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Short communication

Spectroscopic studies on Co(II), Ni(II), Cu(II) and Zn(II) complexes with a N₄-macrocylic ligands

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Abstract

Complexes of cobalt(II), nickel(II), copper(II) and zinc(II) with a new tetraaza macrocyclic ligand have been synthesized and characterized by microanalyses, molar conductance, magnetic susceptibility, mass, thermogravimetric (TGA), IR, ¹H and ¹³C NMR, electronic and ESR spectral studies. All the complexes are found to have the formula [MLX₂]·nH₂O and are six-coordinated with distorted octahedral geometry. © 2007 Elsevier B.V. All rights reserved.

Keywords: Macrocyclic ligands; Transition metal complexes; Mass spectroscopy; ¹H NMR; Electronic; IR; ESR

1. Introduction

There is a continuing interest in the chemistry of polyaza macrocycles because of their ability to interact with both metal cations and anionic species [1-3]. Transition metal complexes of polyaza macrocyclic ligands with functional groups have been synthesized in order to investigate how the functional groups affect their coordination geometry and chemical properties [4,5]. Complexes of macrocyclic ligands have become very important building blocks of ligand-bridged complexes that possess various dimensional structures and fascinating magnetic properties [6-9]. The large polyazamacrocyclic molecules, containing six or more nitrogen atoms, are known to form stable metal complexes, with one or more metal ions, due to their large number of nitrogen atoms [10]. They find applications in different areas such as catalysis, bioinorganic, biomimetic and coordination chemistry [11]. Metal complexes of macrocycles are also tested in medicine, radio immunotherapy [12–14] cancer diagnosis and treatment of tumor [15]. The complexes of manganese and iron with macrocyclic ligands are used as antimicrobial, antifertility, anti-inflammatory and analgesic agents [16,17]. In view of the interest and importance of nitrogen macrocycles, we have reported the preparation of new tetraaza macrocycles of variable

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ring sizes by non-template synthetic methods [18]. Herein, we report the preparation and characterization of the complexes of Co(II), Ni(II), Cu(II) and Zn(II) with three new ligands: dibenzo[e,m][1,4,8,11]tetraazacyclotetradecine-5,14-dione (L₁), dibenzo[e,n][1,4,8,12]tetraazacyclotetradecine-6,15-dione (L₂) and tribenzo[b,f,m][1,4,8,11]tetraazacyclotetradecine-5,14-dione 5,14-dione (L₃).

2. Experimental

All the chemicals used were of AnalaR grade, and purchased from Sigma–Aldrich. Metal salts were procured from E. Merck and were used as received. The preparation of ligands was described elsewhere [18].

2.1. Synthesis of complexes

The general method used for the preparation of the complexes is: to 10 ml warm solution of the corresponding metal salt [0.001 mol, chloride in the case of Co(II), Ni(II) and Cu(II) and acetate in the case of Zn(II)] the solution (10 ml) of the respective ligand (0.001 mol) in methanol was added and refluxed for 5 h at 60 °C. The solid complex obtained was collected on a fine frit and washed with cold methanol and then with acetone. The complexes were dried in vacuo over fused calcium chloride till no change in weight was noticed.

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2.2. Physical measurements

The percentages of C, H and N were determined using a PerkinElmer CHN analyzer-2400. Molar conductance was measured on the Digisun digital DI-909 conductivity bridge. TGA curves were recorded using Mettler-Toledo, DSC and TGA 822e series instrument. Magnetic susceptibility was measured at room temperature on a Gouy balance using Hg[Co(CNS)₄] as callibrant. The mass spectrum was recorded on CEC-21-110B and Finnigan MAT-1210 mass spectrometers. ¹H NMR spectrum was recorded using a Jeol 200 MHz FT-NMR spectrometer in d_6 -DMSO. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra were recorded on a PerkinElmer BX series spectrometer using KBr pellets in the IR region and as nujol mulls between CsI plates in the far-IR region. The electronic spectra were recorded in DMF solutions on a Shimadzu UV-vis spectrophotometer model 2401 PC. ESR spectra of the Cu(II) complexes were recorded at liquid nitrogen temperature on JEOL-JES-PE-3X ESR spectrometer using DPPH as the g-marker.

3. Results and discussion

3.1. Complexes

All the complexes are stable, non-hygroscopic and soluble in DMF and DMSO but insoluble in methanol, ethanol, acetone and benzene. The analytical data of the metal chelates presented in Table 1 indicate that the metal ions are coordinated to one ligand molecule and two chloride or acetate ions. The low molar conductivities of all the complexes in DMF indicate that they are non-electrolytic in nature [19].

