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EPR, IR and electronic spectral studies on Ni(II) and Cu(II) complexes with N-donor tetradentate [N_4] macrocyclic ligand

Sulekh Chandra*, Archana Gautam

Department of Chemistry, Zakir Husain College, University of Delhi, JLN-Marg, New Delhi 110002, India

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Abstract

Nickel(II) and copper(II) complexes are synthesized with a novel tetradentate macrocyclic ligand, i.e. 2,6,12,16,21,22-hexaaza;3,5,13,15-tetraphenyltricyclo[15,3,1,1^{7-11}] docosa;1(21),2,5,7,9,11(22),12,15,17,19-decaene (L) and characterized by the elemental analysis, magnetic susceptibility measurements, mass, ^{1}H NMR, IR, electronic and EPR spectral studies.

All the complexes are non-electrolytic in nature. Thus, these may be formulated as [M(L)X_2] [M = Ni(II), Cu(II) and X = Cl^-, NO_3^- and (1/2)SO_4^{2-}]. Ni(II) and Cu(II) complexes show magnetic moments corresponding to two and one unpaired electron, respectively.

On the basis of IR, electronic and EPR spectral studies an octahedral geometry has been assigned for Ni(II) and tetragonal geometry for Cu(II) complexes.

Keywords: Macrocycle; Nickel(II); Copper(II)

1. Introduction

The complexes of transition metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems such as porphyrins and cobalamines [1,2]. The main interest in new macrocyclic bifunctional chelating agents arises due to their use in labeling monoclonal antibodies with radioactive metals [3–5] and for cancer diagnosis [6,7].

The synthesis and characterization of coordination compounds with aza-macrocyclic ligands have evolved as a main research area during recent years [8,9]. Aza-type ligands appear to be very promising for catalysis and have been discussed as chelating systems in the literatures [10,11]. The complexation capabilities of polyaza macrocycles are mainly governed by the macrocyclic ring size [12].

Aza-macrocyclic ligands, as well as their coordination and organometallic compounds, play important roles in catalytically activating small molecules in electrochemically assisted reactions with several substrates [13,14].

In this paper, we report the spectral studies on Ni(II) and Cu(II) complexes with a new aza-macrocyclic ligand (Fig. 1). On the basis of analytical, magnetic and spectral data an octahedral geometry for Ni(II) whereas tetragonal geometry for Cu(II) complexes has been assigned.

2. Experimental

All the chemicals used were of AnalaR grade, and procured from Fluka and Sigma–Aldrich. Metal salts were purchased from E. Merck and were used as received.

2.1. Synthesis of ligand

Hot ethanolic solution (20 mL), of dibenzoylmethane (4.48 g, 0.02 mol), and a hot ethanolic solution (20 mL), of 2,6-diaminopyridine (2.18 g, 0.02 mol) were mixed slowly with constant stirring. This mixture was refluxed at 80 °C for 6 h in presence of few drops of concentrated hydrochloric acid. On cooling, light brown precipitate formed, which was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}. Yield 70%, m.p. 85 °C. Elemental analysis found (%): C 80.82; H 5.09; N 14.17. Calculated for $C_{40}H_{30}N_6$ (atomic mass 594) was C 80.80; H 5.05 and N 14.14%.

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* Corresponding author. Tel.: +91 11 22911267; fax: +91 11 23215906.
E-mail addresses: schandra_00@yahoo.com (S. Chandra), archanagautam_00@yahoo.com (A. Gautam).

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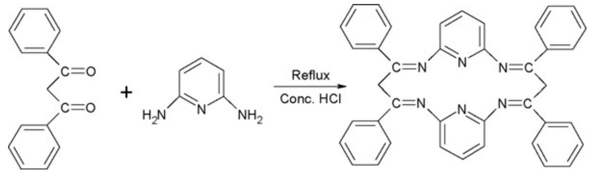

Fig. 1. Preparation and structure of the ligand (L).

2.2. Synthesis of complexes

Hot ethanolic (20 mL) solution of ligand (0.594 g, 0.001 mol) and hot ethanolic solution of corresponding metal salts (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5–8 h at 70–80 °C. On cooling, coloured complex precipitated out. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}.

