

Synthesis and Physicochemical Properties of Schiff Base Macrocyclic Ligands and Their Transition Metal Chelates

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ABSTRACT. Tetraaza Schiff base macrocyclic ligands, L^1, L^2 and their transition metal chelates have been synthesized and characterized by elemental analyses, IR, electronic, EPR and ^1H NMR spectra, TGA and magnetic measurements. The molar conductance of one milli-molar solution of the complexes measured in DMF indicates that the divalent metal complexes are nonelectrolyte while those of trivalent metal ion, are 1:1 electrolytic in the same solvent. The reduction of Racah parameter from the free ion value confirms the presence of considerable covalence of metal ligand sigma bond in the Co(II) and Mn(II) complexes. The EPR spectra of Cu(II) complexes at room temperature shows axial symmetry indicating a $d_{x^2-y^2}$ ground state with significant covalent character. The thermal analysis suggests that the complexes do not contain water molecules because only the metal is left as residue.

Key words: Spectroscopic measurements, Triethylenetetramine, Macrocyclic ligands

INTRODUCTION

Complexes of metal ions with synthetic macrocycles assume importance because it possesses a controlled geometry. These have been widely studied because of their applications in biological systems.¹ For example, manganese complexes involving tetradentate Schiff base derivatives are most versatile and interesting synthetic systems.² Some of these types of complexes were found to be artificial mimics of the biological enzymes such as Mn-catalase,³ Mn-superoxide dismutase, Mn-ribonucleotide reductase and in particular, the Mn-peroxidase that protects cells against hydrogen peroxide induced oxidative stress. It has been observed that the catalytic activity of the Schiff base complexes is very sensitive to minor structural changes. Photophysical and catalytic properties of the Schiff base complexes have also been studied.^{4,5}

Recently, pentadentate (N_3O_2) ligands with several ring substituted salicylaldehydes have been prepared and their complexes with a variety of metal ions have been thoroughly explored.¹

In the last decade, Schiff base ligands have received more attention mainly because of their wide application in the field of synthesis and catalysis.⁶ The attraction is still growing, such that a considerable research effort is today devoted to the synthesis of new Schiff base complexes with transition⁷ and main group metal ions⁸ to further develop applications in both catalysis and material chemistry.⁹

We report, in this communication the complexes of Mn(ii), Fe(ii), Co(ii) and Cu(ii) ions with N_4 Schiff base macrocycles derived from the condensation of triethylenetetramine with benzil (L^1) and acetylacetonate (L^2).

EXPERIMENTAL

Acetylacetonate, benzil (Fluka), triethylenetetramine (Merck), hydrated metal chlorides (BDH) were used as received. Methanol was distilled and dried by conventional methods.

Elemental analyses (C, H, N) were carried out with a 1106 Carlo Erba analyzer. The metals were determined by complexometric titration using EDTA and chlorine was determined gravimetrically. The IR spectra ($4000\text{--}450\text{ cm}^{-1}$) were recorded on a RXI FT-IR spectrometer as KBr discs. The conductivity measurements were carried out with a CM-82T Elico conductivity bridge in DMF. The electronic spectra were recorded on a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were done with a 155 Allied Research vibrating sample magnetometer at room temperature. ^1H NMR spectrum was recorded on a Bruker ACF 300 spectrometer at 300.12 MHz, using TMS as a reference in DMSO- d_6 . EPR spectra of polycrystalline samples were recorded on a RE-2X Jeol EPR spectrometer fitted with 100 KHz field modulation. The TGA was performed with a Perkin Elmer thermal analyzer. The experiment was done in nitrogen atmosphere using calcinated Al_2O_3 as reference material.

The weight of the sample taken was 8 mg and the heating rate was kept at $10\text{ }^{\circ}\text{C min}^{-1}$.

