

Synthesis, Spectral and Antimicrobial Studies of Demi-macrocycles of Ligands N₂O₂ with Co(II), Ni(II) and Cu(II) Ions

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Abstract: Macrocyclic complexes of the type $[M(C_{14}H_{30}N_2O_2)(ClO_4)_2]$, where, $M = Co(II), Ni(II)$ and $Cu(II)$ ions were synthesized by the condensation reactions. The complexes were characterized with the aid of elemental analysis, conductance, magnetic susceptibility measurements and spectroscopic methods. The complexes were tested for their *in vitro* antibacterial activity. The minimum inhibitory concentration shown by these complexes were compared with standard drugs.

Keywords: inhibitory, incorporated, incur, polydentate, *in vitro*.

1. INTRODUCTION

In the recent years, demi-macrocyclic chemistry has attracted national and internal laboratories and drawn the attention due to their academic importance. The demi-macrocyclic are polydentate ligands with donor atoms commonly linked to a cyclic backbone. The macrocyclic ligands find vast and wide applications in chemical, biochemical and pharmacological^[1] industrial laboratories. By virtue of their utility we report here the synthesis, and characterization of demi-macrocyclic complexes of Co(II), Ni(II) and Cu(II) ions with donor ligand N₂O₂.

2. MATERIALS AND METHODS

The standard solutions employing analytical grade reagents were prepared. The elemental analysis (C,H, and N) of the sample were performed by micro-analytical methods whereas oxygen was measured by different methods. The conductance and magnetic moments were determined at room temperature. DMSO conductivity meter and Evan balance at 8000 G, employing Co[(Hg(SCN)₄)] as calibrant were used.

(a) Synthesis of Ligand

The donor ligand N₂O₂ (4,4,9,9-tetramethyl-5,8-diazoniumdiodeca-2,11-dione diperchlorate) was synthesized by addition of Ethane-1,2-diamine (33.83) ml with acetone (36.80) ml followed by perchloric acid below 5° C under freezing condition. The insoluble fine crystals of product after 48 hrs obtained. At last colourless ligand is obtained which was air dried, the yield was 85% (Table 1).

Table1. C₁₄H₃₀N₂O₁₀Cl₂, 457.30 Calcd. Mass (M)

% Calculated Mass	% Observed Mass
C = 36.77	C = 36.24
H = 6.61	H = 6.59
N = 6.61	N = 6.15
O = 34.98	O = 34.92
Cl = 15.50	Cl = 15.49

Synthesis of Demi-macrocyclic Complexes

(b) Syntheses of Cobalt(II) Complex

4,4,6,6-Tetramethyl-5,18- diazadodeca-2,11-dione Cobalt (II) complex

Cobalt(II) perchlorate^[2-5] (20 ml) was dissolved in water followed by [amke + H₂] (ClO₄)₂ (24 gm, 0.052 mol.). The mixture was refluxed until the colour of the solution changed from green to red. After sometime, the product was filtered, recrystallised from methanol and evaporated to dryness in vacuum (Table 2).

Table2. C₁₄H₂₈N₂O₁₀Cl₂ Co, 519.94 Cal. Mass (M)

% Calculated Mass	% Observed Mass
C = 32.34	C = 32.36
H = 5.42	H = 5.43
N = 5.38	N = 5.37
O = 30.77	O = 30.73
Cl = 13.63	Cl = 13.63
Co = 11.33	Co = 11.32

IR KBr cm⁻¹

V(M-N) 530, V(M-O) 452 cm⁻¹

d-d Spectra (DMSO)

7870 Ti (F) → ⁺T₂ g (F)

15542 → ⁺A₂ g (F)

19160 → ⁺T₁ g (P)

35689 → CT

Dq = 892

B = 803

β = 827

IR Spectral data of Ligand

IR (KBr) ν_{as} (C-H) 2960 (M), ν_s (C-H) 2909 cm⁻¹, ν (-C -(CH₃)₂) 1385, 1565 (s)

ν (C=O) 1685 (s), ν (N-H) 3370, ν (N-C) 1260,

ν_{as} (CH₂) 2985, ν_s (CH₂) 3007, δ_S (CH₃) 1348 cm⁻¹, δ_{as} (CH₃) 1445 cm⁻¹

δ_S (CH₂) 1473 cm⁻¹ ν (ClO₄⁻) 1105, 655 cm⁻¹

(c) Synthesis of Ni(II) Complex

4,4,9,9-Tetramethyl-5,8- diazadodeca-2,11-dione Nickel (II) complex

Nickel (II) sulphate hexahydrate (1.31gms) was dissolved in water (18ml) followed by respective ligand (4.57gms). The mixture was stirred until the liquid dissolved, the colour of the solution gradually changed from blue to red and the orange product crystallized.^[6] After several hours the solution was cooled in ice and the product was filtered off and washed with ice cold water, yield (3 gms, 80%) recrystallised from hot 1:1 water methanol or from hot acetonitrile /propanol-2. The compound was also formed by reacting respective ligand with nickel acetate tetrahydratpin methanol (Table 3).