2.3. Physical measurements

The C, H and N were analysed on a Carlo-Erba 1106 elemental analyzer. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4{\cdot}5H_2O$ as a calibrant. Electron impact mass spectra were recorded on TOF MS ES+ mass spectrometer. ^1H NMR spectra were recorded on Hitachi FT-NMR, model R-600 spectrometer using DMF as a solvent, chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (KBr) were recorded on a FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMF on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline sample and in the solution of DMSO, at room temperature for Cu(II) complexes on E4–EPR spectrometer using the DPPH as the *g*-marker.

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 measurements of the complexes in DMF correspond to non-electrolytic nature. These complexes may be formulated as $[M(L)X_2]$ [M = Ni(II), Cu(II) and X = Cl^-, NO_3^- and $(1/2)SO_4^{2-}$]. The electron impact mass spectra (Fig. 2) of ligand (L) confirm the proposed formula by showing a peak at 616 amu (i.e. atomic mass 594 corresponding to the macrocyclic moiety $(C_{40}H_{30}N_6)^+$ + 23 atomic mass of Na^+ ion). It also shows a series of peaks, i.e. 300 amu, 326 amu, 367 amu, 466 amu, 472 amu, 480 amu, 524 amu and 582 amu, etc. corresponding to various fragments. Their intensity gives an idea of stability of fragments. The ^1H NMR spectrum of the ligand does not give any signal attributable to primary diamine or alcoholic protons. The presence of a sharp multiplet in the region, δ 7.28 may be assigned for the benzenoid hydrogen (6H) having the same chemical shift and thus these behave as equivalent [15]. A signal at δ 1.80–2.20 ppm may be assigned for (C–CH_2–C, 4H) and a strong triplet appeared for (C–C_6H_5, 20H). No IR spectral bands appear corresponding to the free primary diamine or hydroxyl group [16], which suggests the complete condensation of keto group with amino group. The vibrations corresponding to υ(C=C) and υ(C=N) skeletal are present in the region 1560 cm^{-1} shoulder and 1602 cm^{-1}. The bands appearing at 924–805 cm^{-1} may be assigned to ring breathing mode, C–H deformations, respectively. The strong frequencies 1597 cm^{-1} are usually associated to υ(CN) coupled with phenyl ring vibrations. The band appearing at 1620–1580 cm^{-1} may be assigned to symmetric or asymmetric υ(C=N) vibrations. The shifting of the υ_{CN} bands toward the lower side in the complexes indicate that the coordination take place through the nitrogen of $\upsilon_{C=N}$ group, thus implying that the ligand is tetradentate.

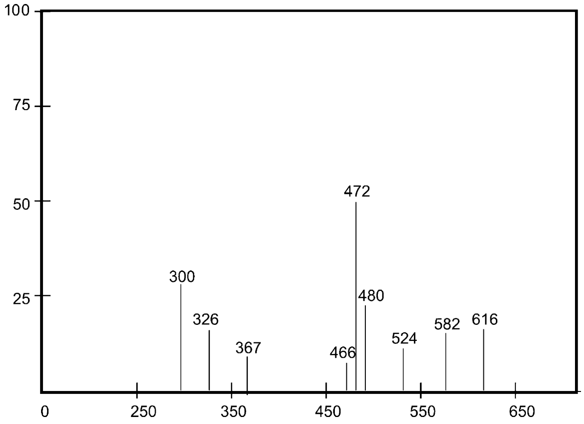

Fig. 2. Electron impact mass spectrum of the ligand (L).

3.1. IR bands due to anions

IR spectra of nitrato complexes display three stretching bands at 1455–1483 cm^{-1}, 1228–1231 cm^{-1} and 926–999 cm^{-1}

