitions involving $^6A_{1g}$ ground electronic state to the various high energy states with different spin multiplicities i.e. ^4E_g, $^4T_{2g}$, $^4T_{1g}$ and $^4A_{1g}$. The resulting electronic transitions in the octahedral geometry around Fe^{3+} ion are $[^4A_{1g}, {}^4E_g]\leftarrow{}^6A_{1g}$, $[^4T_{2g}]\leftarrow{}^6A_{1g}$ and $[^4T_{2g}, {}^4T_{1g}]\leftarrow{}^6A_{1g}$. The Electronic transitions with their assignments for the complexes (**1**) and (**2**) are shown in **Table 1**.

The X- band EPR spectra of **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 neighboring nuclei or negligible interaction [39].

Minimum energy perspective 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_1ClH_2O] (**1**) and $[FeL_2ClH_2O]$ (**2**), which indicate that the metal ions acquire a hexa- coordinate geometry as shown in **Fig. 1**. The ligand H_2L_1 and H_2L_2 both act as tetradentate $[N_2O_2]$ 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_2O. The overall geometry is distorted octahedral around the Fe^{3+} ions in both the complexes. Although this is apparent from **Scheme 1** that the ligand moiety has seven possible electron rich binding sites to coordinate to metal ions. However, the minimum energy plot **(Fig. 1)** 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_2L_1 and H_2L_2 both act as tetradentate $[N_2O_2]$ chelating agent involving the amido nitrogen and the hydroxyl oxo sites that is [N,N,O,O] in binding the Fe^{3+} ion.

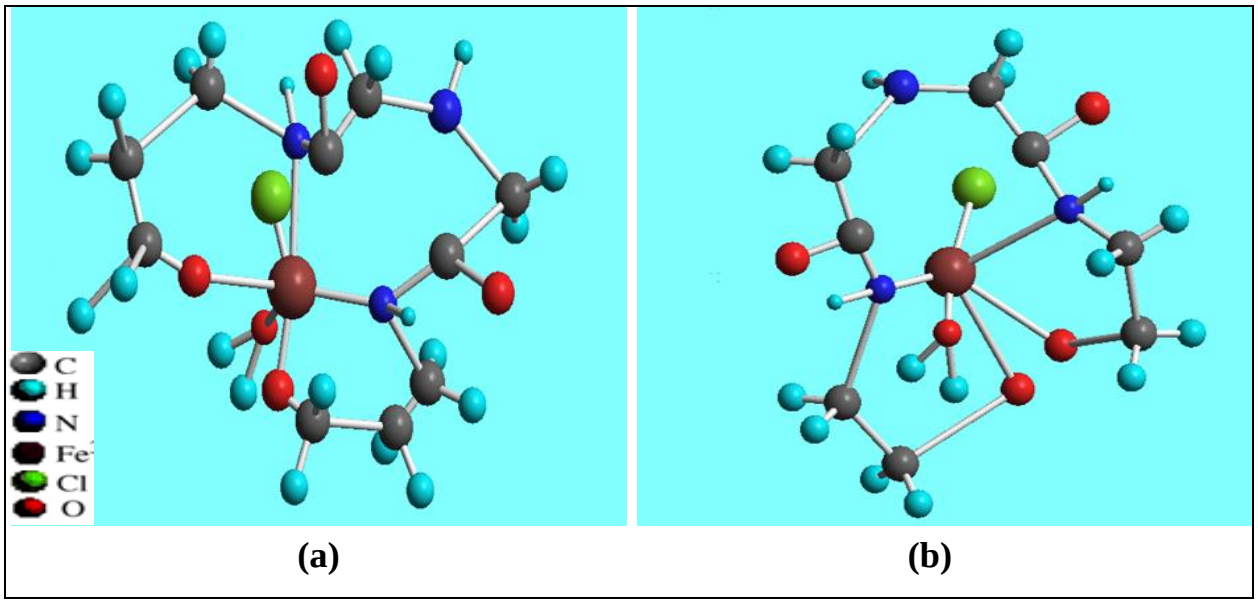


Figure 1. Optimized view of the complexes **1** and **2**.

The equatorial sites of the octahedron of the six coordinated geometry involve [N,N,O,O] donors and the remaining axial coordination involve Cl and H_2O as indicated in **Fig. 1.** Important calculated bond lengths (A°) and bond angles (°) in the complexes **1** and **2** are given in **Table 2**.

