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Mass, EPR, IR and electronic spectroscopic studies on newly synthesized macrocyclic ligand and its transition metal complexes

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Abstract

Manganese(II), cobalt(II), nickel(II) and copper(II) complexes have been synthesized with a new tetradentate ligand viz. 1,3,7,9-tetraaza-2,4,8,10-tetraketo-6,12-diphenyl-cyclododecane (L) and characterized by the elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, ¹H NMR, IR, electronic and EPR spectral studies. The molar conductance measurements of the complexes in DMF correspond to be nonelectrolytic nature for Mn(II), Co(II) and Cu(II) while 1:2 electrolytes for Ni(II) complexes. Thus, these complexes may be formulated as $[M(L)X_2]$ and $[Ni(L)]X_2$ (where M = Mn(II), Co(II) and Cu(II) and $X = Cl^-$ and NO_3^-).

On the basis of IR, electronic and EPR spectral studies an octahedral geometry has been assigned for Mn(II) and Co(II) complexes, squareplanar for Ni(II) whereas tetragonal for Cu(II) complexes. The ligand and its complexes were also evaluated against the growth of bacteria and pathogenic fungi in vitro.

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1. Introduction

Synthetic macrocycles are a growing class of compounds with varying chemistry a wide range of different molecular topologies and sets of donor atoms [1–5]. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Transition metal macrocyclic complexes have received much attention as a active part of metalloenzymes [6] as biomimic model compounds [7] due to its resemblance with natural proteins like hemerythrin and enzymes. In view of the above in the present paper, we report the synthesis and characterization of macrocyclic complexes by the urea containing nitrogen donor macrocyclic ligand (L) (Fig. 1).

2. Experimental

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

2.1. Synthesis of ligand

The hot ethanolic solution (20 mL), of ethylcinnamate (3.52 g, 0.02 mol), and a hot ethanolic solution (20 mL), of urea (1.20 g, 0.02 mol) were mixed slowly with constant stirring. This mixture was refluxed at ~75 °C for 9h in the presence of few drops of concentrated hydrochloric acid (pH ~4–5). Cooling give a cream precipitate, which was filtered, washed with cold EtOH, and dried under vacuum over P₄O₁₀. Yield 69%, mp 274 °C. Elemental analysis found %(found 381 u), C 63.03; H 5.33; N 14.82. Calculated for C₂₀H₂₀N₄O₄ (calculated 380 u), C 63.16; H 5.26 and N 14.74%.

2.2. Synthesis of complexes

The hot ethanolic (20 mL) solution of ligand (0.76 g, 0.002 mol) and hot ethanolic (20 mL) solution of

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Fig. 1. Preparation and structure of the ligand.

corresponding metal salts (0.002 mol) were mixed together with constant stirring. The mixture was refluxed for 6–14 h at 60–85 °C. Cooling gives a colored complex. 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. Molar conductance was measure on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄·H₂O as a callibrant. Electron-impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrometer. ¹H NMR spectra were recorded on Hitachi FT-NMR, model R-600 spectrometer using CDCl₃ as 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 DMF solution, at liquid nitrogen temperature for Co(II) and at room temperature for Mn(II) and Cu(II) complexes on E₄-EPR spectrometer using the DPPH as the g-marker.

3. Results and discussion

3.1. Ligand

The EI Mass spectrum of free ligand confirm the proposed formula by showing a peak at 381 u corresponding

Table 1 Molar conductance and elemental analysis data of the complexes



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

to the macrocyclic moiety (C₂₀H₂₀N₄O₄). It also shows a series of peaks, i.e. 58, 77, 104, 132, 175, 190, 248, 303 and 381, etc., corresponding to various fragments. Their intensity gives an idea of stability of fragments Fig. 2. The ¹H NMR spectrum of the ligand (L) does not gives any signal corresponding to primary amine and alcoholic protons. It gives a doublet in the region 8.56 ppm, which is due to the amide group (-NH-CO-, 2H) protons [8]. Signals appear in the region 1.54, 2.41 and 7.25 ppm, correspond to methyne (-CH-CH2-), methylene (-CH2-CO-) and benzenoid protons, respectively. The presence of another signal at δ 5.16 ppm is due to the protons of –NH group [9]. IR spectrum of the ligand does not exhibit any band corresponding for the free primary diamine and hydroxyl group [5]. The absorption in IR spectrum of (L) in the range of $715-756 \text{ cm}^{-1}$ and $1432-1633 \text{ cm}^{-1}$ [10,11] is due to the presence of phenyl group. Four new bands appear in the spectrum of the free ligand in the regions 1628, 1592, 1239 and 771 cm^{-1} assignable to amide I [ν (C=O)], amide II [ν (C-N) + δ (N-H)], amide III [δ (N–H)] and amide IV [ϕ (C=O)] bands respectively [11–13]. A sharp band observed \sim 3276 cm⁻¹, may be assigned to ν (N–H) of he secondary amino group [14–15].

