



## Synthesis, Spectral and Electrochemical behavior of Co (II) Complexes with New Schiff Base Ligands in Non-aqueous media at the Surface of Solid Electrode

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### ABSTRACT

A series of Co(II) complexes with new Schiff bases ligand and various amino acids in aqueous methanol solution have been synthesized. The synthesized Schiff bases and their Co(II) complexes have been characterized by various sophisticated analytical instruments for their magnetic susceptibility, thermal, spectral and electrochemical analysis. These ligands act as tetradentate species with N and O as donor atoms and facilitate the metal to center. The plausible octahedral structures have been allotted to these complexes. A typical cyclic voltammogram obtained in the potential range of -1.6 V to +1.6 V (Ag | AgCl) on GCE for [Co<sub>2</sub>(CMAIPA)(H<sub>2</sub>O)<sub>4</sub>] using in TEAP an irreversible oxidation peak at ~ 0.850 V and another quasi reversible reduction peak at ~-1.250 V are observed.

**Keywords:** Orthophthalaldehyde; Schiff-bases; Co(II) complexes; Spectral studies; Electrochemical studies and antimicrobial activity.

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## **INTRODUCTION**

Coordination chemistry is one of the broad areas that cover various applications [1-3]. This field has now been emerged into various areas of science and technology like, analytical chemistry, medicinal chemistry, metallurgy, and industrial chemistry, so on and so forth [4]. It is a well-known fact that, alkali, alkaline earth metal complexes of crown ethers, acyclic and cyclic ligands play an important role in the biological systems [5].

Among coordination compounds, those with Schiff bases were found to have numerous crucial capacities such as photosynthesis and transport of oxygen in mammalian and other respiratory frameworks [6]. On the other hand, transition metal complexes with a wide assortment of Schiff bases having donor atoms such as nitrogen and oxygen around the metal atoms have been utilized as catalysts for different natural processes [7, 8]. In our search for the versatile aldehydes to design new Schiff-base ligands, we turned our attention towards the combination of orthophthalaldehyde and amino acids as there were no reports available as on time

Orthophthalaldehyde (OPA) can be utilized as a starting material for condensation reactions. The Schiff base compounds can be synthesized from OPA by template or non-template synthesis, owing to the association of two aldehyde groups. It is also used as an intermediate in synthesis of pharmaceuticals, medicines and other organic compounds [9]. OPA is a good chemical sterilant that received FDA clearance in October 1999. It has a superior mycobactericidal activity in comparison with glutaraldehyde. OPA is effective against a wide range of microorganisms, including glutaraldehyde-resistant mycobacterium and *Bacillus subtilis* spores. It can destroy all viable bacteria within 5 minutes of exposure [10]. OPA is convenient and easy to use since it does not produce noxious fumes. However, exposure to its vapours may be irritating to the respiratory tract and eyes[11]. OPA is used as tanning agent in leather industry [12]. It is also useful for sterilization of endoscope instruments, thermometers, which cannot be sterilized by heating [13].

Orthophthalaldehyde is used for the synthesis of acyclic, macro cyclic and other condensation products. Reactions of OPA with nucleophiles were extensively reviewed by Zuman et.al., [24]. Most of the substituted benzaldehydes and di-ketones showed a limited reactivity with weak nucleophiles [15]. Acetalization of OPA was achieved in methanol containing triethylamine as a base using  $TiCl_4$  as a catalyst [16]. Under preparative conditions in cold DMSO, reaction of OPA with ammonia to give isoindole derivative which subsequently undergone dehydration, rearrangement and afforded phthalimidine [17]. In ethanol, reaction of primary amines with OPA at 0 °C and produced both imines and diimines

However, 2-alkylisoindolines were formed selectively when OPA was treated with amines in the presence of tetracarbonylhydrido ferrate as reducing agent [18]. Reaction of OPA with hydrazine yielded a fluorescent species at pH 4-6 [19].

Nilesh et al synthesized and characterized Schiff base complexes of Co(II), Ni(II), Cu(II), and Cd(II) with bis(acetophenone) ethylenediamine and 5-chlorosalicylideneaniline or 5-bromo salicylideneaniline [20],

## **EXPERIMENTAL**

In the present investigations, Co(II) complexes were synthesized by treating the above four Schiff base ligands with cobalt acetate. The Co(II) complexes were characterized by elemental, UV, IR, (<sup>1</sup>H & <sup>13</sup>C) NMR and mass spectral analysis.

### **Synthesis of Schiff bases:**

All the organic solvents, amino acids and metal salts used in this study were of AR grade. All the studies were carried out using double distilled water. All the four ligands used in this work were prepared and characterized by various techniques such as elemental analysis and spectral analysis.

The ligands CEIMPA, CPMIMP, DCPIMP and CMAIPA were synthesized by treating orthophthalaldehyde (OPA) with L-Alanine, Methyldopa, Sodium glutamate, and Glycyl-Glycine respectively in 1:2 ratios.

