

## Synthesis and Spectroscopic Characterization of Manganese(II), Iron(III) and Cobalt(III) Complexes of Macrocyclic Ligand. Potential of Cobalt(III) Complex in Biological Activity

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**ABSTRACT.** A new series of manganese(II), iron(III) and cobalt(III) complexes of 14-membered macrocyclic ligand, (3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine) have been prepared and characterized by elemental analyses, IR, UV-VIS,  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectra, magnetic susceptibilities, conductivities, and ESR measurements. Molar conductance measurements in DMF solution indicate that the complexes are electrolytes. The ESR spectrum for cobalt(III) complex in  $\text{CD}_3\text{OD}+10\%\text{D}_2\text{O}$  after exposure to  $^{60}\text{Co}$ - $\gamma$ -rays at 77 K using a  $0.2217\text{ M rad h}^{-1}$  vicrad source showed  $g_{\perp} > g_{\parallel} > g_e$ , indicating that, the unpaired electron site is mainly present in the  $d_{z^2}$  orbital with covalent bond character. In this case, the ligand hyperfine tensors are nearly collinear with  $\gamma$ -tensors, so there is no major tendency to bend. Therefore, little extra delocalization via the ring lobe of the  $d_{z^2}$  orbital occurs. However, the ESR spectrum in solid state after exposure to  $^{60}\text{Co}$ - $\gamma$ -rays at 77 K showed  $g_{\parallel} > g_{\perp} > g_e$ , indicating that, the unpaired electron site is mainly present in the  $d_{x^2-y^2}$  ground state as the resulting spectrum contains a large number of randomly oriented molecules provided that, the principle directions of  $g$  and  $A$  tensors. Manganese (II) complex **2**,  $[\text{H}_{12}\text{LMn}]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ , showed six isotropic lines characteristic to an unpaired electron interacting with a nucleus of spin 5/2, however, iron(III) complex **3**,  $[\text{H}_{12}\text{LFe}]\text{Cl}_5 \cdot \text{H}_2\text{O}$ , showed spectrum of a high spin  $^{57}\text{Fe}$  ( $I=1/2$ ),  $d^5$  configuration. The geometry of these complexes was supported by elemental analyses, IR, electronic and ESR spectral studies. Complex **1** showed exploitation in reducing the amount of electron adducts formed in DNA during irradiation with low radiation products.

**Key words:** Macrocyclic complexes, Spectral studies, magnetism,  $^{60}\text{Co}$ - $\gamma$ -rays on metal complexes and DNA

### INTRODUCTION

There has been considerable interest in the chemical properties, structures and coordination behaviors of polyazamacrocyclic compounds because they can play an important role in various fields such as in biological, medical chemistry, catalysis and chemical industry.<sup>1-6</sup> In general, chemical properties and structures of such compounds are strongly influenced by the nature of encapsulated metal ion and the nature and number of functional groups. The polyazamacrocyclic chelates can be used in the determination of certain cation levels in cells and tissues. The size of the macrocycle ring is selective towards different metal cations in biological systems. Copper(II) and nickel(II) complexes of polyazamacrocyclics bearing pendent amide groups have been prepared and characterized.<sup>4,5,7</sup> Copper(II) complexes of 14-membered tetraza macrocyclic compounds bearing pendent  $\text{N-CH}_2\text{CH}_2\text{CONH}_2$  groups have been prepared and spectrally investigated.<sup>6</sup> Encapsulated transition metal complexes are also of consider-

able importance in biological studies since they have very high binding constants, meaning that the possibility of releasing of the metal cations is negligibly small. Also, there is no easy access for active ligands such as hydrogen peroxide, and hence fenton type reactions to occurs, thereby reducing potential toxicity. A long term aim of this study was to find transition metal complexes having high non-localized, positive charges and high stability for two redox states of the metal ion. It seemed possible that, some of the  $\text{H}_{10}\text{L}$  complexes that were designed and studied.<sup>8-10</sup> would be suitable for biological studies. Generally, macrocyclic complexes are of the synthetic flexibility involved in their preparation which allows for systematic variation in parameters such as ring size, the nature of the donor atoms and the steric and electronic effects associated with the groups located on the periphery of the macrocyclic ring.<sup>11</sup> Increasing interest in the macrocyclic metal complexes as model compounds for active sites in enzymes comprising corrin or porphyrin moieties has resulted in various preparative routes to such compounds. Earlier work had demonstrated