Synthesis of Ligand L¹

Distilled triethylenetetramine (1.42 mL, 10 mmol) was added drop wise to a methanolic solution (100 ml) of benzil (2.10 g, 10 mmol) with stirring. The resulting mixture was heated at $80\text{ }^{\circ}\text{C}$ for 3 to 4 h in a 250 ml round bottomed flask equipped with the reflux condenser protected from atmospheric moisture. The reaction mixture was then permitted to stand at room temperature overnight. The light yellow precipitate deposited was removed by filtration under suction pressure. It was washed thrice with cold methanol and dried in vacuo. Yield, 1.86 g (58%).

Synthesis of Ligand L²

Distilled triethylenetetramine (1.42 mL, 10 mmol) was added dropwise to a methanolic solution (100 ml) of acetylacetone (1.03 mL, 10 mmol) with stirring. The resulting mixture was heated at $80\text{ }^{\circ}\text{C}$ for 3 to 4 h in a 250 ml round bottomed flask equipped with the reflux condenser protected from atmospheric moisture. The reaction mixture gradually turned orange. The reaction mixture was then permitted to stand at room temperature overnight. The precipitate deposited was removed by filtration under suction pressure. It was washed thrice with cold methanol and dried in vacuo. Yield, 1.12 g (53%).

Synthesis of Complexes of Ligand L¹

Distilled triethylenetetramine (1.42 mL, 10 mmol) was added drop wise to a methanolic solution (100 mL) of benzil (2.10 g, 10 mmol) with stirring. The resulting mixture was heated at $80\text{ }^{\circ}\text{C}$ for about half an hour in a 250 ml round bottomed flask equipped with the reflux condenser protected from atmospheric moisture. Calculated amount of fresh hydrated metal chloride dissolved in the methanol (50 ml) was added. The mixture was heated under reflux for next 3 to 4 h and then the volume was reduced to half. The solid complexes that separated out were filtered, washed with cold methanol, recrystallized from a DMF-DMSO mixture (1:1) and dried in vacuo. Yield (63-76%).

Synthesis of Complexes of Ligand L²

Distilled triethylenetetramine (1.42 mL, 10 mmol) was added drop wise to a methanolic solution (100 mL) of acetylacetone (1.03 mL, 10 mmol) with stirring. The resulting mixture was heated at $80\text{ }^{\circ}\text{C}$ for about half an hour in a

250 ml round bottomed flask equipped with the reflux condenser protected from atmospheric moisture. Calculated amount of fresh hydrated metal chloride dissolved in the methanol (50 ml) was added. The mixture was heated under reflux for next 3 to 4 h and then the volume was reduced to half. The coloured solid complexes that separated out were filtered, washed with cold methanol, recrystallized from a DMF-DMSO mixture (1:1) and dried in vacuo. Yield, (56-79%).

RESULTS AND DISCUSSION

The ligands were synthesized by refluxing a mixture of triethylenetetramine with benzil (L¹) and acetylacetone (L²). The contents were left overnight which yielded the ligand. Metal complexes were synthesized directly by the addition of hydrated metal chloride solutions to the ligand solution in the same solvent (*Figs. 1-4*). Since the yield of the complexes was too poor (10 to 15%), the template method was employed. In this method the ligand was not isolated. The metal chloride was added to the ligand under preparation. All the complexes were formed in 1:1 ratio. They are stable in air and decompose at high temperature (*Table 1*). The ligands are hygroscopic whereas all the complexes are non hygroscopic in nature. It may be rationalized in the following way. The lone pair of electron of free amino group takes up the water molecule through hydrogen bonding and gets stabilized. But when the complex is formed these lone pair of electrons is used up in complex formation with metal ions.

The molar conductance of one millimolar solution of the complexes measured in DMF indicated that divalent complexes are non electrolyte while those of Fe(III) are 1:1 electrolyte¹⁰ (*Table 1*).