3.2. Complexes

On the basis of elemental analysis, the complexes were assigned to possess the composition shown in Table 1. The molar conductance measurements of the complexes in DMF correspond to be nonelectrolytic nature for Mn(II), Co(II) and Cu(II) while 1:2 electrolytes for Ni(II) complexes. Thus, these complexes may be formulated as $[M(L)X_2]$

Complex			Color	mp (°C)	Yield (%)	Elemental analysis data found (calculated)%			
						Metal	С	Н	N
$[Mn(L)Cl_2] C_{20}H_{20}MnN_4O_2S_2Cl_2$	506	10.03	Brown	295	66	10.93 (10.87)	47.52 (47.43)	4.02 (3.95)	11.01 (11.07)
$[Mn(L)(NO_3)_2] C_{20}H_{20}MnN_6O_8S_2$	559	12.09	Light brown	285	71	9.96 (9.84)	43.04 (42.93)	3.50 (3.58)	14.97 (15.03)
$[Co(L)Cl_2] C_{20}H_{20}CoN_4O_2S_2Cl_2$	510	10.06	Lotus pink	290	67	11.64 (11.57)	47.00 (47.06)	3.98 (3.92)	11.09 (10.98)
[Co(L)(NO ₃) ₂] C ₂₀ H ₂₀ CoN ₆ O ₈ S ₂	563	6.92	Rose pink	288	73	10.36 (10.48)	42.69 (42.63)	3.49 (3.55)	15.01 (14.92)
[Ni(L)]Cl ₂ C ₂₀ H ₂₀ NiN ₄ O ₂ S ₂ Cl ₂	510	225	Purple red	280	60	11.50 (11.57)	46.98 (47.06)	3.84 (3.92)	10.89 (10.98)
[Ni(L)] (NO ₃) ₂ C ₂₀ H ₂₀ NiN ₆ O ₈ S ₂	563	218	Shiny orange	286	62	10.59 (10.48)	42.55 (42.63)	3.61 (3.55)	14.80 (14.92)
[Cu (L)Cl ₂] C ₂₀ H ₂₀ CuN ₄ O ₂ S ₂ Cl ₂	515	8.18	Blue	>300	59	12.58 (12.43)	46.71 (46.60)	3.96 (3.88)	11.00 (10.87)
[Cu (L)(NO ₃) ₂] C ₂₀ H ₂₀ CuN ₆ O ₈ S ₂	568	10.11	Shiny blue	290	63	11.15 (11.27)	42.16 (42.25)	3.60 (3.52)	14.92 (14.79)

and $[Ni(L)]X_2$ (where M=Mn(II), Co(II), and Cu(II) and $X = Cl^-$ and NO_3^-). In the IR spectra of complexes, the shifting in lower side of the band $[\nu(N-H)]$ and the band of amides II and III, suggest the coordination through nitrogen of -NH group (N₄).

3.3. IR bands due to anions

IR spectra of nitrato complexes display three (N–O) stretching bands at ~1415–1431 cm⁻¹ (ν_5), 1306–1317 cm⁻¹ (ν_1) and 1006–1019 cm⁻¹ (ν_2). The separation of two highest frequency bands ($\nu_5 - \nu_1$) is 109–114 cm⁻¹. Suggesting that both the nitrate groups are coordinated to the central metal ion [14].

However, the IR spectrum of Ni(II) nitrate complex displays a sharp and strong band at 1391 cm^{-1} which suggests that the nitrate group is uncoordinated.