that use of a difunctional macrocycle in such reactions resulted in the production of polymers that were highly cross-linked and hence insoluble.<sup>12</sup> The aim of this preliminary study was the production of manganese(II), iron(III) and cobalt(III) complexes of 14-membered macrocyclic ligand, (3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine) containing a single reactive  $\text{NH}_3^+$  functional site. Our other interest lies in finding efficient radiation protection agents for nuclear DNA. One approach is to make use of the results,<sup>8,13</sup> that obtained using ESR spectroscopy at low temperatures, which suggest that DNA effectively ionizes, giving initially, radical-cations centered on the purine bases (A,G) and radical-anions centered on the pyrimidine bases (C, T). We are designing agents which will rapidly reverse this process before irreversible events make this impossible. Thus, we require an agent that can redox cycle, such as Co(III)/Co(II) and Fe(III)/Fe(II) complexes. However, this agent must have a high DNA affinity, but must not bind too strongly, since it is required to read the DNA searching for damage sites.

## EXPERIMENTAL

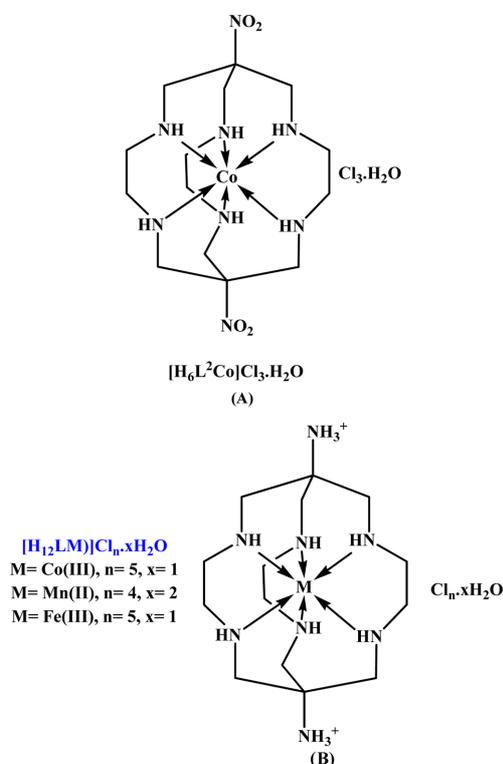
All chemicals and solvents were reagent grade and used as received, C, H, N, Cl and M analysis were determined at the analytical Unit of Cairo University, Egypt (Table 1). The complexes were dried in the air. IR spectra (as KBr pellets) and (as nujol mull between CsBr prisms) were recorded on a Perkin-Elmer 681 spectrophotometer. Electronic spectra in 200-900 nm region were recorded on a Perkin-Elmer 550 spectrophotometer. <sup>1</sup>H- and <sup>13</sup>CNMR spectra were obtained with a Perkin-Elmer R32-90 MHz spectrometer using TMS as internal standard. Magnetic susceptibilities were measured at 25 °C by Gouy method using mercuric tetrathiocyanato-cobaltate(II) as the magnetic standard. Diamagnetic corrections were estimated from Pascal's constant. The magnetic moment susceptibilities were calculated from the following equation  $\mu_{\text{eff}} = 2.84 \times (\chi_m^{\text{corr}} \times T)^{1/2}$ . Molar conductances were measured on a Tacussel type CD<sub>6</sub>NG conductivity bridge using 10<sup>-3</sup> M DMF. The ESR spectra of the complexes at room temperature and in CD<sub>3</sub>OD+D<sub>2</sub>O (10%) in the form of small

beads at 77 K were measured using a varian E-109 spectrometer. The cobalt(III) complex and DNA molecules were exposed to <sup>60</sup>Co- $\gamma$ -rays at 77 K using a 0.2217 M radh<sup>-1</sup> dose for 5 h (Leicester University, England). DPPH was used as the marker.

### Preparation of macrocyclic complexes

**Preparation of [Co(en)<sub>3</sub>]Cl<sub>3</sub>:** [Co(en)<sub>3</sub>]Cl<sub>3</sub> was prepared and resolved by conventional procedures.<sup>13</sup>

**Preparation of [H<sub>6</sub>LCo]Cl<sub>3</sub>.H<sub>2</sub>O:** The cobalt(III) complex [H<sub>6</sub>LCo]Cl<sub>3</sub>.H<sub>2</sub>O, H<sub>6</sub>L=1,8-dinitro-3,6,10,13,16,19-hexaazabi-cyclo[6.6.6]icosane (Fig. 1A) was prepared and characterized previously.<sup>8</sup> Nitromethane (190 g) was added to a solution of [Co(en)<sub>3</sub>]Cl<sub>3</sub> (163 g) in water (5 mL) and the solution stirred until the CH<sub>3</sub>NO<sub>2</sub> had completely