IR Spectra

The solid state IR spectra of the ligands (*Table 2*) show a single absorption band in $3396\text{-}3428\text{ cm}^{-1}$ region corresponding to free secondary amino group. It is shifted to lower wave number by about $50\text{ to }100\text{ cm}^{-1}$ after coordination of the metal ions with nitrogen atoms of the ligands.¹¹

Generally the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ absorb in the $1600\text{-}1650\text{ cm}^{-1}$ and $1350\text{-}1450\text{ cm}^{-1}$ ranges respectively, although in a highly conjugated system the $\nu(\text{C}=\text{N})$ appears at lower wave number as has been found by Patra and Goldberg¹² in such systems. However, these bands have been found to be shifted to lower wave number in the complexes (*Table 2*).

Table 1. Physical Properties and Analytical Data for L¹, L² and its Metal Chelates

	Compounds (Formula weight)	Yield (%)	Colour	M.p. (°C)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	% Analysis Found (Calcd)			
						C	H	N	Cl
	C ₂₀ H ₂₄ N ₄ (L ¹) (320.44)	58	Yellow	140	–	74.0 (74.9)	7.2 (7.5)	27.9 (17.5)	–
(1)	C ₂₀ H ₂₄ Cl ₂ MnN ₄ [MnL ¹ Cl ₂] (446.28)	63	Brown	210	16	54.1 (53.8)	5.5 (5.4)	12.8 (12.5)	16.3 (15.9)
(2)	C ₂₀ H ₂₄ Cl ₃ FeN ₄ [FeL ¹ Cl ₂]Cl (482.64)	59	Brown	195	92	50.1 (49.7)	4.7 (5.0)	12.0 (11.6)	21.6 (22.0)
(3)	C ₂₀ H ₂₄ Cl ₂ CoN ₄ [CoL ¹ Cl ₂] (450.27)	68	Brown	220	38	53.7 (53.3)	5.0 (5.4)	12.8 (12.4)	15.2 (15.7)
(4)	C ₂₀ H ₂₄ Cl ₂ CuN ₄ [CuL ¹ Cl ₂] (454.88)	76	Green	243	42	52.9 (52.8)	5.9 (5.3)	11.9 (12.3)	16.0 (15.6)
	C ₁₁ H ₂₂ N ₄ (L ²) (210.33)	53	Orange	155	–	62.3 (62.8)	10.7 (10.5)	26.9 (26.6)	–
(5)	C ₁₁ H ₂₂ Cl ₂ MnN ₄ [MnL ² Cl ₂] (336.17)	69	Brown	190	35	39.5 (39.3)	6.3 (6.6)	16.4 (16.7)	19.8 (21.1)
(6)	C ₁₁ H ₂₂ Cl ₃ FeN ₄ [FeL ² Cl ₂]Cl (372.53)	61	Pale Yellow	175	83	35.1 (35.5)	6.3 (5.9)	14.4 (15.0)	29.1 (28.5)
(7)	C ₁₁ H ₂₂ Cl ₂ CoN ₄ [CoL ² Cl ₂] (340.16)	56	Brown	178	46	38.4 (38.8)	6.8 (6.5)	16.8 (16.5)	20.3 (20.8)
(8)	C ₁₁ H ₂₂ Cl ₂ CuN ₄ [CuL ² Cl ₂] (344.76)	79	Green	160	29	38.7 (38.3)	6.1 (6.4)	15.9 (16.2)	20.7 (20.5)

Table 2. Important IR Bands (cm⁻¹) of Ligands and their Metal Chelates

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C-N})$
L ¹	3396 m	1626 s	1450 s
(1) [Mn(L ¹)Cl ₂]	3073 s	1602 s	1401 m
(2) [Fe(L ¹)Cl ₂]Cl	3343 s	1630 s	1403 s
(3) [Co(L ¹)Cl ₂]	3142 m	1602 m	1402 m
(4) [Cu(L ¹)Cl ₂]	3189 m	1610 s	1443 s
L ²	3428 m	1635 m	1357 m
(5) [Mn(L ²)Cl ₂]	3411 m	1610 m	1357 m
(6) [Fe(L ²)Cl ₂]Cl	3395 s	1610 m	1350 w
(7) [Co(L ²)Cl ₂]	3408 s	1622 s	1355 w
(8) [Cu(L ²)Cl ₂]	3416 w	1579 s	1355 m