3.4. Manganese(II) complexes

Manganese(II) complexes show magnetic moment at room temperature in the range 5.84–5.96 B.M. corresponding to five unpaired electrons. Electronic spectra of Mn(II) complexes, Fig. 3(a–b), exhibit four weak intensity absorption bands in the range 18509–18919 ($\varepsilon = 37-39 \text{ Lmol}^{-1} \text{ cm}^{-1}$), 22550–23100 ($\varepsilon = 41-43 \text{ Lmol}^{-1} \text{ cm}^{-1}$), 29344–29731

 $(\varepsilon = 66-71 \text{ mol}^{-1} \text{ cm}^{-1})$, and 37581-38127 cm⁻¹ ($\varepsilon = 129-133 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$) (Table 2). These bands may be assigned to the transitions: ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g} ({}^{4}G)$, ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}$, ${}^{4}A_{1g} ({}^{4}G)$ (10*B*+5*C*), ${}^{6}A_{1g} \rightarrow {}^{4}E_{g} ({}^{4}D)$ (17*B*+5*C*) and ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g} ({}^{4}P)$ (7B+7C), respectively.

EPR spectra were recorded at room temperature as polycrystalline sample and in solution of DMF. The polycrystalline spectra were isotropic and exhibit the 'g' value in the range 2.0054–2.0099 (Table 3). In DMF solution, Mn(II) complexes give EPR spectra containing the six lines arising due to the hyperfine interaction between the unpaired electron with the ⁵⁵Mn nuclear (l = 5/2). The nuclear magnetic quantum number M_1 , corresponding to these lines are -5/2, -3/2, -1/2, +1/2, +3/2 and +5/2 from low to the high field.

The parameters B and C were calculated from the second and third transitions because these transitions are free from the crystal field splitting and depend on B and C parameters [11,12]. The calculated values of the ligand field parameters are given in Table 4.

3.5. Cobalt(II) complexes

At room temperature the magnetic moment measurements of cobalt(II) complexes lie in the range 4.86–4.93 B.M. corresponding to three unpaired electrons (Table 2).



Fig. 3. Electronic spectra of the complexes. (a) [Mn(L)Cl₂], (b) [Mn(L)4O₃]2, (c) [Ni(L)Cl₂], (d) [Ni(L)(NO₃)₂].

Table 2
Magnetic moment and electronic spectral data of the complexes

Complex	μ_{eff} (B.M.)	$\lambda_{\rm max}~({\rm cm}^{-1})$	$\varepsilon (\mathrm{Lmol^{-1}cm^{-1}})$	
[Mn(L)Cl ₂]	5.84	18509, 22550, 29344, 37581	37, 41, 66, 129	
$[Mn(L)(NO_3)_2]$	5.96	18919, 23100, 29731, 38127	39, 43, 71, 133	
$[Co(L)Cl_2]$	4.86	10173, 14620, 18692, 26596	73, 81, 90, 141	
$[Co(L)(NO_3)_2]$	4.93	11198, 14793, 18657, 32680	72, 81, 92, 139	
[Ni(L)]Cl ₂	Diamagnetic	16178, 22090, 29543	57, 93, 134	
[Ni(L)](NO ₃) ₂	Diamagnetic	16548, 21307, 29825	57, 94, 132	
$[Cu(L)Cl_2]$	1.95	10905, 11249, 16447, 27933	59, 63, 155	
$[Cu(L)(NO_3)_2]$	2.06	10183, 11223, 16260	57, 61, 153	

Table 3

EPR spectral data of the complexes

Complexes	Data as polycrystalline sample					Data in DMF solution			
	Temperature	$g_{ }$	g_{\perp}	$g_{ m iso}$	G	$\overline{g_{ }}$	g_{\perp}	$g_{ m iso}$	G
[Mn(L)Cl ₂]	RT	_	_	2.0054	_	_	_	2.0017	_
$[Mn(L)(NO_3)_2]$	RT	_	_	2.0099	_	_	_	2.0020	_
$[Co(L)Cl_2]$	LNT	2.3268	2.0098	2.1155	_	2.3256	2.0179	2.1205	_
$[Co(L)(NO_3)_2]$	LNT	2.3387	2.0174	2.1245	_	2.3298	2.0053	2.1135	_
$[Cu(L)Cl_2]$	RT	2.0853	2.0597	2.0682	1.4288	2.1329	2.0701	2.0910	1.8959
$[Cu(L)(NO_3)_2]$	RT	2.1182	2.0669	2.0840	1.7668	2.0831	2.0690	2.0737	1.2043