3.2. Mass spectra

The mass spectra of all complexes exhibit high mass peak corresponding to $[(MLX_2)\cdot H_2O]^{7+}$. Another ion that confirms the coordination of the ligand to the metal ion is the appearance of ML^{7+} fragment. The other fragment peaks are as observed in the mass spectrum of the ligand. The mass spectral, analytical and thermal data confirm the formulae of the com-

Table 1			
Analytical and	physicochemical	data of the	complexes

plexes as $[MLX_2] \cdot H_2O$, where M = Co(II), Ni(II) and Cu(II) and $X = Cl^-$. The mass spectrum of $[Zn(L_3)(OAc)_2]$ exhibits the *m*/*z* peaks at 555.2, 496.3 and 437 which are assignable to the species $[Zn(L_3)(OAc)_2]$, $[Zn(L_3)(OAc)]$ and $[Zn(L_3)]$, respectively. Further, all the species containing metal ion were confirmed by good agreements between the observed and calculated isotopic distributions [20].

3.3. Thermal analysis

The thermograms of the complexes of Co(II), Ni(II) and Cu(II) show initial weight loss in the temperature range of 60-150 °C, corresponding to one water molecule. The presence of water molecule in these complexes is further confirmed by an endothermic peak in this temperature range. The loss in the low temperature region indicates that the water molecule is lattice held [21].

On further heating, the complexes exhibit mass loss curve beyond 180 °C and continues to a temperature around 750 °C, after which the TG becomes parallel to the temperature axis. The percentage of the residue left was found to be the respective metal oxide, Co_3O_4 , NiO, CuO and ZnO [22].

3.4. IR spectra

The characteristic absorptions of the N₄-macrocyclic ligands containing two amide and two amine groups have been discussed in an earlier communication [18]. The spectra of the corresponding complexes exhibit these absorptions at different frequencies indicating the coordination of the ligands. The ν (N–H) and amide-II (Table 2) stretching frequencies shift by 50-100 and 20-30 cm⁻¹, respectively, towards lower frequency side. The C=O stretching frequency shifts by $10-20 \text{ cm}^{-1}$ towards high frequency side indicating that the amide oxygen is not coordinated [23]. The IR spectra of Co(II), Ni(II) and Cu(II) complexes exhibit a broad absorption between 3500 and $3250 \,\mathrm{cm}^{-1}$. This broad absorption is the characteristic of ν (O–H) of water molecule. The water molecule in a complex may be as lattice held or as coordinated. The coordinated water molecules exhibit a characteristic absorption around $850 \,\mathrm{cm}^{-1}$ in the IR spectra of complexes. The close examination of the

S. no.	Compound	<i>m/z</i> (amu)	% Yield	Dc. comp.	% M	% C	% H	% N	$\Lambda_{\circ} \; (\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$
1	[CoL ₁ Cl ₂]	475.2 (472)	62	284	12.34 (12.42)	45.71 (45.76)	4.59 (4.66)	11.92 (11.86)	10.2
2	$[NiL_1Cl_2]$	473.82 (472)	64	276	12.52 (12.46)	45.72 (45.76)	4.73 (4.66)	11.79 (11.86)	11.8
3	$[CuL_1Cl_2]$	478.16 (476)	59	288	13.16 (13.23)	45.26 (45.37)	4.56 (4.62)	11.81 (11.70)	12.1
4	$[ZnL_1(OAc)_2]$	507	65	292	12.29 (12.38)	50.19 (50.28)	5.24 (5.33)	10.72 (10.67)	10.6
5	[CoL ₂ Cl ₂]	488.93 (486)	70	254	11.98 (12.06)	46.83 (46.91)	5.01 (4.94)	11.61 (11.52)	13.4
6	$[NiL_2Cl_2]$	487.82 (486)	63	262	12.39 (12.30)	46.86 (46.91)	4.88 (4.94)	11.61 (11.57)	10.9
7	$[CuL_2Cl_2]$	490.8 (490)	68	274	12.89 (12.96)	46.49 (46.53)	4.85 (4.89)	11.51 (11.43)	12.7
8	$[ZnL_2(OAc)_2]$	522.8 (522)	60	268	12.12 (12.06)	51.26 (51.21)	5.63 (5.56)	10.31 (10.39)	11.1
9	[CoL ₃ Cl ₂]	522.2 (520)	59	290	11.27 (11.33)	50.68 (50.79)	4.21 (4.26)	10.69 (10.77)	12.6
10	[NiL ₃ Cl ₂]	520.6 (520)	61	286	11.21 (11.29)	50.76 (50.81)	4.18 (4.26)	10.71 (10.77)	13.2
11	[CuL ₃ Cl ₂]	526.54 (524)	69	278	12.19 (12.11)	50.26 (50.34)	4.18 (4.22)	10.74 (10.67)	9.3
12	$[ZnL_3(OAc)_2]$	555.2 (555)	54	292	11.28 (11.39)	54.35 (54.41)	4.84 (4.92)	9.81 (9.76)	12.5