Electronic spectra

The magnetic moment values and electronic spectral bands are given in Table 3. Cobalt(II) complexes have been widely studied. The electronic spectra of [Co(L¹)Cl₂] and [Co(L²)Cl₂] have identical features, indicating that the stereochemistry around the Co(II) ion in solution are alike. An octahedral Co(II) species exhibits three transitions, but in practice only two transitions have been observed¹³. We, too, have observed two absorption bands at 15,060 and 22,138 cm⁻¹ for [Co(L¹)Cl₂] and at 14,903 and 16,501 cm⁻¹ for [Co(L²)Cl₂] corresponding to ⁴A_{2g}(F)⁴←⁴T_{1g}(F) and ⁴T_{1g}(P)←⁴T_{1g}(F) transitions, respectively. These bands in the visible region are consistent with spin allowed d-d

transition for a six coordinate octahedral Co(II) ion. Various ligand field parameters for the complexes [Co(L¹)Cl₂] and [Co(L²)Cl₂] have been calculated and reported in Table 3. The nephelauxetic parameter β indicates appreciable covalent character in these complexes. The observed magnetic moment values for the [Co(L¹)Cl₂] and [Co(L²)Cl₂] are 3.98 and 4.10 BM respectively. This is consistent with a high-spin octahedral Co(II) ion with considerable orbital contribution to the overall magnetic moment.^{14,15}

It has been reported that the Fe(III) complexes exhibit bands in 23,696 to 23,364 cm⁻¹ region which correspond to a six coordinate Fe(III) system.¹⁶ In the present work, we have observed for the [Fe(L¹)Cl₂]Cl a single absorption band at 22,676 cm⁻¹ while for [Fe(L²)Cl₂] complex a broad band at 23,364 cm⁻¹ corresponding to ⁴T_{2g}←⁶A_{1g} transition have been observed. The experimental magnetic moment in our case falls in the range 5.89-5.97 BM (Table 3) which is very close to that calculated for a high-spin d⁵ ion. The magnetic moment and UV-vis spectra of the pale yellow Fe(III) complex support an octahedral geometry for the Fe(III) ion.

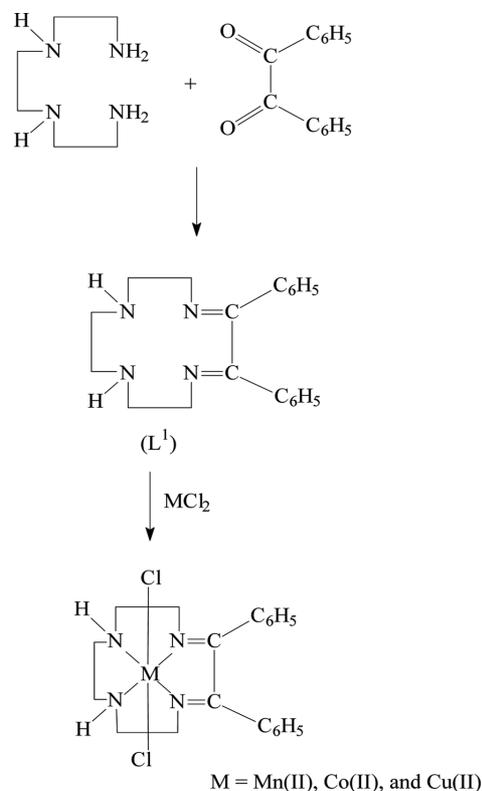
The Cu(II) complexes show one charge transfer band centered at 42,000 to 45,000 cm⁻¹. The band exhibited in the 14,000 to 15,000 cm⁻¹ region has been assigned to the ²T_{2g}←²E_g transition which is characteristic of an octahedral copper(II) ion.¹⁷ It has been reported that the magnetic moment of Cu(II) complexes fall in the region of

Table 3. Magnetic Susceptibility, Electronic Spectra and Ligand Field Parameters of the Complexes