**Fig. 1.** (A) The suggested formulation of the cobalt(III) complex of 1,8-dinitro-3,6,10,13,16,19-hexaazabi-cyclo[6.6.6]icosane [H<sub>6</sub>L<sup>2</sup>Co]Cl<sub>3</sub>.H<sub>2</sub>O. (B) The suggested formulation of the cobalt (III), manganese(II) and iron(III) complexes of 3,6,10, 13,16,19-hexaazabicyclo[6.6.6]-icosane-1,8-diamine.

**Table 1.** Suggested formulation, color and elemental analyses of complexes

Suggested formulation	Color	Found(Calcd.)				
		M	C	H	N	Cl
[H <sub>12</sub> LCo]Cl <sub>3</sub> .H <sub>2</sub> O (C <sub>14</sub> H <sub>36</sub> N <sub>8</sub> CoCl <sub>3</sub> .H <sub>2</sub> O)	Yellow-Orange	10.25(10.33)	29.38(29.46)	6.76(6.71)	19.80(19.63)	30.96(31.06)
[H <sub>12</sub> LMn]Cl <sub>4</sub> .2H <sub>2</sub> O (C <sub>14</sub> H <sub>36</sub> N <sub>8</sub> MnCl <sub>4</sub> .2H <sub>2</sub> O)	Yellow	10.11(10.00)	30.55(30.61)	7.30(7.34)	19.92(20.40)	25.73(25.82)
[H <sub>12</sub> LFe]Cl <sub>5</sub> .H <sub>2</sub> O (C <sub>14</sub> H <sub>36</sub> N <sub>8</sub> FeCl <sub>5</sub> .H <sub>2</sub> O)	Violet	10.21(9.84)	29.48(29.62)	6.40(6.75)	19.56(19.74)	31.28(31.23)

dissolved. Aqueous HCHO solution (1300 g, 37%) and  $\text{Na}_2\text{CO}_3$  (80 g) were then added and stirring was continued until the  $\text{Na}_2\text{CO}_3$  had dissolved. The solution became warm and darkened in color. The solution was left to stand at room temperature for 5 hours, a copious precipitate of orange, needle-like crystals formed. The product was collected, washed with a little ice-cold water and dried in air. The complex was added gradually to hot 3 M HCl (1500 mL), mixing of the solution formed with ethanol (1500 mL), and cooling on ice. Yielded 156 g (69%).

**Preparation of  $[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}$ :**  $[\text{H}_6\text{LCo}]\text{Cl}_3\cdot\text{H}_2\text{O}$  (40 g) was dissolved in water (2 L) and the solution deoxygenated with nitrogen. Under vigorous stirring and maintenance of a nitrogen blanket, zinc dust (40 g) was added, followed by concentrated HCl (200 mL) drop by drop, stirring was continued for 2 hours after the acid addition was complete. The orange solution was warmed on the steam bath for 20 min. and then absorbed on a 20 cm  $\times$  8 cm diameter column of  $\text{H}^+$  Dowex 50 WX2 cation-exchange resin. The column was washed with water (2 L) and 1 M HCl (2 L, to remove  $\text{Zn}^{2+}$ ) and the orange complex then eluted with 3 M HCl. The eluted volume was reduced under vacuum until crystallization commenced and deposition was complete by addition of ethanol. The complex was recrystallized as yellow-orange crystals by dissolution in warm 1 M HCl. Addition of a few drops of ethanol and slow cooling (yield 30 g).

**Preparation of  $[\text{H}_{12}\text{LMn}]\text{Cl}_4\cdot 2\text{H}_2\text{O}$ :** This complex was prepared by extracting cobalt ion from the cage using 8-hydroxyquinoline as follows: In a 3-necked 250 mL round bottomed flask equipped with a condenser, a stirrer and an inlet tube for nitrogen,  $[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}$  (11.49 g) was dissolved in water (75 mL), NaOH (1.6 g) was added to neutralize it and the solution was purged with nitrogen. To this was added a 2 % alcoholic solution of 8-hydroxyquinoline.<sup>14</sup> The mixture was heated to 60-65 °C while stirring under a blanket of nitrogen until the light-brown amorphous cobalt oxinate became crystalline. The latter was allowed to settle at room temperature, filtered off on a sintered-glass. The filtrate was concentrated on water bath; the equimolar concentration of  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  in ethanol (30 cm) was added drop wise. The reaction solution was refluxed for 2 hours and the complex formed was filtered off, washed several times with ethanol and dried in air.

