



# Synthesis, molecular modeling and spectroscopic characterization of nickel(II), copper(II), complexes of new 16-membered mixed-donor macrocyclic schiff base ligand incorporating a pendant alcohol function

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## ARTICLE INFO

### Article history:

Received 25 September 2010

Received in revised form 18 April 2011

Accepted 27 April 2011

### Keywords:

Macrocycles

Schiff base

Copper(II) and Nickel(II) Complexes

UV–vis

EPR spectra

Molecular modeling

## ABSTRACT

Complexes of Cu(II) and Ni(II) of the composition  $[M(L)X]$  [where  $M = \text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $X = \text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ] were synthesized with 1,5-dioxo-9,10-diaza-3,ol-tribenzo-(7,6,10,11,14,15) heptadecane, a  $\text{N}_2\text{O}_2$  macrocyclic ligand. The complexes were characterized by elemental analysis, molar conductance measurements, UV–vis, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EPR and molecular modeling studies. All the complexes are non-electrolyte in nature. On the basis of spectral studies, an octahedral geometry has been assigned for Ni(II) complexes and a tetragonal geometry for Cu(II) complexes.

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## 1. Introduction

Interest in pendant armed macrocycles is growing on account of their unique coordination and structural properties [1]. Macrocyclic ligands containing a hetero atom are important complexing agents for neutral molecules [2–5]. There is an emerging interest in the synthesis of macrocyclic complexes of transition metals and their interesting properties [6]. The formation of macrocyclic complexes depends significantly on the dimension of internal cavity, rigidity of macrocycles, nature of its donor atoms and the complexing properties of the anion involved in coordination [7,8]. Due to their resemblance with natural proteins like hemerythrin enzymes, chemical properties of macrocyclic complexes have received much attention as an active part of metalloenzyme [9–11] as biomimic model compounds [12]. A considerable number of Schiff-base complexes have potential biological interest and are used as more or less successful models of biological compounds [13,14]. Additionally, some of the salicylidene derivatives show photochromism in the solid state [15,16]. It has been suggested that the azomethine linkage is responsible for the biological activities of Schiff bases such as antitumor, antibacterial, antifungal and herbicidal activities [17–20]. Moreover metal complexes of Schiff bases derived

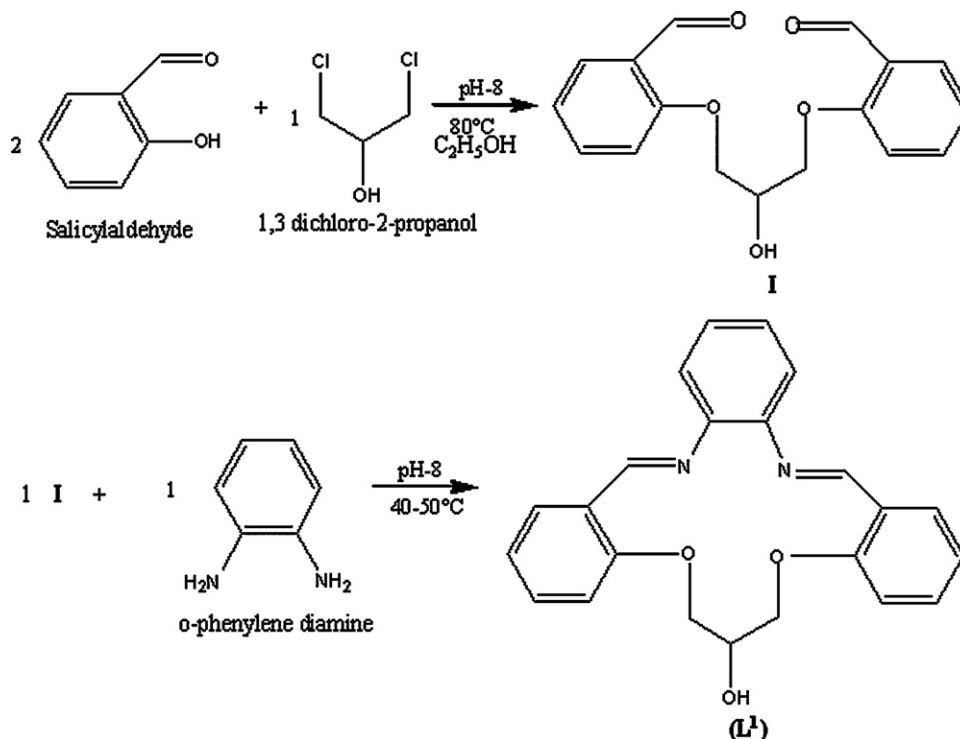
from salicylaldehyde and diamine can increase its dimensionality and can form supramolecular architectures through O–H...N and N–H...O type hydrogen bonds [21]. In this paper we report the synthesis of pentadentate Schiff base ligand, in order to investigate the coordination mode of ligand, complexes of nickel(II) and copper(II) were synthesized and characterized by UV–vis, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EPR and molecular modeling studies.