The electronic spectra of all the cobalt(II) complexes exhibit absorption in the region 10173–11198 $(\varepsilon = 72-73 \text{ mol}^{-1} \text{ cm}^{-1})$, 14620–14793 $(\varepsilon = 81 \text{ L mol}^{-1} \text{ cm}^{-1})$, 18657–18692 $(\varepsilon = 90-92 \text{ L mol}^{-1} \text{ cm}^{-1})$ and 26596–32680 cm⁻¹ ($\varepsilon = 139-141 \text{ L mol}^{-1} \text{ cm}^{-1})$. These bands may be assigned to the transitions: ${}^{4}\text{T}_{1g}$ (F) $\rightarrow {}^{4}\text{T}_{2g}$ (F) (ν_1) , ${}^{4}\text{T}_{1g} \rightarrow {}^{4}\text{A}_{2g}$ (ν_2) and ${}^{4}\text{T}_{1g}$ (F) $\rightarrow {}^{4}\text{T}_{1g}$ (P) (ν_3) , respectively, and the fourth band may be due to charge transfer. The position of bands indicates that these complexes have distorted octahedral geometry [15–18].

EPR spectra of cobalt(II) complexes were recorded as polycrystalline sample and in DMF solution at LNT. 'g' Values are found to be almost same in both cases in polycrystalline sample as well as in the solution (Table 3).

3.6. Nickel(II) complexes

At room temperature these complexes show the diamagnetic behavior, indicating the square planar environment around the Ni(II) ion (Fig. 4).

The electronic spectra of the Ni(II) complexes, Fig. 3(c–d) exhibit three absorption bands in the range 16178–16548 ($\varepsilon = 57 \text{ L mol}^{-1} \text{ cm}^{-1}$), 21307–22090 ($\varepsilon = 93$ –

Table 4	
Ligand field parameters	s of the complexes

Complex	$Dq (cm^{-1})$	$B (\mathrm{cm}^{-1})$	$C(\mathrm{cm}^{-1})$	β	LFSE
					(KJ mol ⁻¹)
$[Mn(L)Cl_2]$	1851.90	613.71	3060.44	0.78	00
[Mn(L)(NO ₃) ₂]	1891.10	518.29	3581.01	0.66	00
$[Co(L)Cl_2]$	1271.62	644.55	_	0.58	121.54
$[Co(L)(NO_3)_2]$	1399.75	574.06	-	0.52	133.79
$[Ni(L)]Cl_2$	1617.80	735.36	_	0.71	231.94
$[Ni(L)](NO_3)_2$	1654.80	752.18	-	0.72	237.25

94 L mol⁻¹ cm⁻¹) and 29543–29825 cm⁻¹ ($\varepsilon = 132-134$ L mol⁻¹ cm⁻¹). An examination of these bands indicates that the complexes have square planar geometry. These bands may be assigned to the three spin allowed transitions: ¹A_{1g} (D) \rightarrow ¹A_{2g} (G) (ν_1), ¹A_{1g} (D) \rightarrow ¹B_{2g} (G) (ν_2) and ¹A_{1g} (D) \rightarrow ¹E_g (G) (ν_3), respectively.

3.7. Copper(II) complexes

The magnetic moment of the Cu(II) complexes at room temperature lie in the range 1.95–2.06 B.M. corresponding to one unpaired electron.

Electronic spectra of copper(II) complexes display three bands (Table 2), corresponding to the transitions $B_{1g} \rightarrow {}^{2}A_{1g}$ $(d_{x^2-y^2} \rightarrow d_{z^2}) v_1, {}^{2}B_{1g} \rightarrow {}^{2}B_{2g} (d_{x^2-y^2} \rightarrow d_{zy}) v_2$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g} (d_{x^2-y^2} \rightarrow d_{zy}, d_{yz}) v_3$, respectively [19,20].