#### **1. 2-((E)-1-(2-((1-carboxyethyl)imino)methyl) phenyl) methylidene) amino propanoic acid (CEIMPA).**

L(+)-Alanine (0.02 mol, 0.58 g), dissolved in MeOH (10 ml), was added slowly with constant stirring to an alcoholic solution (20 ml) of KOH (0.36 g). The solution was stirred for an hour and then filtered. To the filtrate orthophthalaldehyde (0.01 mol, 1.32 g) dissolved in MeOH (20 ml) was added drop wise with constant stirring. The resulting yellowish solution was evaporated under reduced pressure and kept at room temperature for two days. The yellow precipitate (CEIMPA) formed was suction filtered, washed with cold alcohol and diethyl ether. It was recrystallized from ethanol. The product was found to be pure in 2:8 mixtures of methanol using TLC.

#### **2. 2-((E)-1-(2-((1-carboxy-2-(3,4-dihydroxyphenyl)-1-methylethyl) imino) methyl)phenyl)methylidene)amino)3-(3,4-dihydroxyphenyl)-2-methyl propanoic acid (CPMIMP).**

Methyldopa (4.22 g, 0.02 mol) is dissolved in methanol and added to alcoholic KOH

solution. The mixture was stirred for about 1 hour and filtered. To the above collected filtrate, methanolic solution of orthophthalaldehyde (0.01 mol, 1.32g) was added with constant stirring at room temperature. The green precipitate formed was stirred for an hour. The precipitate was washed with ether and recrystallized twice from methanol. The crystals obtained were filtered, washed with diethyl ether. The product gave only one spot upon LC in 3:7 ethylacetate and n-hexane.

**3. 2-[(E)-1-(2-[[1,3dicarboxypropyl]imino]methyl)phenyl)methylidene] amino} pentanedioic acid (DCPIMP).**

A saturated solution of sodium glutamate (3.38g, 0.02 mol) in methanol and was added with 20 mL MeOH solution containing 5 mol KOH by constant stirring at Room temperature. The solution was stirred on a water bath for an hour and then filtered. The filtrate was added drop wise to 10 ml of MeOH solution of orthophthalaldehyde (0.01 mol, 1.32 g) on water bath for two hours, filtered and left to stand. On standing for another six hours, the dark green color solid product formed was collected by vacuum filtration, washed with a minute quantity of diethyl ether and dried in vacuum. The powder formed (DCPIMP) gave only one spot with TLC in 8:2 mixture of ethylacetate and chloroform

**4. 2-({2-[(E)-1{2-[(carboxymethyl)amino]-2-oxoethyl}imino)methyl] phenyl} methylidene)amino}acetyl}amino)acetic acid (CMAIPA).**

Glycyl-glycine (0.64 g, 0.02 mol) dissolved in methanol (10 mL) was added slowly to methanolic KOH solution The solution was stirred for half an hour and then filtered. Orthophthalaldehyde (1.32 g, 0.01 mol) dissolved in MeOH (20 ml) was added drop wise to the filtrate. The resulting reaction mixture was evaporated under reduced pressure and stored for two hours at room temperature. The precipitate obtained was washed with alcohol. The crystals were suction filtered, washed with diethyl ether and dried in vacuum. The product was found to be TLC pure in 7:3 mixture of methanol and chloroform.

The physical properties of Schiff base ligands have been presented in Table-1

**Table 1:** Physical data of Schiff base ligands.

S. No.	Ligand	M. P. (°C)	Color	Yield (g)
1.	CEIMPA	195	Pale yellow	3.042 (78 %)
2.	CPMIMP	200	green	3.713 (88%)
3.	DCPIMP	185	Dark green	2.91 (77 %)
4.	CMAIPA	160	Dirty White	3.65 (80 %)

**Synthesis of Schiff base Co(II) complexes:**

Due to the similarity in structure and properties of the CEIMPA, CPMIMP, CEIMAP, and CMAIPA, a general method of preparation of their cobalt complexes was used. The four ligands and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were used as starting materials.

An arrangement of metal salt (0.005 mol) in methanol (25 ml) was included to an arrangement of the naturally arranged ligand (0.005 mol) in methanol (30 ml) with steady blending. The response blend was refluxed on a water bath for two hours until solid isolated out. The solids were suction filtered, purified by repeated washing with chloroform first and methanol next and dried in vacuum over anhydrous calcium chloride (Yield 70-80 %). Table 2a shows the physical properties of Schiff base Co(II) complexes

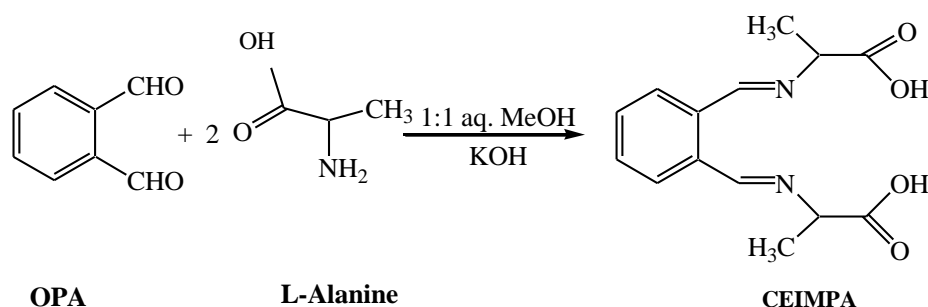
**Table 2a:** Physical data of Schiff base Co(II) complexes.