## 2. Experimental

### 2.1. Chemicals and instruments

Solvents were dried and purified before being used according to published procedures [22]. Other reagents and solvents were purchased from Sigma–Aldrich and used as received. Elemental analysis of C, H and N were performed on a Carlo-Erba EA 1106 elemental analyzer. Molar conductance was evaluated on an ELICO Conductivity Bridge (Type CM82T). Magnetic susceptibility was measured at room temperature on a Gouy balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a callibrant. IR spectra were recorded on Perkin Elmer-137 instrument as KBr pallets. Electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (300 MHz) spectra were recorded on a Bruker Advanced DPX-300 spectrometer using  $\text{CDCl}_3$  as a solvent. EPR spectra of all the complexes were recorded at room temperature (RT) and liquid nitrogen temperature (LNT) on an E4-EPR

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Scheme 1.

spectrometer using the DDPH as the g-marker. The complexes were modeled by MOPAC 2007 program in gas phase using level of theory.

## 2.2. Synthesis of ligand and complexes

### 2.2.1. Synthesis of 2-[3-(*o*-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (**I**)

2-[3-(*o*-Formyl phenoxy)-2-hydroxypropoxy] benzaldehyde was prepared by the method of Lindoy and Armstrong [23] with minor modification. Sodium hydroxide (8.0 g, 0.2 mol) in water (400 mL) was added to salicylaldehyde (20.98 mL, 0.2 mol) in ethanol (20 mL). The mixture was heated up to 60 °C and then 1,3 dichloro-2-propanol (9.54 mL, 0.1 mol) was added. In this mixture sufficient ethanol was added to produce a homogenous solution. The solution was refluxed for 70 h (pH  $\cong$  8) at 80 °C then cooled at 0 °C. The cream colored solid product was recrystallized in 2:1 ethanol–water. The resulting crystals were collected by filtration and dried in a vacuum desiccator over P<sub>4</sub>O<sub>10</sub>.

### 2.2.2. Synthesis of macrocyclic ligand (**L1**)

To a hot ethanolic solution (20 mL) of 2-[3-(*o*-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (6 g, 0.02 mol), a hot solution of *o*-phenyldiamine (2.162 g, 0.02 mol) was added with constant stirring. The solution was heated at 40–50 °C (pH  $\cong$  8) for 5 h. On cooling at 0 °C, an orange colored product was precipitated out. It was filtered, washed several times with cold ethanol and dried over P<sub>4</sub>O<sub>10</sub> (Scheme 1).

### 2.2.3. Synthesis of complexes

The complexes were synthesized by refluxing ethanolic solution (30 mL) of ligand (1 mmol) with an aqueous ethanolic solution (30 mL) of corresponding metal salt (1 mmol) for 8 h at 55 °C. On cooling overnight at 0 °C, the colored complex was precipitated out, which was filtered, washed with cold ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub> (Fig. 1).

