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# Synthesis of some Schiff base metal complexes involving para substituted aromatic aldehydes and glycylglycine: Spectral, electrochemical, thermal and surface morphology studies

# D. Arish, M. Sivasankaran Nair\*

Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli 627 012, India

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#### 1. Introduction

Major advances have been made on the study of transition metal complexes with aromatic carbonyl Schiff base ligands due to their interesting properties and potential applications in the catalytic, analytical and biological fields [1–7]. Ru(II) Schiff base complexes were found to be useful catalysts in many reactions [8-10]. There is a continuing interest in metal complexes of amino acid Schiff bases [11,12], because of the presence of both hard nitrogen and oxygen and soft sulphur donor atoms in the backbones of these ligands. They readily coordinate with transition metal ions yielding stable and intensely coloured metal complexes and have been shown to exhibit interesting physical, chemical, and potentially beneficial chemotherapeutic properties [13-16]. For e.g., Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from 4-hydroxysalicylaldehyde and amino acids have been shown to have stronger anticancer activity against Ehrlich ascites carcinoma (EAC) [17]. Many reports are available for the preparation and properties of model complexes with amino acid Schiff bases. However, little attention has been paid to systems in which the Schiff bases are derived from dipeptides, and few such compounds have been synthesized and structurally characterized [18-23]. In continuation to our interest in metal complexes of Schiff bases

#### ABSTRACT

Two Schiff base ligands, cumi-gg(L) and pcb-gg(L<sup>1</sup>) were prepared via condensation of cuminaldehyde (*p*-isopropylbenzaldehyde)/*p*-chlorobenzaldehyde and glycylglycine. The ligands were characterized based on elemental analysis, mass, <sup>1</sup>H and <sup>13</sup>C NMR, IR and UV–Vis spectra. Co(II), Ni(II), Cu(II), Zn(II) and Ru(II) metal complexes are reported and characterized based on elemental analysis, mass, <sup>1</sup>H and <sup>13</sup>C NMR, molar conductance, IR, UV–Vis, magnetic moment, CV, ESR and thermal analyses, powder XRD and SEM. All the complexes were found to be non-electrolytic in nature. IR spectra show that the ligands are coordinated to the metal ions in a tridentate manner. The geometrical structures of these complexes are found to be octahedral. The thermal behavior of the synthesized complexes indicates the presence of lattice as well as coordinated water molecules in the complexes. The SEM image of  $[CoL^1(H_2O)_3]$  complex exhibit nano rod structure.

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[24–26], the present study describes the synthesis and characterization of two novel Schiff base ligands viz cuminaldehyde (*p*-isopropylbenzaldehyde)-glycylglycine (cumi-gg) and *p*-chlorobenzaldehyde-glycylglycine (pcb-gg)) and their Co(II), Ni(II), Cu(II), Zn(II) and Ru(II) complexes.

# 2. Experimental

#### 2.1. Materials

Glycylglycine was purchased from Sigma and used without further purification. Cuminaldehyde and *p*-chlorobenzaldehyde were obtained from Himedia. Co(II), Ni(II), Cu(II), Zn(II) and Ru(III) chlorides were Merck samples. All other reagents and solvents were purchased from commercial sources and were of analytical grade.

# 2.2. Synthesis of cumi-gg (L)

A solution of glycylglycine (10 mmol) and KOH pellets (10 mmol) in 50 mL of MeOH is kept under continuous stirring in a 100 mL RB flask. A solution of cuminaldehyde (10 mmol) in 50 mL MeOH is then added slowly to the flask. The reaction mixture was vigorously stirred at room temperature for 15 min and then refluxed at 70–80 °C for 8 h. The yellow solution is reduced to 1/3 of its original volume by rotary evaporation. The concentrated filtrate thus obtained is poured into diethyl ether. A yellow



<sup>\*</sup> Corresponding author. Tel.: +91 944 3540046; fax: +91 462 23334363. *E-mail address:* msnairchem@rediffmail.com (M. Sivasankaran Nair).

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precipitate was formed, which is collected by vacuum filtration and washed several times with anhydrous ether and then dried in *vacuo* over anhydrous CaCl<sub>2</sub>. The yield of the isolated ligand is found to be 72%.

# 2.3. Synthesis of $pcb-gg(L^1)$

A solution of glycylglycine (10 mmol) and KOH pellets (10 mmol) in 50 mL of MeOH is kept under continuous stirring in a 100 mL RB flask. A solution of *p*-chlorobenzaldehyde (10 mmol) in 50 mL absolute MeOH is then added slowly to the flask. The reaction mixture was vigorously stirred and then refluxed at 70–80 °C for 8 h. After 2 days an air sensitive dark yellow precipitate was formed, which is collected by vacuum filtration and washed several times with anhydrous ether and then dried in *vacuo* over anhydrous CaCl<sub>2</sub>. The yield of the isolated ligand is found to be 80%.

# 2.4. Synthesis of Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes

A solution of cumi-gg/pcb-gg (2 mmol) in MeOH (20 mL) was added to a solution of metal(II) chloride (2 mmol) in 20 mL of aqueous MeOH, and the reaction mixture was stirred and then refluxed for 2 h. The resulting solution was cooled to room temperature and the volume was reduced to half of the initial volume under reduced pressure. The precipitate was filtered off, washed several times with cold EtOH, ether and then dried in *vacuo* over anhydrous CaCl<sub>2</sub>.