**Preparation of  $[\text{H}_{12}\text{LFe}]\text{Cl}_5\cdot\text{H}_2\text{O}$ :** This complex was prepared in ethanol-water solvent from the 1:1 molar ratio reaction of the ligand with  $\text{FeCl}_3\cdot 4\text{H}_2\text{O}$  using the procedure described above. This complex was washed several times with warm ethanol and dried in air. The formulae of the

complexes, colors and the elemental analyses are collected in Table 1.

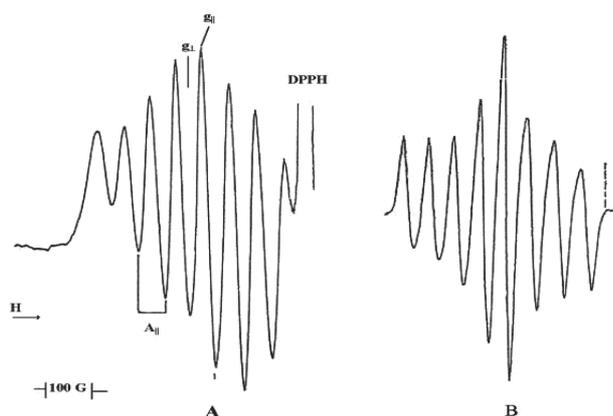
## RESULTS AND DISCUSSIONS

### Cobalt(III) complexes

The cobalt(III) complex  $[\text{H}_6\text{L}^2\text{Co}]\text{Cl}_3\cdot\text{H}_2\text{O}$ , gave strong absorption bands characteristic of the  $\text{NO}_2$  groups at 1555 and 1353  $\text{cm}^{-1}$  and the electronic spectrum in 0.1 M HCl shows two peaks with  $\lambda_{\text{max}}=473.5$  nm ( $\epsilon=146$   $\text{M}^{-1}\text{cm}^{-1}$ ) and  $\lambda_{\text{max}}=343.5$  nm ( $\epsilon=124$   $\text{M}^{-1}\text{cm}^{-1}$ ). The reduction of  $\text{NO}_2$  groups was made using zinc dust under nitrogen atmosphere to give cobalt(III) complex  $[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}$ . This complex was prepared and characterized by elemental analyses (Table 1), magnetic moment, molar conductivity, electronic and IR spectral studies and ESR measurements. The suggested structure is shown in Fig. 1B.

The IR spectrum of this complex shows a broad absorption at 3070  $\text{cm}^{-1}$  characteristic to  $^1\text{NH}_3$ .<sup>15</sup> The bands corresponding to  $\text{NO}_2$  groups were absent, a broad band appearing in the high energy region at ca 3500-3410  $\text{cm}^{-1}$  assignable to NH group.<sup>16,17</sup> The appearance of two bands at 2680 and 2720  $\text{cm}^{-1}$  characterized to  $\text{CH}_2$  group. The molar conductance is 330  $\Omega^{-1}\text{cm}^2\text{Mol}^{-1}$ , indicates electrolytic nature of this complex.<sup>18,19</sup> Also, this complex is diamagnetic, confirms cobalt(III) species.<sup>17</sup> The electronic spectrum was measured in nujol mull and in 0.1 M HCl. In nujol mull, the complex shows several bands at 370, 480 and 510 nm. The first one is within the ligand and the other peaks are assigned to  $^1\text{A}_{1g}\rightarrow^1\text{T}_{2g}$  and  $^1\text{A}_{1g}\rightarrow^1\text{T}_{1g}$  transitions respectively, which are typical of octahedral complexes.<sup>20-22</sup> However, in 0.1 M HCl solution, the complex exhibits absorption bands at  $\lambda_{\text{max}}=475$  nm ( $\epsilon=149$   $\text{M}^{-1}\text{cm}^{-1}$ ) and  $\lambda_{\text{max}}=344$  nm ( $\epsilon=130$   $\text{M}^{-1}\text{cm}^{-1}$ ), which confirm the octahedral geometry.<sup>8</sup> The  $^1\text{H-NMR}$  spectrum shows the characteristic protons in their expected chemical shift regions. In  $\text{D}_2\text{O}$  (after N deuteration which was complete on dissolution) strong resonances were detectable at 2.84 (8H) ppm ascribed to the ethylenediamine methylene protons, another two peaks appear at 3.43 and 3.53 ppm corresponding to the methylene groups of the caps, a single symmetrical resonance appears at 7.8 ppm assigned to NH groups.<sup>20</sup> The  $^{13}\text{C-NMR}$  of this complex. The spectrum shows two absorptions at 53.71 and 57.54 ppm. The former signal is ascribed to the carbon atoms of methylene groups in the ethylenediamine skeleton and the latter to the carbon atoms in the caps.<sup>20,21</sup>