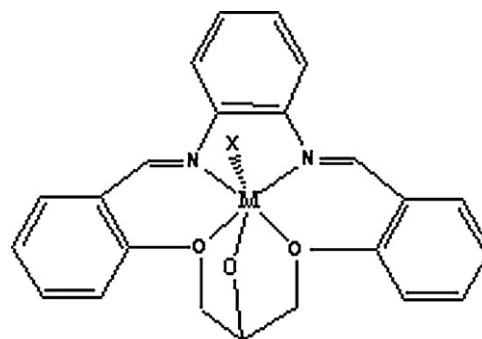
## 3. Result and discussion

On the basis of elemental analysis the complexes were assigned to possess the composition as shown in Table 1. The molar conductance data for Ni(II) and Cu(II) complexes revealed that these complexes behave as non-electrolytes [24]. Thus the general formula of the complexes may be given as [M(L)X] where M = Cu, Ni and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>.

### 3.1. IR spectra

In ligands (**I**) bands corresponding (OH) and C=O groups appeared at 3447 cm<sup>-1</sup> and 1636 cm<sup>-1</sup> and in ligand (**L1**) bands corresponding to OH and C=N groups appeared at 3294 cm<sup>-1</sup> and 1612 cm<sup>-1</sup> respectively.

On complexation the absence of band corresponding to OH indicate the coordination of O with metal. A band corresponding to  $\nu(\text{C}=\text{N})$  shifts to the lower wave number (20–30 cm<sup>-1</sup>)



Where M = Ni, Cu  
X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>

Fig. 1. Structure of the complexes.

**Table 1**  
Molar conductance and elemental analysis data of ligand and its complexes.

Ligand/complexes	Molar cond. ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Color	M.P. ( $0^\circ \text{C}$ )	Yield (%)	Elemental analysis found (calculated) %			
					M	C	H	N
$L_1 = (\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_3)$	–	Orange	144	70	–	74.70 (74.67)	5.08 (5.12)	7.69 (7.63)
$[\text{Ni}(\text{L})\text{Cl}] (\text{NiC}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{Cl})$	10	Redish Brown	>300	65	12.71 (12.64)	59.35 (59.32)	4.11 (4.09)	5.97 (6.03)
$[\text{Ni}(\text{L})\text{NO}_3] (\text{NiC}_{23}\text{H}_{18}\text{N}_3\text{O}_6)$	14	Brown	>300	62	11.91 (11.96)	56.18 (56.24)	3.83 (3.87)	8.53 (8.55)
$[\text{Ni}(\text{L})\text{CH}_3\text{COO}] (\text{NiC}_{25}\text{H}_{21}\text{N}_2\text{O}_5)$	12.6	Redish Brown	>300	75	12.06 (12.03)	61.57 (61.51)	4.36 (4.30)	5.68 (5.74)
$[\text{Cu}(\text{L})\text{Cl}] (\text{CuC}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{Cl})$	11	Brown	217	68	13.53 (13.53)	58.78 (58.84)	4.02 (4.05)	6.02 (5.97)
$[\text{Cu}(\text{L})\text{NO}_3] (\text{CuC}_{23}\text{H}_{18}\text{N}_3\text{O}_6)$	9.7	Brown	222	70	12.86 (12.81)	55.67 (55.70)	3.87 (3.83)	8.42 (8.47)
$[\text{Cu}(\text{L})\text{CH}_3\text{COO}] (\text{CuC}_{25}\text{H}_{21}\text{N}_2\text{O}_5)$	13.5	Dark Brown	>300	78	12.80 (12.86)	60.98 (60.91)	4.22 (4.26)	5.61 (5.68)