# 2.5. Synthesis of Ru(II) Schiff base complexes

 $RuCl_3$ ·3H<sub>2</sub>O (1 mmol) and an excess LiCl (1 g) were dissolved in ethanol (20 mL) and the mixture was refluxed for 30 min. A solution of Schiff base ligand cumi-gg/pcb-gg (1 mmol) was added drop wise to the above dark brown ruthenium solution. Immediately, a blackish green precipitate was formed, which was further refluxed for 2 h on a water bath. The precipitate was filtered off, washed

# several times with cold EtOH, ether and then dried in *vacuo* over anhydrous CaCl<sub>2</sub>.

#### 2.6. Physical measurements

Elemental analysis was done using a Perkin-Elmer elemental analyzer. The Mass spectra of the Schiff base ligand and its complexes were recorded on a JEOL SX 102/DA-600 mass spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the Schiff base ligand were recorded in JEOL GSX 400 FT-NMR spectrometer. Molar conductance of the complexes were measured in MeOH  $(10^{-3} \text{ M})$  solutions using a coronation digital conductivity meter. IR spectra were recorded in KBr disc on a JASCO FT/IR-410 spectrometer in the 4000-400 cm<sup>-1</sup> region. The electronic spectra were recorded on a Perkin Elmer Lambda-25 UV-Vis spectrometer. Room temperature magnetic measurements were performed on a Guoy balance by making diamagnetic corrections using Pascal's constant. The X-band ESR spectrum of Cu(II) complex was recorded on a Varian E112 X-band spectrometer using TCNE as standard. Cyclic voltammetric measurements were carried out in a Bio-Analytical system (BAS) model CV-50 W electrochemical analyzer. The three electrode cell comprised of a reference Ag/AgCl, auxiliary platinum and working glassy electrodes. Tetrabutylammonium perchlorate was used as supporting electrolyte. Thermal analysis was carried out on SDT Q 600/V8.3 build 101 thermal analyzer with the following conditions; temperature calibration-pure metal standards, sample mass 6–8 mg, heating rate 20 °C/min and nitrogen atmosphere (flow rate 20 mL/min). Powder XRD was recorded on a Rigaku Dmax X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda_{K\alpha}$  = 1.5406 Å). SEM images were recorded in a Hitachi SEM analyzer.

# 3. Result and discussion

The analytical and physical data of cumi-gg(L) and pcb- $gg(L^1)$  and their complexes are listed in Table 1. The proposed structure of the

#### Table 1

Analytical and physical data of the Schiff ligand and its complexes.

Compound	Empirical formula	Colour	Elemental analysis found (calcd)%				$\Lambda c (Ohm^{-1} cm^2 mol^{-1})$	$\lambda_{max}$ (nm)	$\mu_{\mathrm{eff}~(\mathrm{BM})}$
			С	Н	Ν	М			
Cumi-gg (L)	KC <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O <sub>3</sub>	Yellow	55.87 (55.98)	5.65 (5.70)	9.45 (9.33)	-	-	220, 268, 302, 356	-
$[CoL(H_2O)_3]$	$CoC_{14}H_{22}N_2O_6$	Brown	45.21 (45.05)	6.01 (5.94)	7.43 (7.51)	15.63 (15.79)	12	630, 690	5.11
[NiL(H <sub>2</sub> O) <sub>3</sub> ]	$NiC_{14}H_{22}N_2O_6$	Light green	44.93 (45.08)	6.01 (5.94)	7.42 (7.51)	15.68 (15.73)	09	1100, 710, 400	3.23
[CuL(H <sub>2</sub> O) <sub>3</sub> ]	$CuC_{14}H_{22}N_2O_6$	Deep Green	44.39 (44.50)	5.68 (5.87)	7.56 (7.41)	16.74 (16.82)	15	720	1.92
[ZnL(H <sub>2</sub> O) <sub>3</sub> ]	$ZnC_{14}H_{22}N_2O_6$	Light yellow	44.73 (44.28)	5.48 (5.84)	7.66 (7.38)	17.01 (17.22)	07	345	Dia
$[RuL(H_2O)_3]\cdot H_2O$	$RuC_{14}H_{24}N_2O_7$	Blackish green	38.65 (38.80)	5.72 (5.58)	6.39 (6.46)	23.25 (23.32)	12	420, 530, 610	Dia
Pcb-gg (L <sup>1</sup> )	$KClC_{11}H_{10}N_2O_3$	Bright yellow	(45.06) (45.13)	(3.32) (3.44)	(9.68) (9.57)	-	-	250, 270, 328	-
$[CoL^{1}(H_{2}O)_{3}]$	$CoClC_{11}H_{15}N_2O_6$	Brown	(36.37) (36.13)	(4.03) (4.14)	(7.69) (7.66)	(16.28) (16.12)	08	630, 692	5.03
$[NiL^1(H_2O)_3]$	NiClC <sub>11</sub> H <sub>15</sub> N <sub>2</sub> O <sub>6</sub>	Green	(36.07) (36.16)	(4.08) (4.14)	(7.82) (7.67)	(16.17) (16.06)	12	1100, 710, 380	2.98
$[CuL^{1}(H_{2}O)_{3}]\cdot 2H_{2}O$	$CuClC_{11}H_{19}N_2O_8$	Green	(32.65) (32.52)	(4.79) (4.71)	(6.98) (6.90)	(15.38) (15.64)	15	850	2.01
$[ZnL^1(H_2O)_3]\cdot H_2O$	$ZnClC_{11}H_{17}N_2O_7$	Light yellow	(33.59) (33.87)	(4.32) (4.39)	(7.32) (7.18)	(16.72) (16.76)	04	320	Dia
$[RuL^1(H_2O)_3]\cdot 2H_2O$	$RuClC_{11}H_{19}N_2O_8$	Blackish green	29.68 (29.77)	4.44 (4.32)	6.39 (6.31)	22.85 (22.77)	08	423, 525, 620	Dia