Table 1
Elemental analysis data of the complexes

Complex	Atomic mass	Colour	m.p. (°C)	Yield (%)	Elemental analysis data found (calculated) (%)			
					Metal	C	H	N
Ligand (L) $C_{40}H_{30}N_6$	594	Light brown	85	70	–	80.82 (80.80)	5.09 (5.05)	14.17 (14.14)
$[Ni(L)Cl_2]$ $NiC_{40}H_{30}N_6Cl_2$	724	Light green	248	64	8.13 (8.11)	66.32 (66.30)	4.17 (4.14)	11.62 (11.60)
$[Ni(L)(NO_3)_2]$ $NiC_{40}H_{30}N_8O_6$	777	Light green	240	62	7.58 (7.55)	61.76 (61.78)	3.84 (3.86)	14.44 (14.41)
$[Ni(L)SO_4]$ $NiC_{40}H_{30}N_6O_4S$	749	Light green	270	67	7.86 (7.84)	64.05 (64.08)	4.05 (4.00)	11.24 (11.21)
$[Cu(L)Cl_2]$ $CuC_{40}H_{30}N_6Cl_2$	729	Green	285	61	8.75 (8.78)	65.87 (65.84)	4.15 (4.12)	11.49 (11.52)
$[Cu(L)(NO_3)_2]$ $CuC_{40}H_{30}N_8O_6$	782	Green	282	60	8.15 (8.18)	61.34 (61.38)	3.81 (3.84)	14.35 (14.32)
$[Cu(L)SO_4]$ $CuC_{40}H_{30}N_6O_4S$	754	Green	280	62	8.45 (8.49)	63.62 (63.66)	3.95 (3.98)	11.17 (11.14)

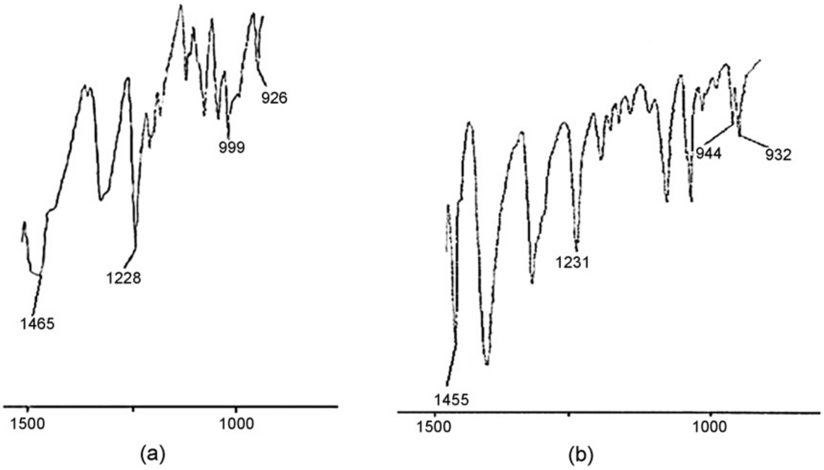

Fig. 3. IR spectral bands due to anions. (a) [Ni(L)(NO$_3$)$_2$], (b) [Cu(L)(NO$_3$)$_2$].

(Fig. 3). The position of the bands suggests that both the nitrate groups are coordinated in unidentate manner.

In the sulphato complexes, the presence of medium intensity bands in the region 944–999 cm^{-1}, 430–438 cm^{-1} and another strong band appears in the region 1170–1183 cm^{-1}, which splits into two bands that suggest the coordinated behaviour of sulphate group in unidentate manner.

4. Nickel(II) complexes

Magnetic moment of the Nickel(II) complexes at room temperature lie in the range 2.93–2.98 BM (Table 2). These values are in tune with a high spin configuration and show the presence of an octahedral environment [17] around the Ni(II) ion in the complexes (Fig. 5).

The electronic spectra of the complexes (Fig. 4), exhibit four bands in the range 10,395–10,526 cm^{-1}, 18,621–18,460 cm^{-1}, 27,932–28,571 cm^{-1} and 36,231–38,022 cm^{-1}. An examination of these bands indicates that the complexes have an octahedral geometry and might possess D$_{4h}$ symmetry [18]. The ground state of Ni(II) in an octahedral coordination is $^3A_{2g}$. Thus, these bands may be assigned to the three spin allowed transitions [19,20], $^3A_{2g}$ (F) → $^3T_{2g}$(F), $^3A_{2g}$(F) → $^3T_{1g}$(F), $^3A_{2g}$(F) → $^3T_{1g}$(P), respectively and fourth one may be considered as charge transfer band (Fig. 5).