S. No.	Co(II) complex formed	Reaction time (min)	Decomp. temp. ( $^{\circ}\text{C}$ )	Color	Yield (g)
1	$[\text{Co}(\text{CEIMPA})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	75	248	Pale pink	0.357 (80%)
2	$[\text{Co}(\text{CPMIMP})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	90	260	Light pink	0.500 (78%)
3	$[\text{Co}(\text{DCPIMP})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	105	245	Dark pink	0.396 (76 %)
4	$[\text{Co}_2(\text{CMAIPA})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$	95	255	Light brown	0.500 (80 %)

## RESULTS AND DISCUSSION

### Characterization of Ligands

In the present investigations four new Schiff base ligands were synthesized by condensation of orthophthalaldehyde with different amino acids and peptides in the basic medium. These ligands were used for the synthesis of metal complexes. The synthesis of CEIMPA treating OPA with L-Alanine in 1:2 ratios is presented in Scheme-1.



**Scheme- 1: Synthesis of CEIMPA.**

### a) Elemental analysis:

The percentage of carbon, hydrogen, and nitrogen of all these ligands were determined experimentally using CHN analyzer. The physical and analytical data (Table-2b) is in good concurrence with the proposed molecular formulae.

**Table 2b:** Analytical data of Schiff bases.

S. No.	Schiff base	Molecular Formula	Found (Calcd.)%		
			C	H	N
1.	CEIMPA	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	60.76 (60.86)	5.74 (5.84)	10.01 (10.14)
2.	CPMIMP	C <sub>28</sub> H <sub>28</sub> N <sub>2</sub> O <sub>8</sub>	64.55 (64.61)	5.38 (5.42)	5.26 (5.38)
3.	DCPIMP	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub>	55.10 (55.12)	5.08 (5.14)	7.10 (7.16)
4.	CMAIPA	C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub>	53.04 (58.84)	5.01 (4.94)	15.48 (15.46)

**b) Mass spectral analysis:**

The mass spectra of Schiff base ligands viz., CEIMPA, CPMIMP, DCPIMP, and CMAIPA showed the molecular ion peaks at m/z (M<sup>+</sup>) 276(12%), 520(9%), 392(5%), and 362(14%) respectively. This data is in good agreement with the respective molecular formulae. The FAB mass spectrum of CEIMPA shows a parent peak at m/z 276(12%), which supports the formation of 1:2 condensed products from orthophthalaldehyde and L-alanine corresponding to the molecular formula C<sub>14</sub>H<sub>16</sub> N<sub>2</sub>O<sub>4</sub>. The FAB mass spectrum shows major fragments at m/z values of 276(15%), 270(4%), 264(10%), 252(9%), 208(18%), 197(5%), 192(5%), 121(9%), 116(12%) and 94(10%) respectively.

**c) Infrared spectral analysis:**

A strong intensity band is appeared in the IR spectra of Schiff base ligands, in the range of 1643-1618 cm<sup>-1</sup> which is attributed to  $\nu_{C=N}$  provides strong evidence for the condensation of phthalaldehyde with the -NH<sub>2</sub> group of amino acids in all the ligands [21]. The spectra of the ligands also contain characteristic bands in the range of 1720-1710 cm<sup>-1</sup> of  $\nu(C=O)$  belongs to free carboxyl group of amino acids [22]. Aromatic ring stretching frequencies were observed for all the ligands in the range of 1446-1385 cm<sup>-1</sup> and wagging frequencies were observed in the range of 3098-3010 cm<sup>-1</sup> [23]. The infrared spectral data of all these ligands is presented in table 3.

**Table 3: Infrared spectral data of Schiff base ligands.**

S. No.	Ligand	Selected IR bands (cm <sup>-1</sup> )			
		$\nu_{C=N}$	$\nu_{NH}/\nu_{OH}$ *	$\nu(C=O)$ of COOH/Amide*	Aromatic
1.	CEIMPA	1640	-	1720	3065/1420
2.	CPMIMP	1620	3425*	1718	3040/1385
3.	DCPIMP	1619	-	1715	3041/1403
4.	CMAIPA	1643	3318	1720, 1632*	3010/1440

**d) <sup>1</sup>H NMR spectral analysis:**

In the spectra of all the ligands a singlet was appeared from CH=N protons (2H) in the range of 8.04-8.24  $\delta$  suggest the condensation of OPA with amino acids [14]. This fact was also supported by the disappearance of peaks around 9.98  $\delta$  corresponding to aldehydic protons. Multiples were observed in the range of 6.10-8.00  $\delta$  have been assigned to the aromatic protons [25]. The individual <sup>1</sup>H peak positions of selected protons of all the ligands are presented in table 4.