Schiff base ligands are shown in Fig. 1. The Schiff base ligands are air sensitive in nature and soluble in all common organic solvents. The CuL·3H<sub>2</sub>O complex is air sensitive, hydroscopic in nature and soluble in water, DMF and DMSO, while other complexes are stable towards air and moisture and soluble in acetonitrile, DMF and DMSO. The molar conductance values (Table 1) of metal complexes measured in DMSO at  $10^{-3}$  M reveal their non-electrolytic nature [27].

# 3.1. Mass spectra

The EI mass spectrum of the Schiff base ligand, cumi-gg (L) and pcb-gg (L<sup>1</sup>) shows a well-defined molecular ion peak at m/z = 301.26 (Relative Intensity = 23%) and 292.87 (18%), respectively. There are consistent with the proposed molecular formulae of the ligands. The FAB mass spectrum of CoL·3H<sub>2</sub>O, NiL·3H<sub>2</sub>O, CuL·3H<sub>2</sub>O, ZnL·3H<sub>2</sub>O and RuL·4H<sub>2</sub>O complexes shows a peak at m/z 375.46 (7%), 373.31 (11%), 378.50 (12%), 382.27 (14%) and 433.37 (29%) respectively, corresponding to their molecular weight. The spectrum of CoL<sup>1</sup>·3H<sub>2</sub>O, NiL<sup>1</sup>·3H<sub>2</sub>O, CuL<sup>1</sup>·5H<sub>2</sub>O, ZnL<sup>1</sup>·4H<sub>2</sub>O and RuL<sup>1</sup>·5H<sub>2</sub>O complexes shows a molecular ion peak (M<sup>+</sup>) at m/z 366.13 (12%), 368.59 (11%), 407.11 (8%), 390.78 (26%) and 443.29 (4%), respectively. The mass spectrum of all the complexes indicates that the complexes are monomeric confirming the metal to ligand ratio to be 1:1 in the complexes.

# 3.2. NMR spectra

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data of the Schiff base ligands and their Zn(II) complexes are given in Table 2. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of cumi-gg and its Zn(II) complex is shown

respectively in Fig. 2a and b. <sup>1</sup>H NMR spectra of cumi-gg and pcbgg show a peak at 8.48 and 8.50 ppm characteristic of azomethine proton (-CH=N-). The peaks at 9.98 and 10.08 ppm are assignable to the peptide linkage – NH– proton for cumi-gg and pcg-gg, respectively. The aromatic ring protons are observed in the 7.1–8.2 ppm range as expected. In the <sup>1</sup>H NMR spectrum of Zn(II) complexes, the -CH=N- proton peak is slightly shifted to downfield. This difference in (-CH=N-) peak position could arise due to the coordination of its neighbouring nitrogen atom which indicates the metal to coordinate the ligand through azomethine nitrogen atom. The peptide plexes. This supports the proposal that the ligands have coordinated with the metal ion in the deprotonated form. In addition, the spectra of ZnL·3H<sub>2</sub>O and ZnL<sup>1</sup>·4H<sub>2</sub>O complexes show a broad peak centered at 4.73 and 4.86 ppm, respectively. There are characteristic of water molecule present in the complexes.

The <sup>13</sup>C NMR spectrum of Schiff base ligands and their Zn(II) complexes revealed the presence of expected number of signals corresponding to different types of carbon atoms. The <sup>13</sup>C NMR spectrum of cumi-gg and pcb-gg shows a peak at 164.29, 175.85 ppm for cumi-gg and 171.37, 181.45 ppm for pcb-gg respectively. There are assignable to azomethine carbon (-CH=N-) and carboxylato carbon. This peaks are slightly shifted to down field region in the Zn(II) complexes (Table 2) indicating involvement of azomethine nitrogen and carboxylato oxygen atoms on coordination.

# 3.3. IR spectra



Fig. 1. Proposed structure of Schiff base ligands (a) cumi-gg and (b) pcb-gg.

Table 2				
<sup>1</sup> H and <sup>13</sup> C NMR s	pectral data of Sc	hiff base ligands and	their Zn(II)	complexes.