Room temperature EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in the solution of the DMF, on X-band at frequency 9.5 GHz under the magnetic field strength 3400 G. Polycrystalline spectra exhibit a single



Fig. 4. Suggested structures of the complexes where M = Mn(II), Co(II), and Cu(II) and $X = Cl^-$ and NO_3^-).

broad signal. No band corresponding to $\Delta Ms = \pm 2$ transitions was observed in the spectrum suggesting Cu–Cu interaction [21,22]. The absence of above transition can be explained by proposing interaction between two paramagnetic centers is negligible [23]. The analysis of spectra gives the values for $g_{||} = 2.0831-2.1329$ and $g_{\perp} = 2.0597-2.0701$. The observed $g_{||}$ values for the complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{||} > g_{\perp} > 2.0023$ observed for the complexes indicate that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectral figures are characteristic of axial symmetry. Tetragonaly elongated structure are confirmed for the Cu(II) complexes (Fig. 4).

 $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. According to Hathaway [24,25] if G > 4, the exchange interaction is negligible but G < 4 indicates considerable exchange interaction in the solid complexes. In the complexes, reported in this paper the 'G' value are <4 indicating the exchange interaction in solid complex.

3.8. Ligand field parameters

Various ligand field parameters were calculated for the complexes and are listed in Table 4. The values of Dq in Co(II) complexes were calculated from transition energy ratio diagram using the v_3/v_2 ratio [17]. Our results are in agreement with the complexes reported earlier [18,21]. The Nephelauxetic parameter β was readily obtained by using the relation:

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

where B(free ion) for Mn(II) is 786 cm⁻¹, for Ni(II) is 1041 cm⁻¹ and for Co(II) is 1120 cm⁻¹ [11,12]. The values of β lie in the range of 0.54–0.81. These values indicate the appreciable covalent character of metal ligand ' σ ' bond.

3.9. Antimicrobial screening

The ligand (L) and its transition metal complexes were evaluated against different species of bacteria and fungi [26,27].

3.10. Antibacterial screening

The antibacterial action of the ligand and the complexes of Mn(II), Co(II), Ni(II) and Cu(II) was checked by the disc diffusion technique. This was done on Sarcina lutea (gram-positive) and *Escherchia coli* (gram-negative) bacteria at 35 °C. The disc of Whatmann no. 4 filter paper having the diameter 6.00 mm were soaked in the solution of compounds in DMF (1.0 mg cm^{-1}). After drying, it was placed on nutrient agar plates. The inhibition areas were observed after 48 h. DMF was used as a control and Gentamycin as a standard drug.



Fig. 5. Biological screening of the ligand and complexes: (a) antibacterial and (b) antifungal activity.

Hundred percent growth of bacteria which is represented as +, 50% growth by ++, less then 50% growth by +++ and noble inhibition by ++++. The bacterial growth inhibition capacity of the complexes follow the order Cu(II) > Ni(II) > Mn(II) > Co(II), given in Fig. 5(a) and Table 5.

3.11. Antifungal screening

The antifungal activity of the ligand and its complexes was checked, by the agar plate technique for the *Aspergillus niger* and *Aspergillus glaucus* fungi. The compounds were directly mixed to the medium in different concentrations. The fungus was placed on the medium with the help of the inoculum needle. The pettridishes were wrapped in polythene sheets, containing some drops of EtOH and put in incubator at 31 ± 1 °C for 75–100 h. The growth of fungus was measured by the recording the diameter of fungal colony. The following relation calculated the fungal growth inhibition:

fungal growth inhibition% =
$$\frac{(A - B) \times 100}{A}$$

where *A* is the diameter of fungal colony in control plate and *B* is the diameter of fungal colony in test plate.

Hundred percent growth of fungus which is represented as *, 50% growth by **, less then 50% growth by *** and noble inhibition by ****.

The results of antifungal activity are shown in Table 5. The complexes show fungal inhibition in the following order: Co < Mn < Ni < Cu.

Table 5	
Antimicrobial activity data of the ligand and complexes	

Compound	Bacterial	inhibition (%)	Fungal inhibition (%)		
	Sarcina lutea	Escherichia coli	Aspergillus niger	Aspergillus glaucus	
Ligand	++	++	**	**	
$[Mn(L)Cl_2]$	+++	++	**	**	
$[Co(L)Cl_2]$	++	+	*	**	
[Ni(L)]Cl ₂	+++	++++	**	***	
[Cu (L)Cl ₂]	++++	++++	****	****	

Copper(II) complexes exhibits noble antifungal activity against both the species Fig. 5(b).

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