which indicates that the coordination takes place through the nitrogen atom of azomethine groups. Some new bands appeared at  $360\text{--}390 \text{ cm}^{-1}$  and  $450\text{--}560 \text{ cm}^{-1}$ . These may be due to  $\nu(\text{M}\text{--}\text{N})$  and  $\nu(\text{M}\text{--}\text{O})$  vibrations respectively. Nitrate complexes show bands at  $1458\text{--}1442 \text{ cm}^{-1}$  ( $\nu_5$ ),  $1043\text{--}1020 \text{ cm}^{-1}$  ( $\nu_2$ ) and  $1312\text{--}1303 \text{ cm}^{-1}$  ( $\nu_1$ ) for Cu(II) and Ni(II) complexes [25–27]. The value of  $\Delta(\nu_5 - \nu_1)$ , i.e. 146 and  $139 \text{ cm}^{-1}$  suggests the unidentate coordination of  $\text{NO}_3^-$  ions. The bands corresponding to  $\nu(\text{M}\text{--}\text{Cl})$  are observed at  $345\text{--}320 \text{ cm}^{-1}$  indicating the presence of (M–Cl) bond. IR spectra for acetate complexes of Ni(II) and Cu(II) shows the medium intensity bands at  $1600\text{--}1655 \text{ cm}^{-1}$  and  $1338\text{--}1376 \text{ cm}^{-1}$  assigned to  $\nu_a(\text{C}\text{--}\text{O})$  and  $\nu_s(\text{C}\text{--}\text{O})$  respectively. The difference between two frequencies is  $\sim 289 \text{ cm}^{-1}$  and  $\sim 265 \text{ cm}^{-1}$  respectively for Ni(II) and Cu(II) complexes, which is greater than that for bidentate acetates ion by  $\sim 217 \text{ cm}^{-1}$  and for uncoordinated acetate ion by  $\sim 143 \text{ cm}^{-1}$ . It supports strongly that one acetates ions are coordinated to the metal ion in unidentate fasion [28].

### 3.2. Mass spectra

The electron impact mass spectra show a peak at 372 amu, which is also the molecular ion peak, corresponding to the molecular mass 371 amu. It also shows a series of peaks, i.e. 197 amu, 212 amu, 319 amu, 322 amu corresponding to various fragments as shown in Fig. 2. Their intensity gives an idea of stability of fragments.

**Table 2**  
Magnetic moment and electronic spectral data of the complexes.

Complex	$\mu_{\text{eff}}$ (B.M.)	$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )
$[\text{Ni}(\text{L})\text{Cl}]$	3.20	9671, 13,140, 22,123, 26,736
$[\text{Ni}(\text{L})\text{NO}_3]$	3.18	9285, 13,140, 22,075, 25,906
$[\text{Ni}(\text{L})\text{CH}_3\text{COO}]$	3.01	9671, 11,111, 16,075, 25,109
$[\text{Cu}(\text{L})\text{Cl}]$	1.95	9671, 11,098, 27,397
$[\text{Cu}(\text{L})\text{NO}_3]$	1.92	9671, 12,804, 28,818
$[\text{Cu}(\text{L})\text{CH}_3\text{COO}]$	2.02	9758, 11,098, 27,548

### 3.3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.643 (s, 1H, HC=N); 7.32–7.40 (m, 4H, ArH); 7.22–7.26 (2d, 2H, ArH); 7.01–7.07 (1d, 1H, ArH); 6.90–6.98 (t, 2H, ArH); 5.29–5.45 (quintet, 1H, CH); 5.09–5.19 (d, 4H,  $\text{CH}_2$ ); (1H OH washed out by  $\text{D}_2\text{O}$ ) ppm.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  163.601 (C=N); 161.264, 132.292, 125.405, 119.142, 114.444 (Ar); 146.426, 127.656, 123.620 (Ar); 69.429 ( $\text{OCH}_2$ ); 67.585 (CHOH); ppm.