Ligand/ complexes	Nucleus	-CH <sub>3</sub>	-CH <sub>2</sub>	—CH	Aromatic (—CH)	—CH=N	—NH	-C=0
Cumi-gg	<sup>1</sup> H	1.312 (d, <i>I</i> = 6.9 Hz, 6H)	4.014 (s, 2H) 5.472 (d, I = 14.7 Hz, 2H)	2.995 (m, 1H)	7.2–7.6 (d, <i>J</i> = 8.1 Hz, 2H; d, <i>J</i> = 7.8 Hz, 2H	8.488 (s, 1H)	9.984 (s, 1H)	_
	<sup>13</sup> C	23.610	43.13, 53.691	33.880	126–152	164.291	-	171.626 (pep) 175.851 (carbo)
Zn(II)	<sup>1</sup> H	1.301 (d, / = 6.9 Hz, 6H)	4.167 (s, 2H) 5.401 (s, 2H)	2.975 (m, 1H)	7.1–7.8 (d, <i>J</i> = 8.1 Hz, 2H; d, <i>J</i> = 7.5 Hz, 2H)	8.602 (s, 1H)	-	-
	<sup>13</sup> C	23.653	43.462, 53.714	33.903	126–152	165.045	-	171.679 (pep) 176.624 (carbo)
Pcb-gg	<sup>1</sup> H	-	4.272 (s, 2H) 5.526 (d, <i>I</i> = 14.9 Hz, 2H)	-	7.4–8.1 (d, <i>J</i> = 8.1 Hz, 2H; d, <i>J</i> = 7.8 Hz, 2H)	8.501 (s, 1H)	10.085(s, 1H)	-
	<sup>13</sup> C	-	46.358, 54.397	-	129–152	171.370	-	175.971(pep) 181.459 (carbo)
Zn(II)	<sup>1</sup> H	-	4.306 (s, 2H) 5.665 (s, 2H)	-	7.4–8.2 (d, <i>J</i> = 8.1 Hz, 2H; d, <i>I</i> = 7.5 Hz, 2H)	8.742 (s, 1H)	-	-
	<sup>13</sup> C	-	46.433, 54.415	-	129–152	165.939	-	176.001 (pep) 182 329 (carbo)

The IR spectral data of the Schiff base ligands and their complexes are given in Table 3. IR spectrum of cumi-gg and pcb-gg show the strong band respectively at 1665 and 1638 cm<sup>-1</sup>. These are assigned to azomethine stretching frequency. During complexation, these bands are shifted to lower frequency indicating the

coordination of azomethine nitrogen to the metal ion. In the spectrum of Schiff bases, the sharp band present in the region  $\sim$ 3300 and  $\sim$ 1520 cm<sup>-1</sup> is due to peptide N—H stretching frequency



Fig. 2. (a) <sup>1</sup>H NMR spectrum of cumi-gg (L) and (b) [ZnL·(H<sub>2</sub>O)<sub>3</sub>].

Table 3
R spectral data of the Schiff base ligands and their complexes $(cm^{-1})$ .

Compound	v <sub>azo</sub> (C=N)	$v_{asym}(COO^{-})$	$v_{sym}(COO^{-})$	v <sub>peptide</sub> (N–H)	v(H <sub>2</sub> O)	v(M—O)	v(M—N)
Cumi-gg (L)	1665	1608	1385	3298	-	-	-
$[CoL(H_2O)_3]$	1647	1596	1371	-	3387	520	434
$[NiL(H_2O)_3]$	1645	1590	1370	-	3385	526	440
$[CuL(H_2O)_3]$	1640	1592	1375	-	3398	534	438
$[ZnL(H_2O)_3]$	1653	1598	1370	-	3390	522	430
$[RuL(H_2O)_3] \cdot H_2O$	1645	1592	1372	-	4000	520	434
Pcb-gg (L <sup>1</sup> )	1638	1590	1378	3270	-	-	-
$[CoL^{1}(H_{2}O)_{3}]$	1632	1584	1372	-	3395	528	425
$[NiL^{1}(H_{2}O)_{3}]$	1628	1582	1368	-	3380	524	427
$[CuL^{1}(H_{2}O)_{3}]\cdot 2H_{2}O$	1628	1584	1371	-	4010	530	431
$[ZnL^{1}(H_{2}O)_{3}]\cdot H_{2}O$	1630	1580	1365	-	4003	526	429
$[RL^{1}(H_{2}O)_{3}]\cdot 2H_{2}O$	1625	1578	1365	-	4008	530	435

[28]. In the complexes, the peptide  $v_{(NH)}$  bands disappeared indicating the metal ion to coordinate through deprotonated nitrogen atom [29]. The new broad band appeared at  $\sim$ 3400 cm<sup>-1</sup> can be attributed to the stretching vibration of the water molecule. Further, the band at  $\sim 800 \text{ cm}^{-1}$  in the complexes is assigned to coordinated water molecule [30]. The strong bands present in the region 1608 and 1590 cm<sup>-1</sup> respectively, cumi-gg and pcb-gg can be assigned to an asymmetric stretching frequency of carboxylato group. The Schiff base ligands also display bands at 1385 and 1378 cm<sup>-1</sup> respectively, due to symmetric stretching vibration of carboxylato group [28]. On complexation, the asymmetric and symmetric stretching bands are shifted to lower frequency for all the complexes, which reveals the formation of a linkage between the metal ion and carboxylato oxygen atom. Moreover, the large difference (~200) between the asymmetric and symmetric stretching modes indicates the monodentate binding of the carboxylato group in the complexes [31].

The spectrum of all the metal complexes show new bands in the  $520-540 \text{ cm}^{-1}$  and  $420-440 \text{ cm}^{-1}$  regions, which may probably be due to the formation of M—O and M—N bonds, respectively [28].