Table 2	
Infrared spectral data (cm^{-1}) and their assignment	

S. no.	Complex	ν(N–H)	Amide bands			ν(M–N)	v(M–Cl)	ν(M–O)
			I	II	III			
1	$[CoL_1Cl_2]$	3447	1674	1560	1224	447	342	_
2	$[NiL_1Cl_2]$	3435	1671	1595	1245	450	354	_
3	$[CuL_1Cl_2]$	3458	1654	1591	1238	418	350	_
4	$[ZnL_1(OAc)_2]$	3364	1654	1586	1253	472	-	372
5	$[CoL_2Cl_2]$	3424.5	1664	1588	1227	332	452	_
6	[NiL ₂ Cl ₂]	3432	1658	1572	1242	358	448	_
7	$[CuL_2Cl_2]$	3436	1656	1546	1234	444	342	_
8	$[ZnL_2(OAc)_2]$	3408	1664	1584	1256	490	-	390
9	[CoL ₃ Cl ₂]	3382	1644	1561	1231	438	348	_
10	[NiL ₃ Cl ₂]	3368	1658	1594	1229	458	354	_
11	$[CuL_3Cl_2]$	3354	1670	1612	1219	421	352	_
12	$[ZnL_3(OAc)_2]$	3408	1664	1546	1246	503	-	403

spectra of the complexes did not reveal any new absorption around 850 cm⁻¹ indicating that the water molecule is not coordinated. Hence, it may be proposed that the water molecule is lattice held and the thermal data (loss of mass in the low temperature region) also confirms the same. The absorption between 418 and 450 cm⁻¹ in the far-IR spectra of the complexes may be attributed to ν (M–N), and it provides a strong evidence for the involvement of nitrogen atoms in coordination [24]. The spectra of Co(II), Ni(II) and Cu(II) complexes exhibit another absorption around 260 cm⁻¹ characteristic of ν (M–Cl). The far-IR spectra of the Zn(II) complexes show an absorption around 400 cm⁻¹. This may be assigned to ν (M–O) confirming that acetate ions are coordinated to the metal ion [25]. Further, the absorptions at 1606 and 1400 cm⁻¹, confirm the monodentate nature of the acetate ion in these complexes [26].

3.5. Magnetic moment

Table 3

The magnetic moment values of the Co(II) complexes measured at room temperature are found to be 4.94, 4.96 and $4.98\mu_B$ These high spin values of Co(II) complexes confirm that the complexes have octahedral geometry [27].

The magnetic moment values of all the Ni(II) complexes lie in the range 2.97, 2.94 and $3.11\mu_B$ and corresponding to two unpaired electrons. The magnetic moment values are in tune with high spin configuration of octahedral Ni(II) complexes [27].

Electronic spectral absorptions and ligand field parameters of the complexes

The Cu(II) complexes exhibit the magnetic moment values of 1.86, 1.89 and $1.87\mu_B$ corresponding to one unpaired electron. These values are higher than the spin-only value, i.e. $1.73\mu_B$ for one unpaired electron. This reveals that these complexes are monomeric in nature without any of metal–metal interactions [27] but with same orbital contribution at room temperature.

3.6. Electronic spectra

3.6.1. Cobalt complexes

The electronic spectral data of all complexes along with derived parameters are presented in Table 3. The three spectral absorptions of Co(II) complexes may be assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F), {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions. The position of the bands suggests octahedral geometry around the Co(II) ion [27]. The various ligand field parameters were calculated for the Co(II) complexes. The value of D_{q} has been calculated using the ν_{3}/ν_{1} ratio. The nephelauxetic parameter β is obtained using the relation: $\beta = B_{(complex)}/B_{(free ion)}$, where $B_{(free ion)}$ is 1120 cm⁻¹ [28], the value of β is in the range of 0.769–0.82 and this indicates that the covalent character of metal ligand σ bond is low. The LFSE values of the complexes have been evaluated and given in Table 3.