### 3.4. Electronic spectra

Ni(II) complexes show magnetic moments in the range 3.01–3.20 B.M. at room temperature (Table 2). The electronic spectra of the Ni(II) complexes recorded in the DMSO solution at room temperature show bands in the region 9285–13,140,

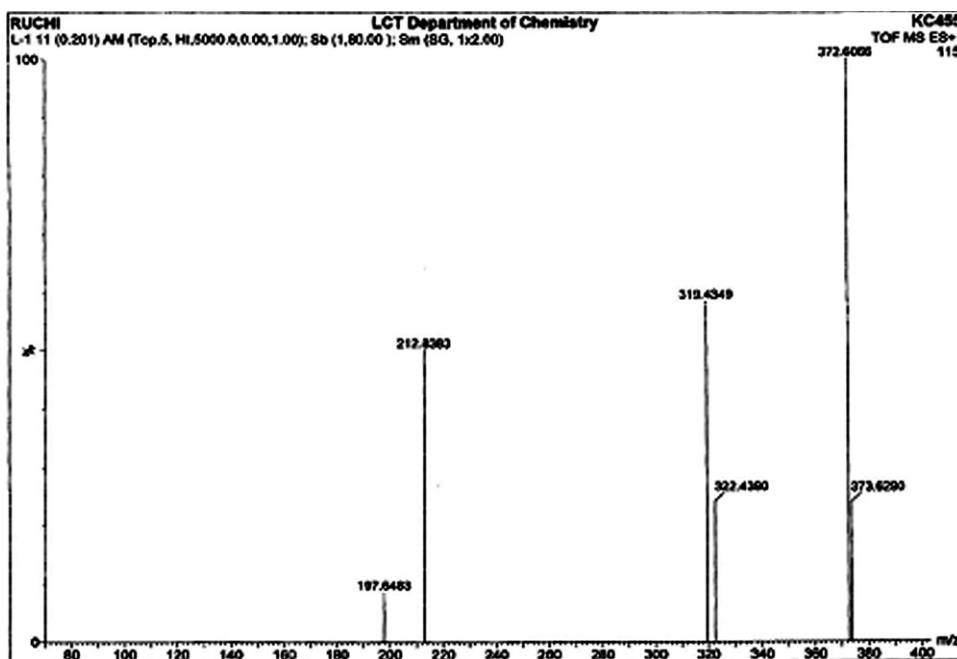


Fig. 2. Mass spectra of ligand.

**Table 3**  
Ligand field parameters of the complexes.

Complex	Dq	B (cm <sup>-1</sup> )	β	LFSE (kJ mol <sup>-1</sup> )
[Ni(L)Cl]Cl	967	416	0.39	138
[Ni(L)NO <sub>3</sub> ]	967	419	0.40	138
[Ni(L)CH <sub>3</sub> COO]	1111	523	0.50	159

16,075–22,172, 25,109–26,736 cm<sup>-1</sup> (Table 2) characteristic of an octahedral geometry [29]. The ground state in Ni(II) octahedral coordination is <sup>3</sup>A<sub>2g</sub>. Thus, these bands are assignable three spin allowed transitions <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) respectively. Various ligand field parameters calculated for Ni(II) complexes are given in Table 3.

The magnetic moment values for Cu(II) complexes lie in the 1.95–2.02 BM range corresponding to one unpaired electron (Table 2). The electronic spectra of these complexes display bands in the range 9671–9758, 11,098–12,804, 27,548–28,818 cm<sup>-1</sup>. These bands may be assigned to the transitions <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> → d<sub>z<sup>2</sup></sub>) (ν<sub>1</sub>), <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> → d<sub>xy</sub>) (ν<sub>2</sub>) and <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub> → d<sub>xy</sub>, d<sub>yz</sub>) (ν<sub>3</sub>) respectively. The complexes may be considered to possess a tetragonal geometry. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn-Teller effect [30].