#### 3.4. Electronic spectra and magnetic measurements

The spectra of free cumi-gg and pcb-gg exhibit a broad band at 380 and 328 nm, respectively, which can be assigned to  $\pi$ - $\pi^*$  transition of the azomethine (>C=N) chromophore. In addition, the other intense absorption band at higher energy, 225–270 nm is due to the  $\pi$ - $\pi^*$  and n- $\pi^*$  transition of the benzene ring of the Schiff base ligands. The electronic spectrum of Co(II) complexes show two absorption bands (Table 1) at 600–700 nm region, which are assignable to  ${}^{4}T_{1}g(F) \rightarrow {}^{4}A_{2}g(F)$  and  ${}^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(F)$  transitions in an octahedral environment [32,33]. The magnetic susceptibility value is found to be 5.11 and 5.03 BM for CoL·3H<sub>2</sub>O and

CoL<sup>1</sup>·3H<sub>2</sub>O, respectively (normal range for octahedral Co(II) complexes is 4.3–5.2 BM), which is indicative of octahedral geometry [34]. The electronic spectrum of the Ni(II) complexes show three bands in the region  $\sim$ 1100,  $\sim$ 700 and  $\sim$ 400 nm (Table 1), attributable to  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{2}g(F)$ ,  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(F)$  and  ${}^{3}A_{2}g(F) \rightarrow {}^{3}T_{1}g(P)$ transitions, respectively, suggesting an octahedral geometry around Ni(II) atom [35]. The NiL·3H<sub>2</sub>O and NiL<sup>1</sup>·3H<sub>2</sub>O complexes reported herein are found to have a room temperature magnetic moment value of 3.23 and 2.98 BM respectively, which are in the normal range observed for octahedral Ni(II) complexes ( $\mu_{eff}$  2.9– 3.3 BM) [34]. The Cu(II) complexes in their spectra display a broad band in the ~800 nm region which can be assigned to  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition, indicating the complexes to have distorted octahedral geometry [32]. The magnetic moment value of 1.92 and 2.01 BM respectively for CuL·3H<sub>2</sub>O and CuL<sup>1</sup>·5H<sub>2</sub>O, falls within the range normally observed for octahedral Cu(II) complexes [33]. The ground state of Ru(II) in an octahedral environment is <sup>1</sup>A<sub>1g</sub>, arising from the  $t_2g$  configuration. The exited state terms are  ${}^{3}T_{1g}$ ,  ${}^{3}T_{2g}$ ,  ${}^{1}T_{1g}$  and  ${}^{1}T_{2g}$ , hence four bands corresponding to the transition  ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{3}T_{2g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  are possible in order of increasing energy. However, the electronic spectrum of Ru(II) octahedral complexes shows in general three to four absorption bands in the region 719-254 nm [36]. The Ru(II) complexes in the present investigation shows an absorption bands at  $\sim$ 420,  $\sim$ 525 and  $\sim$ 620 nm (Table 1). This demonstrates an octahedral geometry for the Ru(II) complex. Further, the magnetic moment values of these complexes manifest their diamagnetic nature with +2 oxidation state.

#### 3.5. Electrochemistry

The cyclic voltammograms were recorded in acetonitrile solution at a scan rate of  $100 \text{ mV s}^{-1}$  in the potential range +2.0 to



Fig. 3. Cyclic voltammagram of (a) [CoL(H<sub>2</sub>O)<sub>3</sub>]; (b) [CoL<sup>1</sup>(H<sub>2</sub>O)<sub>3</sub>]; (c) [NiL(H<sub>2</sub>O)<sub>3</sub>]; (d) [CuL(H<sub>2</sub>O)<sub>3</sub>] complexes.

-2.0 V. The cyclic voltammogram of CoL·3H<sub>2</sub>O, CoL<sup>1.</sup>3H<sub>2</sub>O, CuL·3H<sub>2</sub>O and NiL·3H<sub>2</sub>O complexes are shown in Fig. 3a–d. The Schiff base ligands and their Zn(II) complexes do not show any peaks in this potential range under similar conditions. The cyclic voltammogram of CoL·3H<sub>2</sub>O shows (Fig. 3a) a well-defined redox process corresponding to the formation of the quasi-reversible

Co(II)/Co(I) couple. The cathodic peak at -0.848 V versus Ag/AgCl and the associated anodic peak at -0.640 V corresponds to the Co(II)/Co(I) couple. The peak-to-peak separation ( $\Delta$ Ep) indicates quasi-reversible one electron transfer process. The redox property of CoL<sup>1</sup>·3H<sub>2</sub>O displayed electrochemically irreversible Co(II)/Co(I) reduction at Epc -0.703 V. During the reverse scan the oxidation





of Co(I)/Co(II) occurs in the potential range Epa +0.25. The peak-topeak separation ( $\Delta Ep$ ) is 675 mV indicating the process to be irreversible. The electrochemistry of NiL·3H<sub>2</sub>O is similar to that of NiL<sup>1</sup>·3H<sub>2</sub>O, anodic waves are seen at -0.998 and at -0.983 V and the associated cathodic peaks at -0.543 and -0.536 V respectively, corresponding to the formation of the quasi-reversible one-electron reduction Ni(II)/Ni(I) couple.