3.6.2. Nickel complexes

Electronic spectra of Ni(II) complexes show three transitions in the region $9425-24,690 \text{ cm}^{-1}$ and these transitions may be

Complex	Spectral bands (cm ⁻¹)	v_3/v_1	$Dq (cm^{-1})$	$B (\mathrm{cm}^{-1})$	β	LFSE (kJ mol ⁻¹)		
[CoL ₁ Cl ₂]	8,970, 14,970, 23,152	2.35	711.76	747.46	0.67	68.02		
$[CoL_2Cl_2]$	9,124, 15,002, 24,268	2.23	1232	793.2	0.71	70.84		
$[CoL_3Cl_2]$	8,794, 14,441, 21,902	2.49	996.6	664.1	0.60	72.18		
$[NiL_1Cl_2]$	10,060, 16,103, 24,420	2.43	1006	689.5	0.66	76.92		
[NiL ₂ Cl ₂]	9,425, 15,551, 24,690	2.62	942.5	797.7	0.76	78.67		
[NiL ₃ Cl ₂]	9,695, 16,060, 24,213	2.51	969.5	745.9	0.72	74.56		
$[CuL_1Cl_2]$	14,220	_	_	-	_	_		
$[CuL_2Cl_2]$	14,493	_	_	_	_	_		
[CuL ₃ Cl ₂]	14,588	-	-	-	-	-		
	Complex [CoL1Cl2] [CoL2Cl2] [CoL3Cl2] [NiL1Cl2] [NiL2Cl2] [NiL3Cl2] [CuL1Cl2 [CuL2Cl2] [CuL3Cl2]	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		

assigned to ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F) (\nu_1)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F) (\nu_2)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P) (\nu_3)$, respectively. These transitions are characteristic of the octahedral Ni(II) species [27]. The various ligand field parameters [28] are calculated by using Orgel diagrams and are given in Table 3.

3.6.3. Copper(II) complexes

The electronic spectra of the Cu(II) complexes show a broad absorption in the range 14,220–14,588 cm⁻¹ assignable to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition [29]. This broad absorption suggests distorted octahedral geometry as expected from the Jahn–Teller effect in hexa-coordinated d^{9} metal ion.

3.7. ESR spectra

ESR spectra of Cu(II) complexes are recorded at liquid nitrogen temperature. The absence of Cu–Cu interactions can be explained by proposing transitions, i.e. $\Delta Ms = \pm 2$ between two paramagnetic centers is negligible [30]. The analysis of spectra gave $g_{\parallel} = 2.2301-2.2913$ and $g_{\perp} = 2.078-2.098$. The values $g_{\parallel} > g_{\perp}$ indicates that the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving ²B_{1g} as the ground state. This supports that there is a considerable mixing of ground and excited state terms and also reflected in the magnetic moment values which are slightly greater than the spin-only value for Cu(II), i.e. $1.73\mu_B$, which is indicating the formation of mononuclear copper(II) complexes. The ratio $g_{\parallel} > g_{\perp} > g_{ave} > 2.0023$ evaluated for all Cu(II) complexes, suggests that the unpaired electron is localized in $d_{x^2-y^2}$ orbital and the spectral features are characteristic of tetragonally distorted octahedron.

3.8. ¹H and ¹³C NMR spectra of Zn(II) complexes

The characteristic signals observed in the spectra of the ligands have been described earlier [18]. The ¹H NMR spectra of diamagnetic Zn(II) complexes recorded in d_6 -DMSO exhibit aromatic and methylene protons resonance signals at the same field. The amide (-C=O-NH) protons resonance signal observed at 8.43–8.31 ppm in the spectra of ligands have shifted to down field side. The amine proton resonance signal observed at 4.68–4.85 ppm in the spectra of ligands shifted to 4.98–5.15 ppm. The low field side shift of both amide and amine proton signals indicate that the nitrogen atoms are involved in coordination to the metal ion [31]. The spectra of Zn(II) complexes exhibit one new signal observed at 2.28 ppm, that is attributable to the methyl protons of acetate ions.

¹³C NMR spectra of ligands exhibit signals of $-O=C-NH-CH_2-$ at 168.69 ppm. Aromatic carbon atom signals are found between 147.9 and 113.8 ppm. 147.9 ppm indicates amine attached aromatic carbon ($-C-NH_2-$). The other signals at 44.54 and 43.26 ppm are due to aliphatic carbon atoms of different $-CH_2-$, groups. ¹³C NMR spectra of [Zn(L)(OAc)₂] exhibit the signals corresponding to $-O=C-NH-CH_2-$ and $-C-NH_2-$ at 169.07 and 148.32 ppm, respectively, which are shifted to down field side confirming coordination of N-atoms to metal ion [32]. The spectra of Zn(II)



Fig. 1. Suggested structures of M = Co(II), Ni(II) and Cu(II), $X = Cl^{-}$ and M = Zn(II), $X = CH_3COO^{-}$.

complexes show two new signals at 181.46 and 21.94 which are corresponding to -O-C=O- and CH_3 of acetate ion. The rest of the carbon atoms are similar as found in the spectra of the free ligand.

On the basis of elemental analyses, molar conductance, thermogravimetric analyses, magnetic susceptibility, IR, electronic, ESR and ¹H NMR spectral data the following structure may be proposed for all the complexes (Fig. 1).

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