Compounds	Magnetic moment (B.M.)	Electronic bands (cm ⁻¹)	Log ε (mol ⁻¹ cm ²)	Possible assignments	10Dq (cm ⁻¹)	B (cm ⁻¹)	β
(1) [Mn(L ¹)Cl ₂]	4.41	44,453 30,959 24,012 21,024	4.81 3.07 1.98 1.68	C.T. ⁴ T _{1g} (P)← ⁶ A _{1g} ⁴ E _g (G)← ⁶ A _{1g} ⁴ T _{2g} (G)← ⁶ A _{1g}	8550	750	0.78
(2) [Fe(L ¹)Cl ₂]Cl	5.94	44,443 22,675	4.84 1.93	C.T. ⁴ T _{2g} (G) ⁶ A _{1g}			
(3) [Co(L ¹)Cl ₂]	3.98	43,478 15,060 22,138	4.69 1.98 2.76	C.T. ⁴ A _{2g} (F)← ⁴ T _{1g} (F) ⁴ T _{1g} (P)← ⁴ T _{1g} (F)	9638	989	0.89
(4) [Cu(L ¹)Cl ₂]	2.08	42,553 14,285	4.9 2.0	C.T. ² T _{2g} ² E _g			
(5) [Mn(L ²)Cl ₂]	5.12	44,843 31,112 23,513 22,102	4.52 2.31 1.32 1.12	C.T. ⁴ T _{1g} (P)← ⁶ A _{1g} ⁴ E _g (G)← ⁶ A _{1g} ⁴ T _{2g} (G)← ⁶ A _{1g}	9010	850	0.88
(6) [Fe(L ²)Cl ₂]Cl	5.87	44,444 23,364	4.60 2.76	C.T. ⁴ T _{2g} (G) ⁶ A _{1g}			
(7) [Co(L ²)Cl ₂]	4.18	44,843 14,903 16,501	3.91 2.42 2.38	C.T. ⁴ A _{2g} (F)← ⁴ T _{1g} (F) ⁴ T _{1g} (P)← ⁴ T _{1g} (F)	7450	745	0.67
(8) [Cu(L ²)Cl ₂]	1.97	44,843 14,925	5.00 2.17	C.T. ² T _{2g} ² E _g			

1.73 to 2.20 BM.¹⁵ Our values fall within this region. In the present case, the observed magnetic moments support an octahedral geometry for Cu(II) ion (Table 3).

Three absorption bands have generally been observed for six coordinate Mn(II) complexes.¹⁸ We have also observed three bands at 30,959, 24,012 and 21,024 cm⁻¹ for [Mn(L¹)Cl₂] and at 31,112, 23,513 and 22,102 cm⁻¹ for [Mn(L²)Cl₂] corresponding to the transitions ⁴T_{1g}(P)←⁶A_{1g}, ⁴E_g(G)←⁶A_{1g} and ⁴T_{2g}(G)←⁶A_{1g}, respectively, which is consistent with an octahedral geometry for the Mn(II) ion. The calculated value of B for complexes [Mn(L¹)Cl₂] and [Mn(L²)Cl₂] are 750 and 850 cm⁻¹, respectively. The electron-electron repulsion in these complexes is less than the free ion, resulting in the increased distance between electrons and thus, an effective increase in the size of the orbital will take place. On increasing delocalization, the value of β decreases. This is why the calculated values of β in the present complexes are less than one. This indicates that the complexes under study have appreciable covalent character in the metal-ligand (M-L) bond. Since the magnetic moment value of Mn(II) complexes is lower than the calculated one it is ascribed to an equilibrium between low and high-spin states of Mn(II) ion.