The cobalt(III) complex (**1**) was studied as a frozen solution in  $\text{CD}_3\text{OD}+\text{D}_2\text{O}$  (10%) at 77 K in the form of



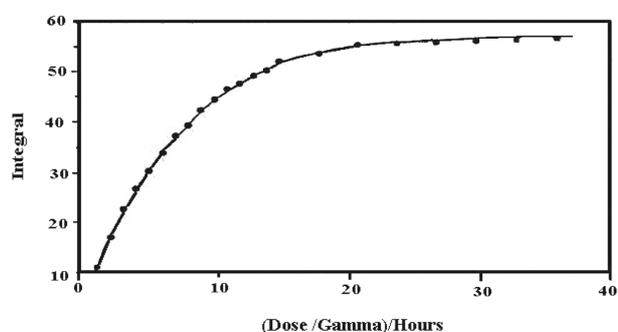
**Fig. 2.** (A) The ESR Spectrum of the  $[[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}]$  in  $\text{CD}_3\text{OD}+\text{D}_2\text{O}(10\%)$  at 77 K. (B) Simulated Spectrum of the  $[[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}]$ .

**Table 2.** ESR parameters of  $[[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}]$  at 77 K

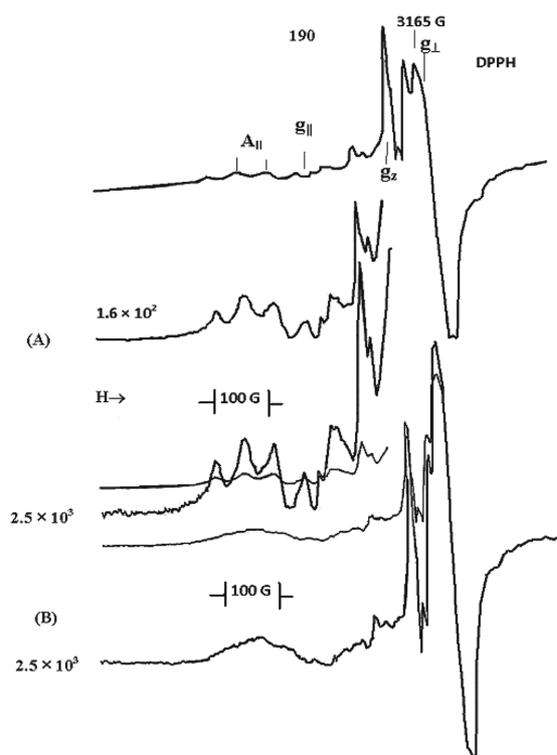
$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$	$A_{\parallel}$	$A_{\perp}$	$A_{\text{iso}}$	$\alpha^2$
2.188	2.197	2.194	38	69.5	59	0.83

small beads. The sample was exposed to  $^{60}\text{Co}$ - $\gamma$ -rays at 77 K using a  $0.2217 \text{ M rad h}^{-1}$  Vicrad source for periods up to 3 h. The ESR spectrum in a frozen solution was recorded at 77 K. It is shown in *Fig. 2A*, and is characteristic of a low spin  $d^7$  configuration eight lines were observed from the interaction of the unpaired electron spin with  $^{59}\text{Co}$  ( $I=7/2$ , 100% abundant). The lines wide are anisotropic. The spectrum exhibits two features, assigned as  $g_{\parallel}$  and  $g_{\perp}$  which are characteristic of species with octahedral symmetry. The ESR parameters are listed in *Table 2*. These parameters show a relation such that  $g_{\perp} > g_{\parallel} > g_e$ , which refers to the unpaired electron site being mainly in the  $d_{z^2}$  orbital.<sup>23-27</sup> with a slight distortion of the symmetry around the Z axis. In this case, the ligand hyperfine tensors are nearly collinear with g-tensors, so there is no major tendency to bend. Therefore, little extra delocalization via the ring lobe of the  $d_{z^2}$  orbital occurs. The spectrum was recorded as a frozen solution in  $\text{CD}_3\text{OD}+\text{D}_2\text{O}$  (10%) at 4 K. No change in the spectrum was observed. On studying the complex in  $\text{H}_2\text{O}$  at 77 K, an identical spectrum although or less intensity was obtained. Simulation of this spectrum gives a similar spectrum to the original *Fig. 2B* but there are some differences in the  $A_{\parallel}$  values. The low temperature irradiated sample was annealed at different temperatures. The sample was studied at 77 K, no change in the spectra were observed when the sample was recorded at the annealing temperatures. The signal intensity decreases as the temperature increases. The signal was lost at  $\sim 115 \text{ K}$ . This fact infers that, the stability of the