**Table 4:** <sup>1</sup>H NMR spectral data of ligands.

S. No.	Ligand	<sup>1</sup> H NMR peak position ( $\delta$ ppm)
1.	CEIMPA	11.25(2H, s, COOH), 8.18(2H, s, CH=N), 7.20-7.68(4H, m, Ar-H), 4.18(4H, q, CH), 1.26(6H, d, CH <sub>3</sub> ).
2.	CPMIMP	11.40(2H, s, COOH), 8.04(2H, s, CH=N), 6.60-7.60 (10H, m, Ar-H), 5.38(4H, s, Ar-OH), 4.09(2H, d, CH), 2.50-2.69(2H, q, CH), 1.72(6H, d, CH <sub>3</sub> ).
3.	DCPIMP	10.59(4H, s, COOH), 8.10(2H, s, CH=N), 7.35-7.52(4H, m, Ar-H), 4.26(2H, t, CH), 3.52(4H, t, CH <sub>2</sub> ), 2.47-2.49 (4H, q, CH <sub>2</sub> ).
4.	CMAIPA	11.56(2H, s, COOH), 8.19(2H, s, CH=N), 7.22-7.54(4H, m, Ar-H), 5.83(4H, s, CH <sub>2</sub> ), 5.60(2H, s, NH), 4.25(4H, d, CH <sub>2</sub> ),

**e) <sup>13</sup>C NMR spectral analysis:**

<sup>13</sup>C NMR spectra of all the ligands contain signals in the range of 152.5-167.4  $\delta$  indicating the presence of carbon, which is doubly bonded to nitrogen [26]. It indicates the conformity of condensation between OPA and amine group. Every ligand except **4** show <sup>13</sup>C NMR signals around 39.9-70.1 $\delta$  attributed to asymmetric  $\alpha$ -methylene carbons. The spectra of every ligand contain signals in the range of 176.0-180.4  $\delta$  corresponding to carboxyl carbon of amino acid [27, 28]. The spectrum of ligand **4** contains a signal at 171.2  $\delta$  indicating the presence of ketonic carbon [29]. Similarly, it also contains a signal at 48.5  $\delta$  corresponding to methylenic carbon adjacent to nitrogen atom, depicting that the presence of N-CH<sub>2</sub> linkage [30]. The aryl carbons are resonated in the range of 117.8-144.6  $\delta$  [31]. The <sup>13</sup>C NMR spectral data of all the ligands are given in table 5.

**Table 5:** <sup>13</sup>C NMR spectral data of ligands.

S. No.	Ligand	<sup>13</sup> C NMR peak position ( $\delta$ ppm)
1.	CEIMPA	16.1(2C, CH <sub>3</sub> ), 70.1(2C, CH), 132.8, 133.9, 136.4 (6C, Ar-C), 163.7 (2C, CH=N), 177.4 (2C, COOH)
2.	CPMIMP	24.1 (2C, CH <sub>3</sub> ), 39.9 (2C, CH), 58.7(2C, CH <sub>2</sub> ), 68.1 (2C, CH) 119.8, 120.0, 126.2, 132.2, 136.1, 144.2 (18C, Ar-C),

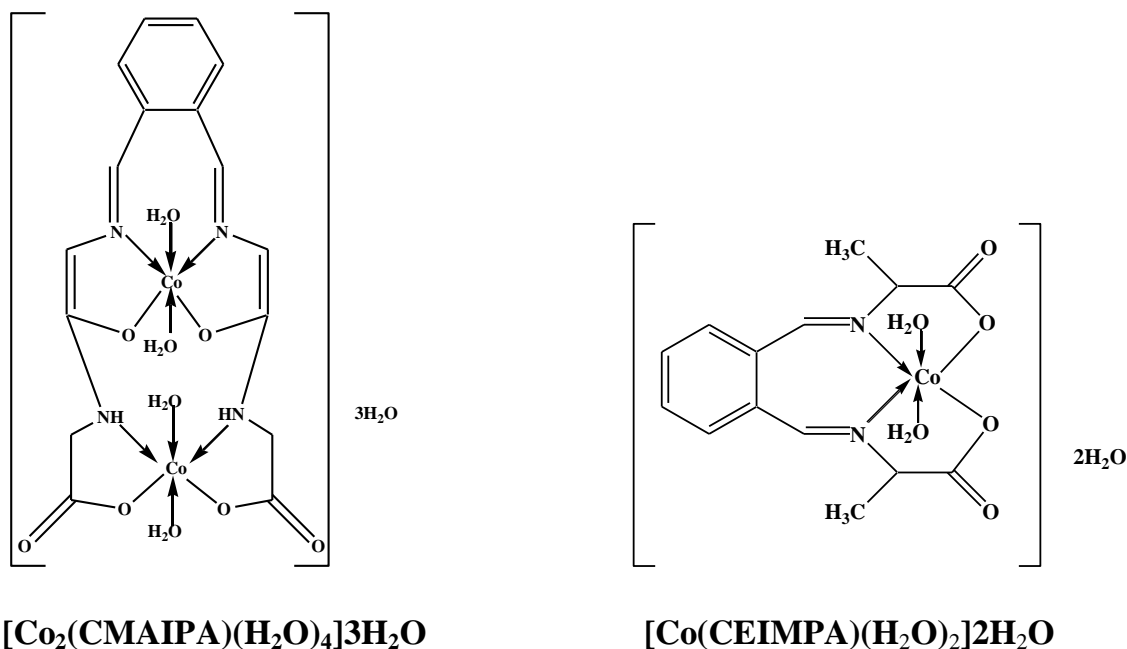
		158.2 (2C, CH=N), 178.1 (2C, COOH).
3.	DCPIMP	32.0(4C, CH <sub>2</sub> ), 65.2 (2C, CH), 132.8, 133.9, 136.8 (6C, Ar-C), 167.4(2C, CH=N), 179.4, 180.2 (4C, COOH).
4.	CMAIPA	48.5 (2C, CH <sub>2</sub> ), 58.3 (2C, CH <sub>2</sub> ), 130.6, 132.3, 136.4 (6C, Ar-C), 163.7(2C, CH=N), 171.2 (2C, C=O), 180.4 (2C, COOH).