### 3.5. EPR spectra

The X-band EPR spectra of Cu(II) complexes were recorded at RT and LNT. The g<sub>iso</sub> values and the geometric parameter G, i.e. the measurement of exchange interaction between the copper centers were evaluated by using the expressions:

$$g_{\text{iso}} = \frac{g_{\parallel} + 2g_{\perp}}{3}$$

$$G = \frac{g_{\parallel} - 2.0023}{g_{\perp} - 2.0023}$$

$$= \frac{4k_{\parallel}^2 \Delta E_{xz}}{k_{\perp}^2 \Delta E_{xy}}$$

The evaluated value of g tensor parameters shows the order as g<sub>∥</sub> > g<sub>⊥</sub> > 2.0023 which reveals that d<sub>x<sup>2</sup>-y<sup>2</sup></sub> is the ground state [31] and also indicates that the unpaired electron is localized in the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital of the Cu(II) ion and the spectral figures are characteristic of the axial symmetry (Table 4). The tetragonal elongated structure is thus confirmed for the aforesaid complexes [32]. The complexes in the present study show the value of G < 4 which indicates the effective interaction between the copper centers [33].

### 3.6. Molecular modeling

#### 3.6.1. Experimental/materials and methods

The molecules (a) ligand, (b) ligand–Cu(II) complex, (c) ligand–Ni(II) complex were modeled by MOPAC 2007 [33] program in gas phase using PM6 level of theory [34]. Selected parts of the complexes not containing the metal ion were preoptimized using molecular mechanics methods. Several cycles of energy minimization had to be carried for each of the molecules. Geometry was optimized using eigen vector following. The Root Mean Square

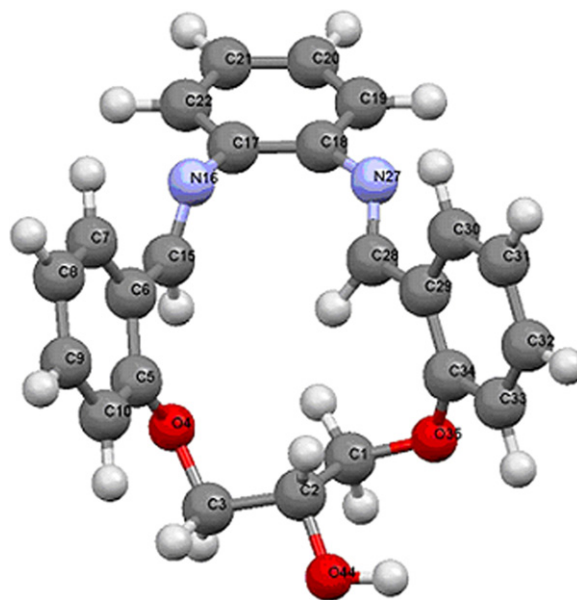


Fig. 3. Geometry optimized structure of ligand.

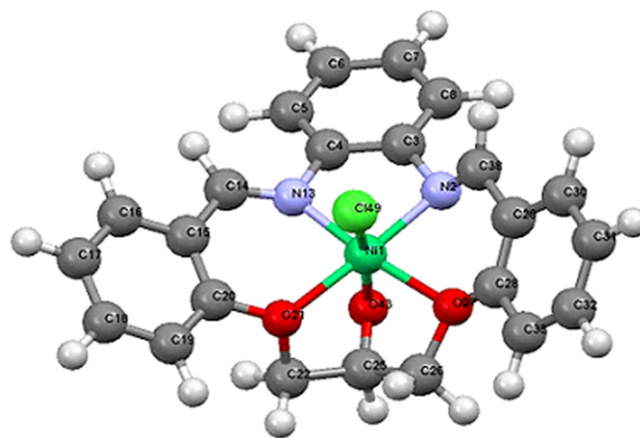


Fig. 4. Geometry optimized structure of ligand–Ni(II) complex.

Gradient for molecules was all less than one. Self Consistent Field was achieved in each case.

#### 3.6.2. Results

The ligand is in highly folded form in the optimized structure (Fig. 3). The mean planes of the two flanking phenyl groups are at an angle of 60.35° with each other and at 67 and 82° with the central phenyl group. The C(sp<sup>2</sup>)–N bond lengths are 1.29 and 1.42 Å the C(sp<sup>2</sup>)–O bonds are 1.39 and C(sp<sup>3</sup>)–O are 1.44 Å are close to literature values. The N–N bond distance is 2.9 Å and O–O distance is 4.2 Å.