**Fig. 1.** Synthesis of Complexes of Ligand L¹.

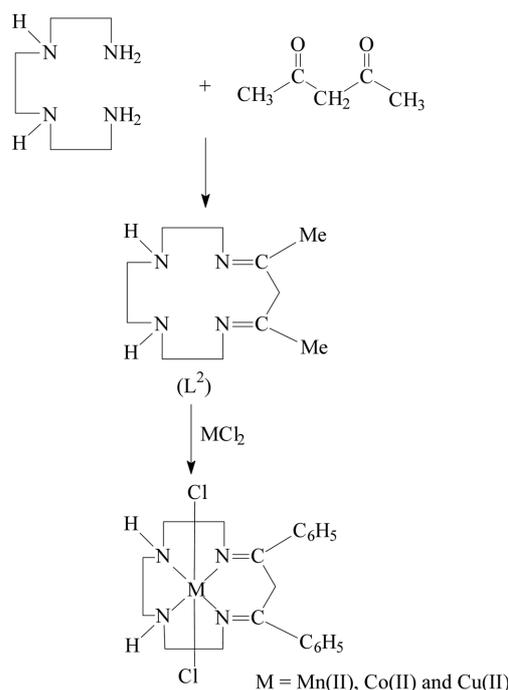


Fig. 2. Synthesis of Complexes of Ligand L^2 .

In cis octahedral complex, the two amino group of triethylenetriamine are trans to each other. So, their condensation with small molecules like benzil or acetylacetone may hardly occur. If macrocycles are formed by their condensation then there is a lot of strain and hence the complexes are unstable.

On the other hand, in trans octahedral complex, the two amino group of triethylenetriamine are cis to each other. So, their condensation with benzil or acetylacetone takes place very easily. The macrocycles so formed are strainless and hence are stable.

In cis octahedral complex, the bond angle between two chlorine atoms is 90° . Due to entropy factor and chelate effect, these two chlorine atoms are also shared by the second metal atom. It means the complex is dimerized. This type of dimerization is also found in Ti complex in Sharpless asymmetric epoxidation.

On the other hand, in trans octahedral complex, dimerization is not possible because Cl atoms are trans to each other.

The magnetic moment value reveals that all the complexes are in monomeric form and not dimerized. Thus we can conclude that the complex is trans octahedral and not cis octahedral.

^1H NMR spectra

^1H NMR spectra of $[\text{Cu}(L^1)\text{Cl}_2]$ and $[\text{Cu}(L^2)\text{Cl}_2]$ were

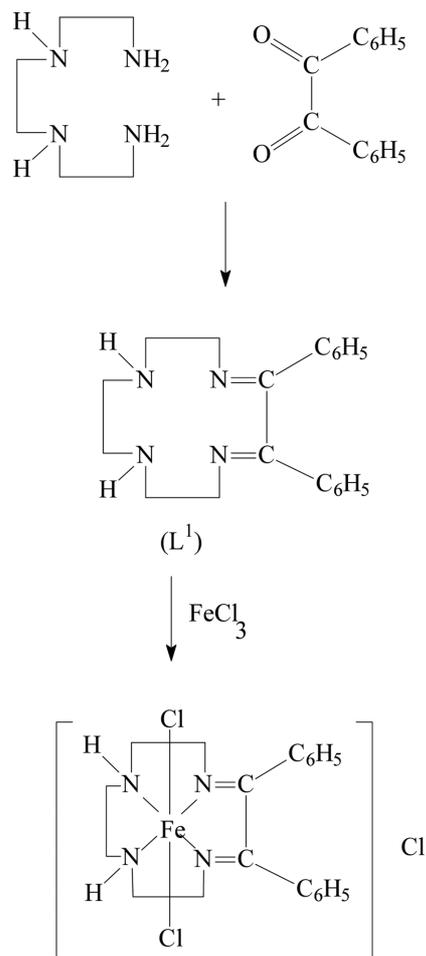


Fig. 3. Synthesis of Fe(III) complex of ligand L^1 .

recorded in DMSO-d_6 and showed NH proton signal at $\delta 8.3$ ppm. The signal at $\delta 7.1$ for $[\text{Cu}(L^1)\text{Cl}_2]$ complex is due to phenyl group. A broad band at about $\delta 1$ to $\delta 2$ ppm indicates the presence of methylene protons present in the complex. Girgis *et al.*¹⁹ have reported that a broadening band is the characteristic of Cu(II) complexes. In our case too, a broad band at $\delta 1$ to $\delta 2$ ppm has been observed.