### Characterization of Co(II) Complexes:

Co(II) with d<sup>7</sup> configuration forms complexes mostly of octahedral and tetrahedral geometry [26-30]. Octahedral complexes are typically pale red or purple, while many tetrahedral ones are intense blue.

#### a) Physical and analytical data:

The general synthetic approach employed in the synthesis of new hexa-coordinated Co(II) compounds in the present investigations, involves the reaction of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with newly synthesized four ligands separately. The percentages of carbon, hydrogen and nitrogen were determined using CHN analyzer. The percentage of cobalt in Co(II) complexes was determined by literature method [32]. The physical and analytical data (Table-2 a, b) is in good accordance with the proposed molecular formulae viz., [Co(II)(L)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O for complexes 1-3 and [Co<sub>2</sub>(II)(L)(H<sub>2</sub>O)<sub>4</sub>]<sub>3</sub>H<sub>2</sub>O for complex 4.



**Scheme-2:** Structure of Co(II) complexes.



#### b) Mass spectral analysis:

The proposed molecular formula of a Co(II) complex is confirmed by the mass spectral analysis by comparing its molecular formula weight with m/z value. The mass spectra contain



molecular ion peaks at  $m/z$  ( $M^+$ ) 404 538 570 and 630. This data is in good concord with the respective molecular formulae.

### **c) Thermal analysis:**

The thermogravimetric analysis data (Table-7) of the Co(II) complexes is obtained using less than 10 mg of the compound. The TG-DTG curves of Co(II) complexes of CEIMPA and CMAIPA.

The thermograms of all the Co(II) complexes show three important clear stages of decomposition, the first two corresponding to loss of water molecules i.e., dehydration and the third corresponding to decomposition of the complex with the loss of organic moiety. Lattice water will usually be lost at temperatures ranging from 70-125 °C whereas coordinated water requires a temperature of 155-200 °C or above. The thermograms of all Co(II) complexes show initial weight loss in the temperature range of 89.9-112.0 °C. Also, the DSC curve of these complexes shows an endothermic peak in the above temperature range further giving evidence for the presence of water molecules. The loss of water molecules in this temperature range indicates that they are present as lattice-held water [37]. The percentage weight loss in this temperature range indicates that there are two water molecules each in Co(II) complexes of CEIMPA and DCPIMP; the Co(II) complexes of CPMIMP have one water molecule and the complex of CMAIPA has three water molecules as lattice-held water. The thermograms of all the Co(II) exhibit weight loss in the temperature range of 178.5-196.0°C. [33,34].

### **d) Infrared Spectra:**

The infrared and far infrared spectra of the complexes were recorded in the wave number region of 4000-200  $\text{cm}^{-1}$  (Table 6). The strong and broad absorption in the 3440-3590  $\text{cm}^{-1}$  region for all the complexes substantiates the presence of coordinated or lattice water molecules in the complexes. In addition, these complexes also show a non-ligand band in the region of 710-760  $\text{cm}^{-1}$  which indicates the presence of coordinated water molecules in these complexes. All the complexes show a strong band at 1600-1630  $\text{cm}^{-1}$ , which is assigned to the  $\nu(\text{C}=\text{N})$  stretching vibration. The disappearance of characteristic  $\nu_{\text{COOH}}$  of carboxylate of amino acid in all ligands at 1720  $\text{cm}^{-1}$  and the appearance of two new absorption bands around 1530-1590, 1340-1396  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{asy}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  in all the complexes supports the participation of carboxylate oxygen of carboxyl group of amino acid in the chelation.

In the IR spectra of the Co(II) complexes of CEIMAP bands due to  $\nu\text{N-H}$  of ring were not changed and indicated the non-coordination of ring nitrogen atoms to the metal ions. On

the other hand, in the case of complex 4 that formed with CMAIPA, the observed negative shift of  $\nu_{\text{N-H}}$  from  $3318\text{ cm}^{-1}$  to  $3158\text{ cm}^{-1}$  describes the coordination of amide nitrogen to Co(II) [40]. In addition to this, the disappearance of  $\nu(\text{C=O})$  of the  $\beta$ -diketone part and the appearance of new band at  $1570\text{ cm}^{-1}$  assignable to  $\nu(\text{C-O})$  which suggest that the carbonyl group involved in coordination in the enol form through deprotonation. This situation indicates the formation of binuclear Co(II) complex using the coordination of nitrogen from C=N of Schiff base and NH of amide group and the oxygens from amide and carboxyl groups of CMAIPA.