The ligand–Ni(II) complex has distorted octahedral geometry with the equatorial positions being occupied by the two O and two N donor atoms (c) (Fig. 4). The Ni(II) ion lies nearly on the mean

**Table 4**  
EPR parameters and orbital reduction parameters of Cu(II) complexes.

Complex	A RT/LNT	g <sub>⊥</sub> RT/LNT	g <sub>∥</sub> RT/LNT	g <sub>iso</sub> RT/LNT	G RT/LNT
[Cu(L)Cl]	95/90	1.9962/2.03185	2.0885/2.03185	2.0269/2.1426	1.0462/1.1636
[Cu(L)NO <sub>3</sub> ]	66/63	1.9847/2.0006	2.1548/2.3221	2.0414/2.1077	1.0857/1.1607

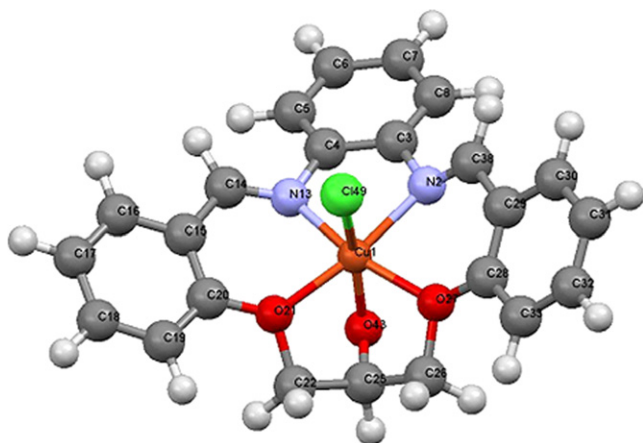


Fig. 5. Geometry Optimized structure of ligand-Cu(II) complex.

plane (0.06 Å above) of the equatorial NNOO donor system. The mean planes of the two flanking phenyl groups are at angle of 73.40° with each other and at 38.3 and 47.9° with the central phenyl group. The N–N and O–O bite distances are 2.77 and 3.22 Å respectively. The equatorial Ni(II)–O distances are 2.12 and 1.95 Å respectively and the Ni(II)–N distances being 1.88 and 1.97 Å. The axial positions are occupied by one oxygen atom of the ligand and a chloride ion. The Cl49–Ni1–O27 bond angle is near to perpendicular (98.93°). The axial Ni(II)–O distance being 1.83 Å and the Ni(II)–Cl distance is 2.15 Å. The Cl149–Ni1–O27 bond angle is near to perpendicular (98.93°).

The ligand–Cu(II) complex has tetragonal geometry with the equatorial positions being occupied by the two O and two N donor atom (Fig. 5). The Cu(II) ion lies on the mean plane of the equatorial NNOO donor system. The mean planes of the two flanking phenyl groups are at an angle of 60.87° with each other and at 36.1 and 39.9° with the central phenyl group. The N–N and O–O bond distances are 2.74 and 3.20 Å respectively. The equatorial Cu(II)–O distances are 2.00 and 1.99 Å respectively and the Cu(II)–N distances being 2.04 and 1.93 Å. The axial positions are occupied by one oxygen atom of the ligand and a chloride ion. The O27–Cu1–Cl49 bond angle is nearly perpendicular (91.1°), while O27–Cu1–O43 angle is 78.6°. The axial Cu(II)–O distance is 1.84 Å and the Cu(II)–Cl distance is 2.24 Å [35–39].

#### 4. Conclusion

Ni(II) and Cu(II) complexes with a pentadentate macrocyclic ligand have been prepared and characterized. On the basis of above spectral studies and molecular modeling a distorted octahedral geometry has been assigned for Ni(II) and tetragonal geometry for Cu(II) complexes. Various ligand field and bonding parameters have been calculated and discussed.

#### Acknowledgements

The authors are grateful to the UGC (New Delhi) for financial support, SAIF, IIT (Bombay) for recording ESR spectra, the Head, App Sci. and Dean FET for recording molecular modeling data.

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