low spin state of cobalt(II) which is produced by  $\gamma$ -irradiation depends much on the temperature. The rapid loss of ESR signals in the 115 K region is quit unexpected. There is no apparent reason for actual loss of the  $\text{Co(II)}$  species and we favor the idea of a structural switch resulting in an undetectably broad signal. This may be because the 77 K species is low spin ( $S=1/2$ ) but this relaxes on annealing to give the high spin ( $S=3/2$ ) species. Since the structural is very symmetrical. The zero fields splitting could be relatively small but sensitivity to thermal fluctuations gives a very broad feature. Attempts were made to study this irradiated complex using Q-band. Unfortunately, no ESR spectrum was observed, this is probably due to increasing the magnetic field.<sup>28</sup> the lines broaden on increasing the magnetic field. The  $\sigma$ -bonding parameter  $\alpha^2$  of this complex (*Table 2*) shows that the bonding is appreciably covalent in nature.<sup>29-31</sup> The attempt was made to study the radiation effect on the cobalt(III) complex at 77 K, by exposing the sample to  $^{60}\text{Co}$   $\gamma$ -rays form a Vicrad source at a dose rate of ca.  $0.2217 \text{ M rad h}^{-1}$  periods up to ca. 35 h. The ESR spectrum was recorded every one hour under the same conditions at 77 K. It was found that, the amount of cobalt(II) species produced increase as  $\gamma$ -rays dose increase as shown in *Fig. 3*. The ESR spectrum of a polycrystalline sample at room and 77 K temperatures were recorded after irradiating the sample with  $^{60}\text{Co}$   $\gamma$ -rays at a dose rate of ca.  $0.2217 \text{ M rad h}^{-1}$  for periods up to ca. 5 h at room temperature, no spectrum was observed even when recorded at 77 K. This may be that the electron transfer process was reversible at room temperature. However, irradiation of a polycrystalline sample at 77 K gave an ESR spectrum which was characteristic of  $^{59}\text{Co}$  ( $I=7/2$ ), a monomeric species. The spectrum is shown in *Fig. 4*, the spectrum shows  $g_{\parallel} > g_{\perp} > g_e$ , indicating octahedral structure with  $d_{(x^2-y^2)}$  ground state.<sup>30</sup> As the resulting spectrum contains a large number of randomly oriented molecules provided that, the principle directions of g and



**Fig. 3.** The effect of  $\gamma$ -rays on  $[[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}]$  complex.



**Fig. 4.** (A) The ESR sSpectrum of the polycrystalline  $[H_{12}LCo]Cl_5 \cdot H_2O$  complex at 77 K. (B) Annealing spectrum at 77 K.

A tensors. The parameters are  $g_{||}=2.26$ ,  $g_{\perp}=2.05$  with  $g_{iso}=2.12$  and  $A_{||}=190$  G,  $A_{\perp}=70$  G with  $A_{iso}=110$  and  $\alpha=0.86$ . The  $g_{||}$ -value indicates covalent bond character which confirms with  $\alpha^2$ -value.<sup>30-32</sup> The low temperature irradiated powdered sample was annealed at room temperature. The Sample was studied at 77 K, a broad signal was observed in the low field region as shown in *Fig. 4*. Once again attempts to record Q-band spectra of this complex were unsuccessful; this again, is probably due to the increase in the magnetic field or the effect of increased temperature.<sup>28</sup>

### Manganese(II) complex

The manganese(II) complex (2),  $[H_{12}LMn]Cl_4 \cdot 2H_2O$  was prepared and characterized by elemental analyses (*Table 1*), magnetic moment, molar conductivity, electronic and IR spectral studies and ESR measurements. The suggested structure is shown in *Fig. 1B*.