**Table 6:** Infrared spectral data of Co(II) complexes.

S. No.	Co(II)Complexes	$\nu$ (C-N)	$\nu$ NH	$\nu$ (C=N) ring	$\nu$ (COO-)	$\nu$ (M- H <sub>2</sub> O)	$\nu$ (M- N)	$\nu$ (M- O)
1	[Co(CEIMPA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	1610	-	-	1530, 1366	751	535	450
2	[Co(CPMIMP)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	1608	-	-	1580, 1350	745	528	440
3	[Co(DCPIMP)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	1609	-	1715**	1543, 1349	725	508	430
4	[Co <sub>2</sub> (CMAIPA)(H <sub>2</sub> O) <sub>4</sub> ] <sub>3</sub> H <sub>2</sub> O	1630	3228	1570*	1583, 1383	725	510	470
* $\nu(\text{C-O})$ of carbonyl    ** $\nu(\text{C=O})$ of COOH								

**e) <sup>1</sup>H NMR spectral analysis:**

<sup>1</sup>H NMR spectral comparison between ligands and Co(II) complexes was made to confirm the binding nature of ligands to Co(II) ion. The integral intensities of each signal in the <sup>1</sup>H NMR spectra of ligands and Co(II) complexes were found to agree with the number of different types of protons present. In all the ligands signals due to CH=N protons in the range of 8.04-8.24  $\delta$  [9] and in the spectra of Co(II) complexes these signals were observed slightly in the up field regions of 8.14-8.42  $\delta$  confirming the coordination of nitrogen atom [35] of this group to Co(II) ion. The ligands containing carboxylic groups show resonance absorptions between 10.17 and 11.80  $\delta$  which is assignable to the carboxylic proton, disappearance of this peak in all the Co(II) complexes indicating the involvement of carboxylate ion oxygen in chelation through deprotonation. In the spectrum of ligand 4, a

signal is appeared at 5.83  $\delta$  corresponding to CH<sub>2</sub> protons. There is an up field shift that was observed at this peak position and appeared at 4.78  $\delta$  and integration showing for only two protons indicating the coordination of carbonyl oxygen to the metal ion in the enol form by deprotonation. There is a peak appeared at 5.6  $\delta$  corresponding to NH protons in this ligand, this band shifted to down field and appeared at 6.0  $\delta$  upon coordination in Co(II) complex. This feature was already seen in the IR spectra to form a binuclear Co(II) complex. The above facts strongly support that there is coordination through nitrogen atom of CH=N group, oxygen of the carboxylic group [36] and NH group [37]. In the spectra of ligands 3 and 4 a signal is appeared around 5.40  $\delta$  corresponding to phenolic protons which show no variation in the peak positions of the Co(II) complexes. There is no appreciable change in the peak positions corresponding to aromatic protons [38]. The individual <sup>1</sup>H peak positions of selected protons of all the Co(II) complexes are shown in table 7. The <sup>1</sup>H NMR spectra of [Co(CEIMPA)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O and [Co<sub>2</sub>(CMAIPA)(H<sub>2</sub>O)<sub>4</sub>]<sub>3</sub>H<sub>2</sub>O

**Table 7:** <sup>1</sup>H NMR spectral data of Co(II) complexes.

S. No.	Co(II) Complexes	<sup>1</sup> H NMR peak position ( $\delta$ ppm)
1	[Co(CEIMPA)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	8.42(2H, s, CH=N), 7.20-7.68(4H, m, Ar-H), 4.17(4H, q, CH), 1.26(6H, d, CH <sub>3</sub> ).
2	[Co(CPMIMP)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	8.14(2H, s, CH=N), 6.62-7.61(10H, m, Ar-H), 5.38(4H, s, Ar-OH), 4.08(2H, d, CH), 2.50-2.69(2H, q, CH), 1.71(6H, d, CH <sub>3</sub> ).
3	[Co(DCPIMP) (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O	10.57(4H, s, COOH), 8.24(2H, s, CH=N), 7.34-7.51(4H, m, Ar-H), 4.26(2H, t, CH), 3.54(4H, t, CH <sub>2</sub> ), 2.47-2.49 (4H, q, CH <sub>2</sub> ).
4	[Co <sub>2</sub> (CMAIPA)(H <sub>2</sub> O) <sub>4</sub> ] <sub>3</sub> H <sub>2</sub> O	8.25(2H, s, CH=N), 7.22-7.54(4H, m, Ar-H), 6.0(2H, s, NH), 4.78(4H, s, CH <sub>2</sub> ), 3.85(4H, d, CH <sub>2</sub> ).

**f) <sup>13</sup>C NMR spectral analysis:**

<sup>13</sup>C NMR signals for the Co(II) complexes are assigned by the comparison with the spectra of corresponding ligands and the chemical shifts in <sup>13</sup>C NMR spectra revealed a consistent pattern. The spectra of all the ligands contain signals in the range of 152.5-168.4  $\delta$  due to the presence of carbon that is doubly bonded to nitrogen [21]. However, in the spectra of Co(II) complexes, a down field shift in peak position was observed in the range of 172.6-178.2  $\delta$  [39] indicating the coordination of Schiff base nitrogen to the metal ion. The spectra of all the ligands contain signals in the range of 176.0-180.4  $\delta$  indicating the presence of

carboxyl carbon. However, the spectra of Co(II) complex showing a down field shift in peak position was observed in the range of 190.3-198.2  $\delta$  [36]. This fact confirms that all the ligands coordinate through the oxygen atoms of carboxylate ions. Appreciable changes in peak positions were not observed with respect to aryl carbons and carbons adjacent to oxygen atom [40]. Further in the spectra of complex 4, the down field of shifting of amide carbonyl (C-O) describes the coordination of this site to the metal ion as mentioned. However, the enolic carbon peak shifted to 115.3  $\delta$  suggesting that coordination of C-O group to the metal centre by deprotonation. The individual  $^{13}\text{C}$  peak positions of carbon atoms of all the Co(II) complexes are shown in the table 8. The  $^{13}\text{C}$  NMR spectra of  $[\text{Co}(\text{CEIMPA})(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$  (Complex-1) and  $[\text{Co}_2(\text{CMAIPA})(\text{H}_2\text{O})_4]3\text{H}_2\text{O}$  (Complex-4) are presented in fig 2-5