TGA

The thermogram of $[\text{Cu}(L^1)\text{Cl}_2]$ can be divided into three major portions showing weight loss of various components. The first step shows the weight loss of about 16% between 137 to 310 $^\circ\text{C}$ which compares well with the calculated value of 15.7% corresponding to two chlorine atoms. The second step runs through 310 to 510 $^\circ\text{C}$ showing a weight loss of nearly 39.6% which is equal to the benzil molecule. The third step (33%) corresponds to the loss of triethylenetriamine molecule compared to 32.8%

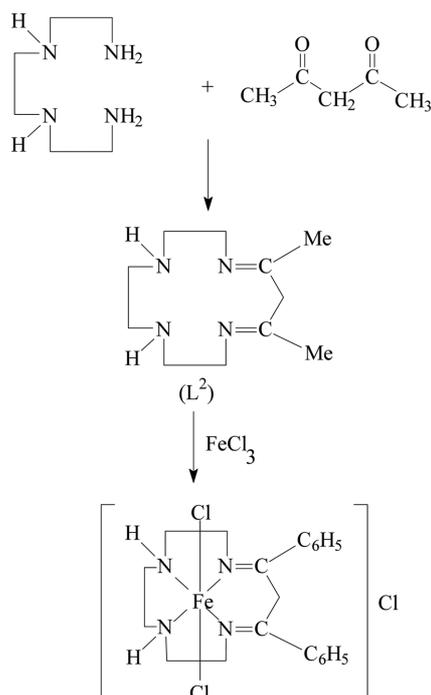


Fig. 4. Synthesis of Fe(III) complex of ligand L^2 .

in the temperature range of 510 to 939 °C. In the end, the residue left is copper metal²⁰ (14%).

EPR spectra

From the EPR spectra of the polycrystalline copper(II) complexes at room temperature, their g_{\parallel} , g_{\perp} and axial symmetry parameter ($G = g_{\parallel} - 2g_{\perp} - 2$) have been calculated. The complexes did not show hyperfine splitting at room temperature. It may be attributed to strong dipolar and exchange interaction between copper(II) ions in the unit cell. The room temperature g values of $[\text{Cu}(L^1)\text{Cl}_2]$ ($g_{\parallel} = 2.2377$ and $g_{\perp} = 2.076765$) and $[\text{Cu}(L^2)\text{Cl}_2]$ ($g_{\parallel} = 2.223$ and $g_{\perp} = 2.083$) suggest that $d_{x^2-y^2}$ may be the ground state for both the complexes.

In trans octahedral complex the two Cl atoms are bonded to metal through z axis. But in cis octahedral complex the N atoms are bonded to the metal through z axis. N atom is hard donor than Cl. It has been reported²¹ earlier that if the hard donor atom is bonded to the Cu through z axis then ground state is d_z^2 orbital and if soft donor atom is bonded to the Cu(II) through z axis then ground state is $d_{x^2-y^2}$. In our case, it has been established from epr spectra that the ground state is $d_{x^2-y^2}$ orbital. It means that the two Cl atoms are bonded to the metal through z axis.

The G value measures the exchange interaction between copper centers in the polycrystalline solid. If $G > 4$,

exchange interaction is negligible while $G < 4$, indicates considerable exchange interaction in the solid complexes.²² For $[\text{Cu}(L^1)\text{Cl}_2]$ and $[\text{Cu}(L^2)\text{Cl}_2]$ the G values are 3.096 and 2.69 respectively, which indicate a considerable exchange interaction in the complexes. It is known that if the G value is less than 4.0, the ligand forming the copper(II) complex is regarded as strong field ligand while a value of G greater than 4.0 indicates weak field ligand. Since the G values are fairly lower (3.096 and 2.69) than 4 they are indicative of strong field strength for the ligands.

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