The cyclic voltammogram of the CuL·3H<sub>2</sub>O complex displayed two reduction couples at +0.054 V and -0.668 V versus Ag/AgCl with the corresponding anodic wave for the first reduction and without the corresponding anodic wave for the second reduction on the reverse scan. The former has a lower peak separation value of 0.030 indicating totally reversible character for the two electron transfer reaction of metal-based Cu(II)/Cu(0) couples and the later one can be assigned to Cu(II)/Cu(I) irreversible reduction process. The CuL<sup>1</sup>·5H<sub>2</sub>O complex displayed two reduction couples at +0.193 V and -0.889 V versus Ag/AgCl with the corresponding anodic waves at +0.556 and at -0.535 V on the reverse scan. The peak separation values ( $\Delta$ Ep = 0.363 and 0.354 V) indicate totally quasi-reversible character for the one electron transfer reaction of metal-based Cu(II)/Cu(I) and Cu(I)/Cu(0) couples. Cyclic voltammogram of the RuL·4H<sub>2</sub>O and RuL<sup>1</sup>·5H<sub>2</sub>O complexes show one quasi-reversible redox processes occurring at negative potential and with a peak-to-peak separation ( $\Delta$ Ep value) of 230 and 253 mV respectively. The redox process occurs with the cathodic peak potential at -0.870 and -0.856 V and anodic peak potential at -0.688 and -0. 527 V.

# 3.6. Electron spin resonance spectra

The X-band ESR spectra of Cu(II) complexes of cumi-gg and pcbgg were recorded on a powder solid at 300 and 77 K. The representative spectrum of CuL·3H<sub>2</sub>O complex at 300 and 77 K are shown in Fig. 4a and b. The spectrum at 300 K shows one intense absorption band at high field, which is isotropic due to the tumbling of the

#### Table 4

molecules. However, the complexes in the frozen state (77 K) exhibit anisotropic signals with g values: (i)  $g_{11} = 2.23$  and  $g_{12} = 2.05$ respectively for CuL·3H<sub>2</sub>O and (ii)  $g_{11} = 2.28$  and  $g_{\perp} = 2.06$  respectively for CuL·5H<sub>2</sub>O, which is characteristic for axial symmetry. The trend  $g_{ll} > g_{\perp} > g_{e}$  shows that the unpaired electron is localized in the  $d_x^2 - d_y^2$  orbital of Cu(II) in complex [37]. The exchange coupling interaction between two Cu(II) ions is explained by Hathaway [38] expression  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ . If the *G* value is larger than 4, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. If the value is less than 4, the exchange interaction is considerable and the local tetragonal axes are misaligned. The observed G for CuL·3H<sub>2</sub>O and CuL<sup>1</sup>·5H<sub>2</sub>O is 4.35 and 4.66 respectively, suggesting that the local tetragonal axes are aligned parallel or slightly misaligned and consistent with a  $d_x^2 - d_y^2$  ground state. Moreover, the absence of a half field signal at 1600 G corresponding to  $\Delta M = \pm 2$  transitions indicates the absence of any Cu-Cu interaction in the complex [39]. Kivelson and Neiman [40] showed that for an ionic environment  $g_{||}$  is normally 2.3 or larger, but for covalent environment  $g_{||}$  is less than 2.3. The observed  $g_{||}$  value for the Cu(II) complexes suggest that the environment is covalent.

#### 3.7. Thermal analysis

The thermal stability data of the complexes are listed in Table 4. The CoL·3H<sub>2</sub>O, NiL·3H<sub>2</sub>O, CuL·3H<sub>2</sub>O and ZnL·3H<sub>2</sub>O complexes undergo similar decomposition mainly in two stages. The first stage takes place in the 160-290 °C ranges with an endothermic DTA peak between 160 and 200 °C. The mass loss observed (Table 4) in this step corresponds to dehydration of three coordinated water molecule. The final decomposition step is represented by the removal of complete organic ligand moiety in the 360-630 °C ranges with the formation of metal oxide as the final product.

The TG curves of the complexes CoL<sup>1</sup>·3H<sub>2</sub>O and NiL<sup>1</sup>·3H<sub>2</sub>O show a weight loss 14.52% (cal.14.77%) and (14.57%) (cal. 14.78%) in the