**Table 8:**  $^{13}\text{C}$  NMR spectral data of Co(II) complexes.

S. No.	Co(II) Complexes	$^{13}\text{C}$ NMR peak position ( $\delta$ ppm)
1	$[\text{Co}(\text{CEIMPA})(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	16.2(2C, $\text{CH}_3$ ), 37.8(2C, C- $\text{CH}_2$ ), 70.1(2C, CH), 132.7 133.9, 136.5(6C, Ar-C), 178.2(2C, CH=N), 198.2(2C, $\text{COO}^-$ ).
2	$[\text{Co}(\text{CPMIMP})(\text{H}_2\text{O})_2]\text{H}_2\text{O}$	24.3 (2C, $\text{CH}_3$ ), 40.0 (2C, CH), 58.6(2C, $\text{CH}_2$ ), 68.3 (2C, CH) 119.9, 120.2, 126.1, 132.2, 136.0, 144.1 (18C, Ar-C), 174.2 (2C, CH=N), 194.1 (2C, $\text{COO}^-$ ).
3	$[\text{Co}(\text{DCPIMP})(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	32.2(4C, $\text{CH}_2$ ), 65.1 (2C, CH), 132.9, 134.2, 136.8 (6C, Ar-C), 176.5(2C, CH=N), 179.5(2C, COOH), 196.2 (4C, $\text{COO}^-$ ).
4	$[\text{Co}_2(\text{CMAIPA})(\text{H}_4)]3\text{H}_2\text{O}$	58.5 (2C, $\text{CH}_2$ ), 115.3 (2C, C=C), 130.6, 132.8, 136.3(6C, Ar-C), 171.2 (2C, C-O), 173.3(2C, CH=N), 196.3 (2C, $\text{COO}^-$ ).

#### g) Electronic spectral analysis:

The electronic spectra of Co(II) complexes with ligands show three d-d move groups within the locales 1040-1090, 518-540 and 426-494 nm allotted to  $^4\text{T}_{2g} \leftarrow ^4\text{T}_{1g}$  (F) ( $\nu_1$ ),  $^4\text{A}_2 g \leftarrow ^4\text{T}_{1g}$  (F) ( $\nu_2$ ) and  $^4\text{T}_{1g}$  (P)  $\leftarrow ^4\text{T}_{1g}$  (F) ( $\nu_3$ ) moves separately. The octahedral geometry of Co(II) complexes is advance backed by  $\nu_2$  to  $\nu_1$  proportion lying within the range of 2.00-2.08. This demonstrates the octahedral geometry for Co(II) complex-4

#### h) Structures of the complexes:

On the basis of analytical and spectral data, octahedral structures have been tentatively proposed for all the Co(II) complexes (Scheme-2). The complexes 1-3 are in mononuclear form whereas the complex 4 is a binuclear complex.

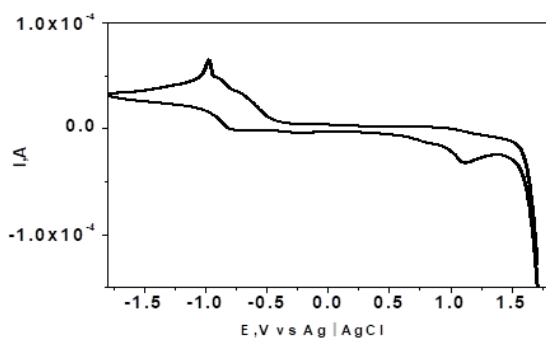
#### i) Electrochemical Studies

A typical cyclic voltammogram obtained in the potential range of -1.6 V to +1.6 V (Ag | AgCl) on GCE for [Co<sub>2</sub>(CMAIPA)(H<sub>2</sub>O)<sub>4</sub>] is presented in Figure 1 and 2. An irreversible oxidation peak at ~ 0.850 V and another quasireversible reduction peak at ~ -1.250 V are observed. The cathodic response is not very clean but seems to be arising from more than one reducible sites. The effect of scan rate, concentration, potential settings, etc on the cyclic voltammetric profiles suggest that the two electron transfer processes are diffusion controlled and that they belong to two different electrophores.