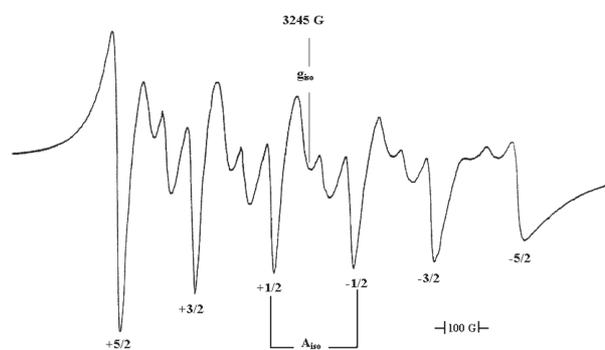
The IR spectrum was made in nujol mull. As expected, it was similar to cobalt complex. The molar conductance is  $260 \Omega^{-1}cm^2 mol^{-1}$ , indicating electrolytic nature of this complex.<sup>18,19</sup> Also, the complex shows magnetic value 5.92 BM indicating high spin Mn(II) complex.<sup>33</sup> The electronic spectrum of this complex in nujol mull shows sev-

eral absorptions at 372, 450, 484 and 516 nm, the first one is due to the ligand and the other bands are corresponding to  ${}^6A_{1g} \rightarrow {}^4E_g$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition respectively, which are typical to octahedral Mn(II) complex. However, in HCl, two absorptions were observed at  $\lambda_{max}=470$  nm ( $\epsilon=152 M^{-1}cm^{-1}$ ) and  $\lambda_{max}=448$  nm ( $\epsilon=119 M^{-1}cm^{-1}$ ) which are characteristic of octahedral geometry.<sup>8</sup>

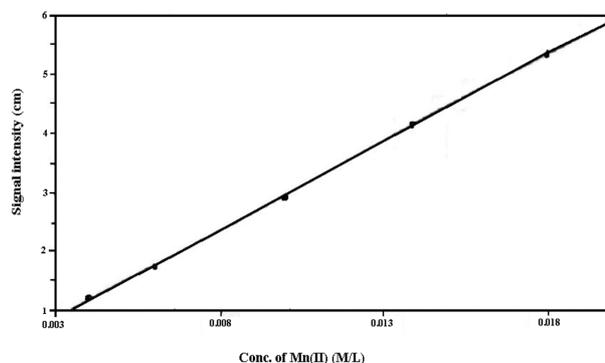
The ESR spectrum was studied in  $CD_3O+D_2O$  (10%) at 77 K in the form of small beads. The spectrum shows six isotropic lines characteristic of an unpaired electron interacting with a nucleus of spin 5/2. The g value is isotropic and is equal to 2.0036,<sup>23,34</sup> the hyperfine coupling constant ( $A_{iso}$ ) is equal to 90 G. There was a series of broad shoulders on the wings of the spectrum with a separation of ca. 22 G which come from forbidden quadruple effect. The ESR spectrum is shown in *Fig. 5*. It was found that, the signal intensity of the manganese(II) complex increased linearly with increase in concentration between 0.005 M and 0.0175 M as shown in *Fig. 6*.

### Iron(III) complex

The iron(III) complex (3),  $[H_{12LFe}]Cl_5 \cdot H_2O$  was prepared and characterized by elemental analyses (*Table 1*),



**Fig. 5.** The ESR spectrum of the  $[H_{12}LMn]Cl_4 \cdot 2H_2O$  complex in  $CDOD+D_2O$  (10%) at 77 K.



**Fig. 6.** Shows the relation between Mn(II) concentration (M/L) with signal intensity (cm).

magnetic moment, molar conductivity, electronic and IR spectral studies and ESR measurements. The suggested structure is shown in Fig. 1B. The IR spectrum was made in nujol mull. As expected, it was similar to cobalt complex. The molar conductance is  $320 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , indicating electrolytic nature of this complex.<sup>18,19</sup> Also, the complex shows magnetic value 5.83 BM indicating high spin Fe(III) complex.<sup>35</sup> The electronic spectrum of this complex in nujol mull shows several absorptions at 370, 451, 482 and 510 nm, the respectively, which are typical to octahedral Fe(III) complex.<sup>36,37</sup> However, in HCl, the complex exhibits two absorptions at  $\lambda_{\text{max}}=471 \text{ nm}$  ( $\epsilon=150.9 \text{ M}^{-1}\text{cm}^{-1}$ ) and  $\lambda_{\text{max}}=340 \text{ nm}$  ( $\epsilon=125 \text{ M}^{-1}\text{cm}^{-1}$ ) which are similar to octahedral iron(III) complexes. The ESR spectrum was studied in  $\text{CD}_3\text{O}+\text{D}_2\text{O}$  (10%) at 77 K in the form of small beads. It is characteristic of a high spin  $^{57}\text{Fe}$  ( $I=1/2$ ),  $d^5$ , configuration. It gives a signal at  $g=4.4$  which is similar to  $\text{Fe}^{3+}$  complexes.<sup>38</sup> The ESR spectrum is shown in Fig. 7. This is not the actual  $g$ -value in the low field half of the zero field splitting feature (No hyperfine splitting was observed. The real  $g$ -value is around 2.0. The  $g$ -value (4.4) is the limit of extreme rhombic distortion. It was found that; increased gamma dose at 77 K tends to decrease the signal intensity. This means that the  $\text{Fe}^{2+}$  species was increased as shown in Fig. 8.