Complex	Temperature range $t$ (°C)	% weight loss Obs. (calcd)	DTA peak t (°C)	Process
$[CoL(H_2O)_3]$	160–286, 365–610, >610	14.02(14.47), 65.23(65.44), 20.71(20.09)	195ª, 341 <sup>b</sup> , 511 <sup>b</sup> , 617 <sup>b</sup>	–3H <sub>2</sub> O(coord), loss of organic moiety, CoO
[NiL(H <sub>2</sub> O) <sub>3</sub> ]	176–280, 368–630, >630	14.13(14.48), 65.13(65.49), 20.68(20.02)	178 <sup>a</sup> , 380 <sup>b</sup> , 540 <sup>b</sup> , 610 <sup>b</sup>	$-3H_2O(coord)$ , loss of organic moiety, NiO
[CuL(H <sub>2</sub> O) <sub>3</sub> ]	188–293, 360–622, >622	14.51(14.29, 65.32(65.65), 21.69(21.05)	175 <sup>a</sup> , 380 <sup>b</sup> , 549 <sup>b</sup> , 623 <sup>b</sup>	–3H <sub>2</sub> O(coord), loss of organic moiety, CuO
$[ZnL(H_2O)_3]$	185–282, 365–616, >616	14.38(14.22), 64.02(64.33), 21.86(21.43)	167 ª, 362 <sup>b</sup> , 534	-3H <sub>2</sub> O(coord), loss of organic moiety, ZnO
$[RuL(H_2O)_3] \cdot H_2O$	60-98,153-266, >359	4.07(4.15), 12.37(12.46),	<sup>b</sup> 102 <sup>a</sup> , 197 <sup>a</sup> , 367 <sup>b</sup> , 607 <sup>b</sup> ,657 <sup>b</sup>	<ul> <li>-H<sub>2</sub>O(lattice)</li> <li>-3H<sub>2</sub>O(coord), unassigned</li> </ul>
$[CoL^{1}(H_{2}O)_{3}]$	150–225, 346–589, >589	14.52(14.77), 68.85(69.10), 20.72(20.49)	224 <sup>a</sup> , 430 <sup>b</sup> , 546 <sup>b</sup>	-3H <sub>2</sub> O(coord), loss of organic moiety, CoO
$[NiL^1(H_2O)_3]$	154–216, 337–600, >600	14.57(14.78), 68.78(69.15), 20.67(20.44)	225 <sup>a</sup> , 430 <sup>b</sup> , 546 <sup>b</sup>	—3H <sub>2</sub> O(coord), loss of organic moiety, NiO
$[CuL^{1}(H_{2}O)_{3}]\cdot 2H_{2}O$	52–120, 147–276, 367–640, >640	8.54(8.86), 13.06(13.29), 61.93(62.19), 20.37(19.58)	133 <sup>a</sup> , 250 <sup>a</sup> , 427 <sup>b</sup> , 576 <sup>b</sup>	-2H <sub>2</sub> O(lattice), -3H <sub>2</sub> O(coord), loss of organic moiety, CuO
$[ZnL^1(H_2O)_3]{\cdot}H_2O$	80–120, 165–247, 355–602, >602	4.36(4.61), 13.72(13.84), 64.08(64.77), 21.11(20.86)	78 <sup>a</sup> , 231 <sup>a</sup> , 466 <sup>b</sup> , 605 <sup>b</sup>	$-H_2O(lattice), -3H_2O(coord),$ loss of organic moiety, ZnO
$[RuL^1(H_2O)_3]{\cdot}2H_2O$	60–110, 180–276, >355	8.23(8.11), 11.98(12.16)	106 <sup>a</sup> , 188 <sup>a</sup> , 360 <sup>b</sup> , 461 <sup>b</sup> , 605 <sup>b</sup> , 688 <sup>b</sup>	$-2H_2O(lattice)$
		-		$-3H_2O(coord)$ unassigned

<sup>a</sup> Endothermic.

<sup>b</sup> Exothermic.

temperature ranges 150–225 and 154–216 °C respectively. This is due to a loss of three coordinated water molecule. The DTA curves of the complexes show endothermic peak in the range 220–225 °C confirming the dehydration process. The second decomposition steps of the complexes in the 346–589 and 337–600 °C range have DTA peaks at 430 and 437 °C, respectively. It brings a weight loss of 68.85% (cal. 69.10%) and 68.78% (cal. 69.15%), which correlate with the loss of coordinated organic ligand. Above this temperature, a horizontal thermal curve has been observed due to formation of metal oxide. The TG curves of the complexes CuL<sup>1</sup>.5 H<sub>2</sub>O and ZnL<sup>1</sup>.4H<sub>2</sub>O show a similar sequence of three decomposition steps. The first stage takes place in the 52–120 °C and 80–120 °C ranges with an endothermic DTA peak at 133 and 78 °C respectively for CuL<sup>1.5</sup> H<sub>2</sub>O and ZnL<sup>1.4</sup>H<sub>2</sub>O complexes. The mass loss observed (Table 4) in this step corresponds to dehydration of lattice water molecule. The second stage starts from 147 °C to 276 °C for CuL<sup>1.5</sup> H<sub>2</sub>O and 165 to 247 for ZnL<sup>1.4</sup>H<sub>2</sub>O complexes with the DTA peak at 250 and 231 °C respectively. The corresponding mass loss (Table 4) is attributed to the decomposition of three coordinated water molecule. The third stage starts from 367 °C to 640 °C for CuL<sup>1.5</sup> H<sub>2</sub>O and 355 to 602 for ZnL<sup>1.4</sup>H<sub>2</sub>O complexes with the DTA peak at 427 and 466 °C respectively. The corresponding mass loss is due



**Fig. 5.** TG–DTA curves of (a)  $[CoL(H_2O)_3]$ ; (b)  $[RuL(H_2O)_3] \cdot H_2O$ ; (c)  $[CuL^1(H_2O)_3] \cdot 2H_2O$  and (d)  $ZnL^1 \cdot 4H_2O$  complexes.