Table 2. Selected calculated bond lengths (A°) and bond angles (°) in **1** and **2.**

Complex 1		Complex 2
	Bond lengths	
N-C	1.453	1.453
C-H	1.113	1.113
C-O	1.208	1.208
O-Fe	1.613	1.341
Fe-Cl	1.452	2.180
	Bond angles	
Cl-Fe-O	99.101	163.704
O-Fe-O	110.738	60.242
N-Fe-O	108.479	61.548
N-Fe-Cl	115.079	133.848

MÖssbauer studies

The ^{57}Fe MÖssbauer spectral data provide ample idea about the oxidation state of iron nucleus as well as the possible coordination environments around the metal ion. The observed representative MÖssbauer spectra along with the important computed parameters like isomer shift (δ), quadruple splitting (ΔE_Q), line widths and peak height ratio (HW_h/HW_l) of **1** and **2** are shown in **Figs. 2 (a)** and **(b)**, 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 quadruple splitted doublets. This is consistent with the presence of a non polymeric/non cluster type, preferably a mononuclear stoichiometry i.e. $[FeL_1ClH_2O]$ (**1**) and $[FeL_2ClH_2O]$ (**2**) of the complexes.

The magnitude of isomer shift (δ) and quadruple splitting (ΔE_Q) parameters of the present complexes are in the range 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 quadruple doublet in each case has nearly the same areas and half widths. The peak height ratio (HW_h/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 $HW_h/HW_l<1$ is indicative of a mononuclear species. $HW_h/HW_l \geq 1$ is suggestive of a dinuclear/ polynuclear nature of the complexes [43, 44]. In the present case, the magnitude of $HW_h/HW_l<1$ confirms its mononuclear nature like other similar Fe^{3+} complexes viz. [Fe(oda)(phen)Cl] and [Fe(oda)(4-picNO)(H_2O)Cl)], reported in literature [45a]. 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 quadruple 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 [45b].

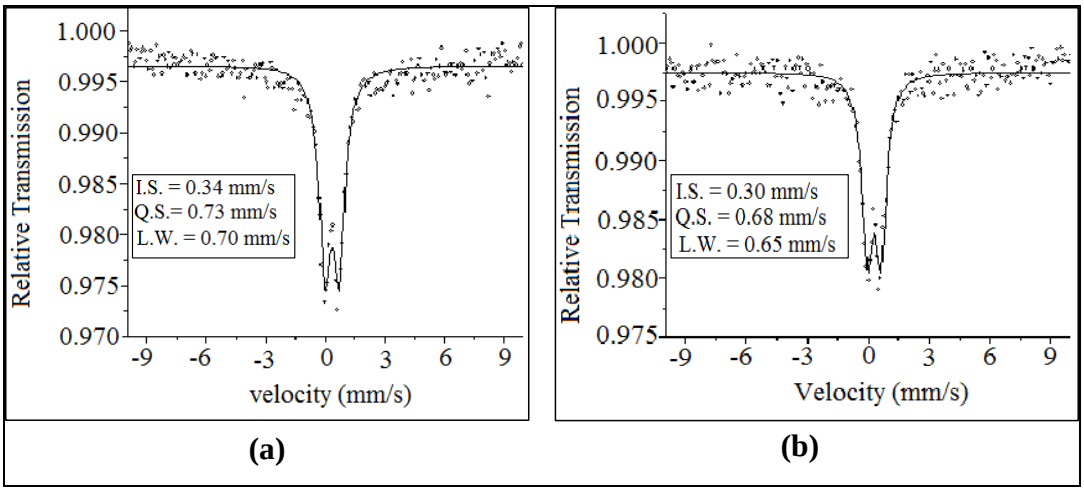


Figure 2. Representative Mössbauer spectrum of (a) $[FeL_1ClH_2O]$ (**1**) and (b) $[FeL_2ClH_2O]$ (**2**) recorded at 298 K.

The nearly asymmetric nature of the quadruple 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 quadruple

doublet components may arise from a paramagnetic relaxation effect on the Mössbauer nucleus. For metal ions having ^6S ($^6A_{1g}$) 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 neighboring 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 data of **1** and **2** at room temperature is provided in **Table 3**.

Table 3. Mössbauer data for **1** and **2** recorded at room temperature.