5. Copper(II) complexes

The magnetic moment measurements of the Cu(II) complexes at room temperature lie in the range 1.95–2.12 BM (Table 2) corresponding to one unpaired electron [16,21].

Electronic spectra of the copper complexes (Fig. 4) recorded in DMSO possess absorption bands in the range 11,013–11,098 cm^{-1}, 16,583–18,621 cm^{-1} and 27,932–28,571 cm^{-1}. These bands may be considered to the following three spin allowed [22] transitions: $^2B_{1g} \rightarrow {}^2A_{1g}(d_{x^2-y^2} \rightarrow d_{z^2})$, $^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} \rightarrow d_{zy})$ and $^2B \rightarrow {}^2E_g(d_{x^2-y^2} \rightarrow d_{zy}, d_{yz})$, these transitions suggest D$_{4h}$ symmetry. The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn–Teller distortion effect.

The EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in the solution of DMSO at room temperature. The spectra of the complexes exhibit a single anisotropic broad signal. The study of the spectra give $g_\parallel$ value in the range 2.0706–2.0906 and $g_\perp$ value in the range 2.0382–2.0510 (Table 3(a) and (b)). The observed $g_\parallel$ value for the Cu(II) complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The values of $g_\parallel$ and $g_\perp$ are closer to 2 and $g_\parallel > g_\perp > 2.0023$. This suggests distortion in the Cu(II) complexes from Oh symmetry to D$_{4h}$ symmetry.

$G = (g_\parallel - 2)/(g_\perp - 2)$, which measure the exchange interaction between the copper centres in a polycrystalline solid has been calculated. According to Hathway and Billing [23,24], if the value of 'G' less 4, indicates a considerable exchange interaction in the solid complex. In the complexes of Cu(II) reported in this paper, the 'G' value are less than 4 indicating the exchange interaction in solid complex.

6. Ligand field parameters

Various ligand field parameters were calculated for the complexes and are listed in Table 4. The values of D_q in Ni(II) complexes were obtained from the first transition. Our results are in agreement with the respective position of anions in the spectrochemical series. The Nephelauxetic parameter β was readily

Table 2
Magnetic moment and electronic spectral data of the complexes

Complex	μ_{eff} (BM)	λ_{max} (cm^{-1})
[Ni(L)Cl$_2$]	2.98	10,416, 18,621, 28,571, 36,231
[Ni(L)(NO$_3$)$_2$]	2.95	10,526, 18,621, 27,932, 36,496
[Ni(L)SO$_4$]	2.93	10,395, 18,621, 28,571, 38,022
[Cu(L)Cl$_2$]	1.98	11,013, 18,621, 28,571
[Cu(L)(NO$_3$)$_2$]	1.95	11,098, 18,621, 27,932
[Cu(L)SO$_4$]	2.12	11,086, 16,583, 28,248

Table 3
EPR spectral data of the complexes

Complexes	(a) Data at LNT and room temperature (as polycrystalline sample)				(b) Data at LNT and room temperature (in solution of DMF)			
	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G
[Cu(L)Cl$_2$]	2.0773	2.0382	2.0512	2.0235	2.0906	2.0446	2.0599	2.0313
[Cu(L)(NO$_3$)$_2$]	2.0773	2.0446	2.0597	1.5156	2.0839	2.0510	2.0619	1.6450
[Cu(L)SO$_4$]	2.0706	2.0446	2.0532	1.5829	2.0906	2.0510	2.0642	1.7764