Where, x = 0 for M =Co(II), Ni(II), Cu(II)and Zn(II); x =1 for Ru(II)

Where x = 0 for  $M = Co(\Pi)$  and  $Ni(\Pi)$ ; x = 1 for  $Zr(\Pi)$ ; x = 2 for  $Cu(\Pi)$  and  $Zn(\Pi)$ 

Fig. 6. Proposed structure of the complexes.

to the decomposition of the organic ligand molecule and which is in agreement with a calculated mass loss (Table 4). The final residue is qualitatively proved to be anhydrous metal oxide. The TG curves of the complexes RuL·4H<sub>2</sub>O and RuL<sup>1</sup>·5H<sub>2</sub>O show a weight loss 4.07% (cal. 4.15%) and 8.23% (cal. 8.11%) in the temperature ranges 60–98 °C and 60–110 °C with an endothermic DTA peak at 102 and 106 °C respectively, corresponding to a loss of lattice water molecule. The second stage starts from 153 °C to 266 °C for RuL·4H<sub>2</sub>O and 180 °C to 276 °C for RuL<sup>1</sup>·5H<sub>2</sub>O complexes with the DTA peak at 197 °C and 188 °C respectively. The corresponding mass loss (Table 4) can be attributed to the decomposition of three coordinated water molecules. Above this temperature, an unassigned mass loss was observed in both ruthenium complexes. This step is accompanied by exothermic and endothermic peaks (Table 4). The representative TG-DTA curves of CoL·3H<sub>2</sub>O, RuL·4H<sub>2</sub>O,  $CuL^{1}$ ·5H<sub>2</sub>O and ZnL<sup>1</sup>·4H<sub>2</sub>O complexes are shown in Fig. 5a–d.

Based on the above studies, the proposed structure of the metal complexes is shown in Fig. 6.

#### 3.8. Powder XRD and SEM

Powder XRD pattern of the Schiff base complexes were recorded over the  $2\theta = 0-80$  range and  $[CoL(H_2O)_3]$ ,  $[CoL^1(H_2O)_3]$  and  $[CuL^1(-H_2O)] \cdot 2H_2O$  are shown in Fig. 7a–c. The  $[CoL(H_2O)_3]$ ,  $[CoL^1(H_2O)_3]$ and  $[CuL^1(H_2O)] \cdot 2H_2O$  complexes display sharp crystalline peaks indicating their crystalline nature, whereas other complexes do not exhibit well-defined crystalline peak due to their amorphous nature. The average crystallite sizes of the complexes  $d_{XRD}$  were calculated using Scherre's formula [41]. The  $[CoL(H_2O)_3]$ ,  $[CoL^1(-H_2O)_3]$  and  $[CuL^1(H_2O)] \cdot 2H_2O$  complexes have an average crystallite size of 48, 61 and 42 nm, respectively, suggesting that the complexes are in nanocrystalline phase.

The SEM micrographs of the  $[CoL^1(H_2O)_3]$ ,  $[CoL(H_2O)_3]$ ,  $[CuL^1(H_2O)] \cdot 2H_2O$  and  $[RuL^1(H_2O)] \cdot 2H_2O$  complexes are shown in

Fig. 8a–d. Taking advantage of metal–ligand coordination interactions, chemists have produced some interesting nano structured complexes [42], which can be demonstrated by SEM or TEM micrographs. Among the complexes, the  $[CuL^1(H_2O)] \cdot 2H_2O$  complex display very good surface morphology with existence of nano rod structure. From the SEM image (Fig. 8b), it is observed that grains are well resolved and circular shape are uniformly distributed in the  $[CoL(H_2O)_3]$  complex. Moreover, the average grain size found from SEM shows that the complex is polycrystalline with nano sized grains. The SEM image of  $[CoL^1(H_2O)_3]$  and  $[RuL^1(H_2O)] \cdot 2H_2O$ complexes show irregularly shaped agglomerated particles of submicron size. All other complexes show irregularly broken stone like surface morphology and the presences of small grains are in micro meter range.

#### 4. Conclusion

Two new Schiff base ligands, cumi-gg(L) and  $pcb-gg(L^1)$  and their Co(II), Ni(II), Cu(II), Zn(II) and Ru(II) complexes were prepared and characterized using various spectral techniques. The results indicate that the complexes are octahedral, with formula  $[ML(H_2O)_3] \cdot xH_2O$  (L = cumi-gg; x = 0 for M = Co(II), Ni(II), Cu(II) and Zn(II); x = 1 for Ru(II) and L = pcb-gg; x = 0 for M = Co(II) and Ni(II); x = 1 for Zn(II); x = 2 for Cu(II) and Ru(II)). The NMR and IR spectra show that the ligands coordinate with metal ion through azomethine nitrogen, deprotonated peptide nitrogen and carboxylato oxygen atoms. All the complexes except Zn(II) display their redox behavior. The thermal behavior of these chelates shows that the hydrated complexes loss water of hydration in first step followed by the loss of coordinated water molecules in the second step. Decomposition of ligand molecules takes place in the subsequent steps. Interestingly, [CoL<sup>1</sup>(H<sub>2</sub>O)<sub>3</sub>] complex exhibit nano rod structure.



Fig. 7. Powder XRD pattern of (a)  $[CoL(H_2O)_3]$ ; (b)  $[CoL^1(H_2O)_3]$  and (c)  $[CuL^1(H_2O)_3]$ ·2H<sub>2</sub>O Complexes.





X2,000 10Mm WD 9

Fig. 8. SEM images of (a)  $[CoL^{1}(H_{2}O)_{3}];$  (b)  $[CoL(H_{2}O)_{3}];$  (c)  $[CuL^{1}(H_{2}O)]\cdot 2H_{2}O$  and (d)  $[RuL^{1}(H_{2}O)]\cdot 2H_{2}O$  complexes.

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