Complex	Temperature	I.S. (mm/s)	Q.S. (mm/s)	Line width
$[FeL_1ClH_2O]$ (1)	RT	0.34	0.73	0.70
$[FeL_2ClH_2O]$ (2)	RT	0.30	0.68	0.65

Thermal studies (TGA)

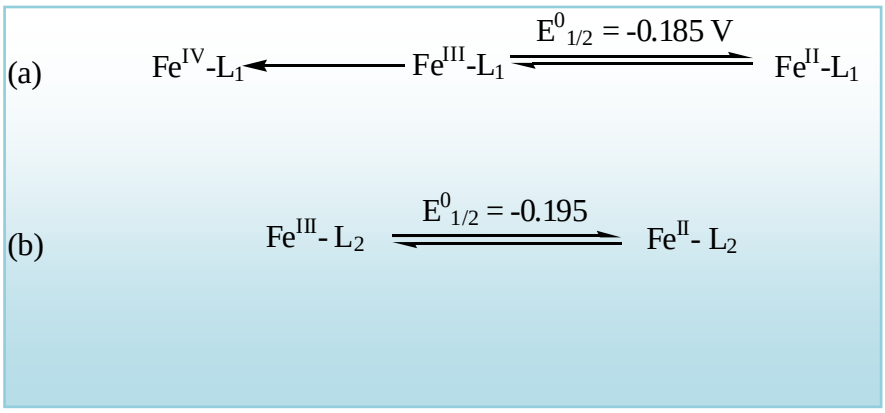
Thermogravimetric studies (TGA) for the complexes were carried out under nitrogen to examine the weight loss which indirectly reveals the gradual decomposition as well as the nature of water molecules. Complex **1** shows weight loss of 10.083% in the range 100-150 °C temperature indicates the release of coordinated Cl^- ion, whereas the weight loss of ~ 24.65% in the temperature range of 150–350 °C corroborates the presence of a metal bound water molecule. Beyond the temperature range of 350-540 °C, complete decomposition of the organic molecules takes place accompanied by formation of metal oxide.

Contrary to the above, complex **2** is shows only two decomposition steps. The initial weight loss of ~ 16.318% in the range of 200-218 °C 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 (**2**) regions are also due to the corresponding loss for the coordinated water molecule.

Cyclic voltammetric (CV) studies

The electrochemical redox behavior of the complexes have been studied using cyclic voltammetry in the potential range from +1.5 to −0.5 V recorded at 0.05 Vs^{-1} scan rate for **1** and potential range from +1.6 to -0.8 V recorded at 0.05 Vs^{-1} 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 (E_p^c), anodic potential (E_p^a) and half wave potential ($E^0_{1/2}$) along with the representative typical scanned cyclic voltammograms have been provided in **Figs. 13S & 14S** (See the supporting Information).

The observed cyclic voltammogram of complex **1** is slightly differ from that of complex **2** in the sense that the former contained an additional irreversible anodic wave at E_p^a = 0.25 V. However, the second anodic peak observed at E_p^a = -0.07 V can be coupled with the cathodic wave E_p^c = -0.3 V to generate a flattened quasi reversible redox couple with $E^0_{1/2}$ = - 0.185 V (**Scheme 3**).



Scheme 3: Electrochemical reactions for (a) complex **1** and (b) complex **2**.

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 indicating the formation of a flattened quasi reversible redox couple with $E^0_{1/2}$ = -0.185V for **1** and $E^0_{1/2}$ = -0.195V for **2**. As indicated by the electrochemical reaction the additional anodic peak in **1** could be assign to the electrochemical disproportionation reaction. The position and nature of the peak indicates the presence as one electron redox process.

4. CONCLUSION

Two ligands (H_2L_1 & H_2L_2) have been synthesized by the reaction of iminodiacetic acid with amino alcohols (propanolamine and ethanolamine), which on reaction with $FeCl_3$ produce mononuclear complexes adopting octahedral geometry around Fe(III) center. The complexes are well characterized by IR, ^{1}H and ^{13}C NMR, FAB Mass, EPR & Mössbauer techniques. The ^{57}Fe Mössbauer spectral data for the complexes confirms the presence of an octahedral asymmetric environment around the iron center. The Mössbauer data are consistent with high spin Fe(III) with the presence of Kramer's double degeneracy. The cyclic voltammograms of the complexes indicate the presence of quasi reversible redox couples (Fe^{III}/Fe^{II}) in solutions. This work provides new synthetic route for the preparation of mononuclear Fe^{3+} complexes in near future by varying the aminoalcohol ligands. New doors would be opened for the possible uses of such Fe(III) complexes in medicinal chemistry and material science.

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SUPPLEMENTARY INFORMATION

For complexes **1** and **2:** complete data for ^{1}H NMR, ^{13}C NMR, TGA analysis, FAB-MS and CV.

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The authors declare no conflict of interest

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