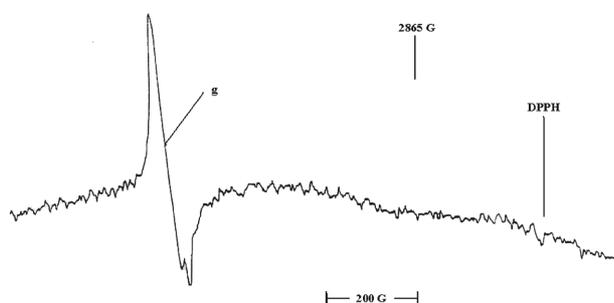


Fig. 7. The ESR spectrum of  $[\text{H}_{12}\text{LFe}]\text{Cl}_5\cdot\text{H}_2\text{O}$  complex in  $\text{CD}_3\text{OD} + \text{D}_2\text{O}$  (10%) at 77 K.

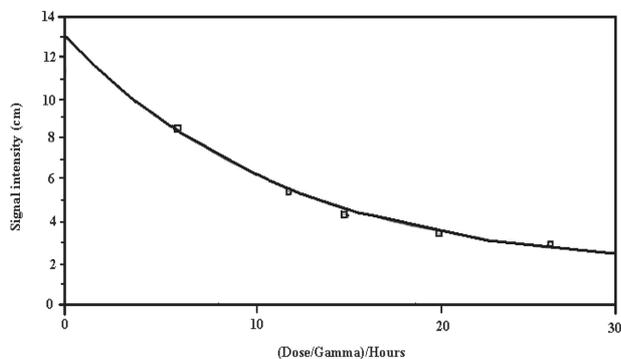


Fig. 8. The relation between Gamma dose (hours) with signal intensity (cm).

### Potential of $[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}$ complex in biological activity

The genetic fingerprint molecule in the replication of cells is deoxyribonucleic acid, DNA. DNA is a long helical structure comprising two intertwined strands of identical arrangements of cytosine, guanine, adenine and thymine. Each strand is made of a pair of strings of phosphodiester linkages to which are attached in regular pairs the four bases. The preponderance of negative charges from the many phosphate groups confers on the molecule a sheath of negative charges which gives it a high affinity for positive charges. Exposure of cells to ionizing radiations initiates a series of electron transfer reactions resulting in the destruction, or at low doses, alteration of the DNA molecule. Replication of such altered DNA molecules invariably leads to the formation of aberrant cells, overproduction of cells, or underproduction of cells. In order to intercept the electron transfer reactions in DNA as a means of mitigating the deleterious effects of ionizing radiations, there is the need for substrates which might act as good electron capture reagents. Such molecules must also have the ability to add on the DNA molecules without any disruption of its native structure. The cobalt(III) complex **1** has a large positive charge due to the central metal ion and the eight nitrogen atoms; this property makes it highly reactive with DNA. Their suitability for electron-capture in any DNA- $[\text{H}_{12}\text{LCo}]\text{Cl}_5\cdot\text{H}_2\text{O}$  complex may be inferred from the results of  $\gamma$ -radiation on cobalt complex. A one-electron-capture event observed by the reduction of Co(III) to Co(II). The efficiency of this reaction may be exploited in reducing the amount of electron adducts formed in DNA during irradiation with less radiation products, the degree of destruction of DNA is exploited to reduce and hence reduction of aberration in cells. It is also clear that using Co(III) complex in the presence of irradiated DNA, we will be able to monitor the initially formed low-spin Co(II) complex using ESR spectroscopy. In the DNA studies this will be exploited by re-cooling after complete loss of DNA radical centers and re-irradiating to convert re-formed Co(III) into low spin Co(II) which is then an assay for the concentration of re-formed Co(III).

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