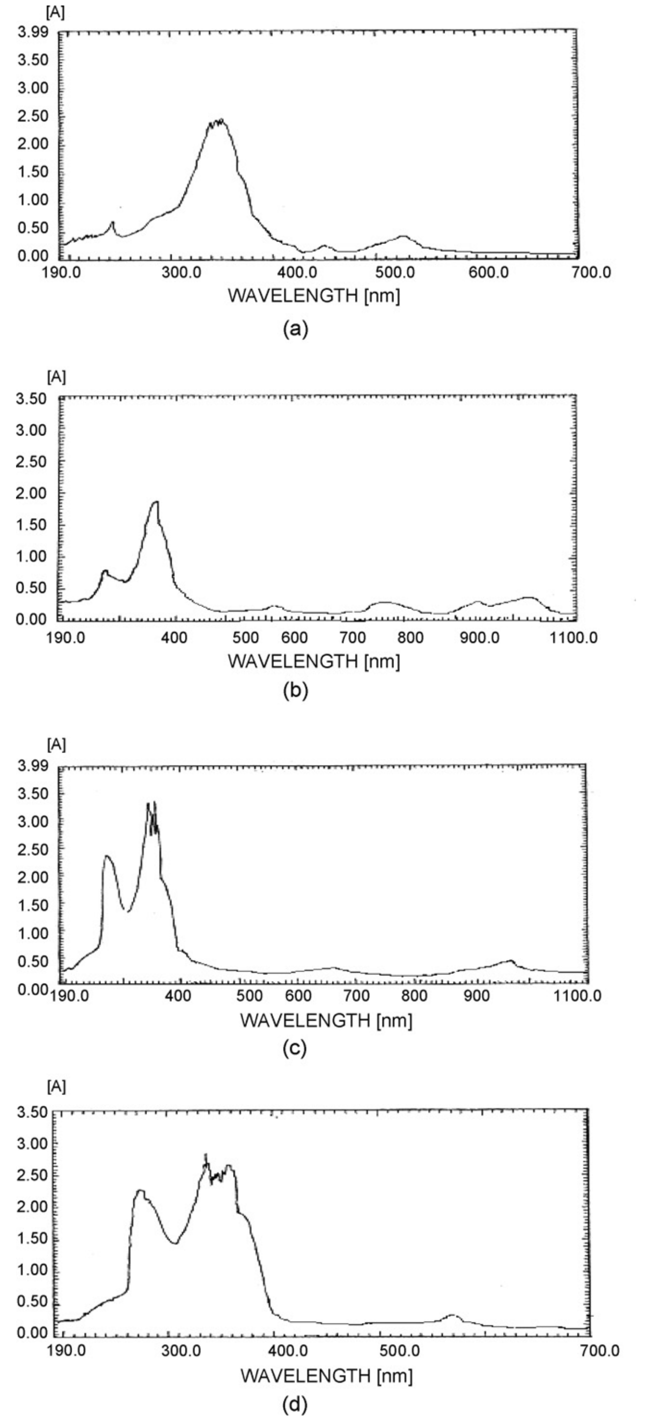

Fig. 4. Electronic spectra of the complexes. (a) [Ni(L)Cl$_2$], (b) [Ni(L)(NO$_3$)$_2$], (c) [Cu(L)Cl$_2$], (d) [Cu(L)(NO$_3$)$_2$].

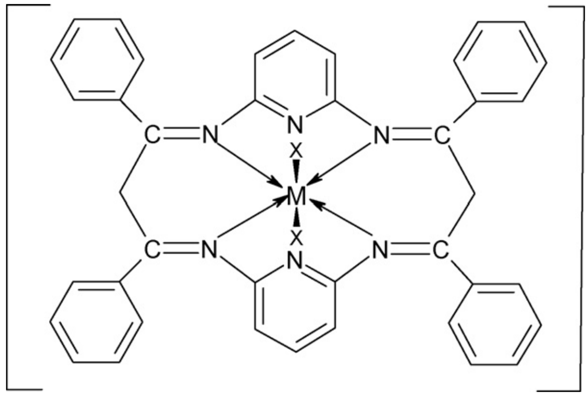

Fig. 5. Suggested structure of the complexes, where M = Ni(II) and Cu(II), X = Cl$^-$, NO$_3$$^-$ and (1/2)SO$_4$$^{2-}$.

Table 4
Ligand field parameter of the complexes

Complex	D_q (cm^{-1})	B (cm^{-1})	β	LFSE (kJ mol^{-1})
[Ni(L)Cl$_2$]	1041.6	1062	1.02	149.51
[Ni(L)(NO$_3$)$_2$]	1052.6	998	0.96	151.09
[Ni(L)SO$_4$]	1039.5	1067	1.02	149.21

obtained by using the relation

$$\beta = B(\text{complex}) \times B(\text{free ion})$$

where B(free ion) for Ni(II) is 1041 cm^{-1}. The values of β indicate the appreciable covalent character of metal ligand 'σ' bond.

7. Conclusion

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

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