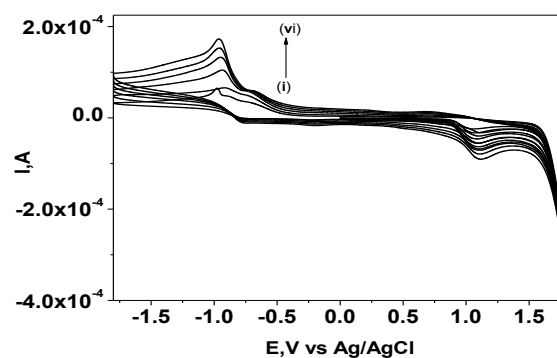
A comparison of the cyclic voltammograms of the complexes with those of the corresponding ligands indicates that the electron transfer processes due to reduction of azomethine group of the ligand framework is slightly more cathodic. Free Co(II)|Co(III) redox couple appears at +1.59 V and Co(II)|Co(0) at -0.54V vs Ag | AgCl in aqueous media. But when Co(II) is complexed, the Co(II)/Co(0) couple has a reduction potential more cathodically shifted such that it might join the hydrogen evaluation. We propose that the multiple (shoulder like) cathodic peaks are due to the reduction of Co(II) and also that to the azomethine. In Figure 3 are shown the cyclic voltammogram of [Co<sub>2</sub>(CMAIPA)(H<sub>2</sub>O)<sub>4</sub>] at various scan rates on the peak current. The fact that both cathodic and anodic current peaks are linear for the square root of scan rate suggests diffusion controlled electron transfer processes. The other Co<sub>2</sub>L<sub>2</sub><sup>1</sup> behave similarly in DMF. Important electrochemical data such as E<sub>p</sub>, i<sub>p</sub>, α<sub>na</sub>, k<sub>h</sub><sup>0</sup>, D, etc, of all Co<sub>2</sub>L<sub>2</sub><sup>1</sup> into Table 9.

**Table 9: Voltametric data of Co<sub>2</sub>L<sub>2</sub><sup>1</sup> complex**

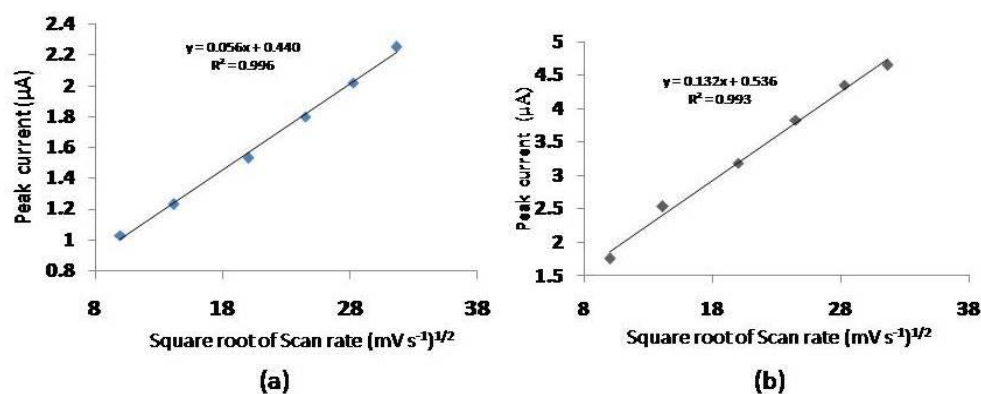
Scan rate (mVs <sup>-1</sup> )	-E <sub>p</sub> (V)	α <sub>na</sub>	k <sub>h</sub> <sup>0</sup> x10 <sup>9</sup> (cm <sup>2</sup> /s)	D <sub>o</sub> x 10 <sup>6</sup> (cm <sup>2</sup> /s)
100	1.056	0.071	0.951	1.28
200	1.075	0.079	0.959	5.41
400	1.082	0.531	0.963	3.19
600	1.107	0.090	0.996	9.30
800	1.108	0.095	1.003	9.91
1000	1.122	0.096	1.012	7.88



**Figure 1:** Cyclic voltammogram of  $[\text{Co}_2(\text{CMAIPA})(\text{H}_2\text{O})_4]$  ( $3.06 \times 10^{-4}$  M) in DMF on GCE at scan rate,  $0.1 \text{ Vs}^{-1}$ , with TEAP (0.1 M)



**Figure 2:** Cyclic voltammograms of  $[\text{Co}_2(\text{CMAIPA})(\text{H}_2\text{O})_4]$  ( $3.06 \times 10^{-4}$  M) in DMF on GCE at different scan rates, (i) 0.1, (ii) 0.2, (iii) 0.4, (iv) 0.6, (v) 0.8, (vi)  $1.0 \text{ Vs}^{-1}$  with TEAP



**Figure 3:** Variation of peak current with scan rate of  $\text{Co}_2\text{L}_2^1$  ( $3.06 \times 10^{-4}$  M) at GCE; (a) for cathodic at  $\sim 0.1 \text{ V}$  and (b) for anodic peak at  $\sim 1.0 \text{ Vs}^{-1}$

### Conclusions:

The ligands CEIMPA, CPMIMP, DCPIMP and CMAIPA were synthesized by treating orthophthalaldehyde (OPA) with L-Alanine, Methyldopa, Sodium glutamate, and Glycyl-Glycine respectively in 1:2 ratios. The complexes of L have the general formulae  $[\text{Co}_2(\text{CMAIPA})(\text{H}_2\text{O})_4]$  has been prepared using neutral tetradentate ligand, coordinating through both the carbonyl oxygens and the azomethine nitrogen. Electronic and spectral studies suggest a octahedral geometry around the Co(II) ion in all the complexes. The electrochemical studies of ligand show a typical cyclic voltammogram for an irreversible process. The most obvious indication is the absence of a cathodic reduction signal. Furthermore, the oxidation signals significantly shift to more positive potentials with faster scan rates. The difference of the peak potentials is significantly bigger than 52 mV and the

separation of the two signals increases with faster scan rates. Therefore the reaction of Co(II) complexes at higher scan rates can be considered to be quasi-reversible.

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