Table3. C₁₄H₂₈N₂ O₁₀Cl, Ni 513.994 Calcd. Mass (M)

% Calculated Mass	% Observed Mass
C = 32.71	C = 32.72
H = 5.49	H = 5.47
N = 5.45	N = 5.43
O = 31.12	O = 31.11
Cl = 13.79	Cl =13.78
Ni = 11.42	Ni = 11.4

IR (KBr)

ν (ClO₄⁻) 1100 s, 620 s

ν (Ni-O) 470 cm⁻¹, ν (Ni-N) 405 cm⁻¹

(d-d) Spectra (methanol) cm⁻¹ 8140 ³A₂ (F) → ³T₂ (F)

13477 ³A₂ (F) → ³T₁ (F)

24000 ³A₂ (F) → ³T₂ (F)

35350 → CT

Dq= 820, B = 873, β= 839

μ_{eH} = 3.51 BM

(d) Synthesis of Cu(II) Complex

4,4, 9, 9-Tetramethyl - 5, 8-diazadodeca-2,11-dione copper (II) complex

Copper (II) sulphate (1.29 gms) was dissolved in water (36 ml) followed by the ligand (4.57 gms). The mixture was refluxed until the ligand dissolved. The color of the solution changed gradually from fast blue to light blue and black colored product crystallized. After several hours, the solution was cooled in ice bath and the product was filtered off and washed with ice cold water, yield (3gms, 76%) recrystallised from 1:1 hot water, methanol or from hot acetonitrile propanol-2. The compound was also formed by reacting the respective ligand with copper acetate tetrahydrate in methanol (Table 4).

Table 4. C₁₄H₂₈N₂O₁₀Cl₂Cu, 524.55 Calcd. Mass (M)

% Calculated Mass	% Observed Mass
C = 32.33	C = 32.34
H = 5.33	H = 5.29
N = 5.27	N = 5.30
O = 31.05	O = 31.10
Cl = 13.50	Cl = 13.54
Cu = 11.19	Cu = 11.24

IR (KBr)

ν (Cu-N) 522 cm⁻¹, ν (Cu-O) 495 cm⁻¹

d-d spectra (DMSO) 10810 E² → ²T₂ Dq= 1081

35010 → CT

= 2.08 BM

Conductivity ohm⁻¹ cm² mol⁻¹ = 13.0

(e) Bacterial Strains

Three different bacteria strains used in this study were originally isolated from patient's samples. The bacterial isolates tested include gram positive species of staphylococcus aureus and gram negative species like Escherichia Coli, and pseudomonas the bacterial strains were identified based on standard phenotypic biochemical tests and grown over night at 37^o C.

Disc Diffusion Assay

Antibacterial activity of the synthesized demi-macrocyclic [M(L) (ClO₄)] complexes was carried out using disc diffusion method. Petri plates were prepared with 20 ml of sterile Muller Hinton Agar (MHA). The test culture were swabbed on the top of solidified media and allows to dry for 30 min. at room temperature for compound diffusion. Negative control was prepared using solvent streptomycin (10 µg/disc) was used as positive control. The plates were incubated for 24 h at 37^o C for bacteria zone of inhibition was recorded in millimeters and experiment was repeated twice.

(f) Determination of Minimum Inhibitory Concentration (Mic.)

Minimum inhibitory concentration studies of synthesized compounds were performed at 250- 0.05 µg/ml using DMSO as solvent system the Mic was performed in 96 well assay concentrations of the synthesized demi-macrocyclic [M (L) (ClO₄)] complex with standard antibiotic positive and DMSO solvent as negative controls. An equal volume of 100 ml of fresh bacterial broth suspension was added to the wells without altering the dilution factor. Mic. plates were incubated at 37^o C for 24 h. The minimum inhibitory concentrations of the synthesized demi-macrocyclic [M(L) (ClO₄)] complex showing different inhibitory effect, and selecting the lowest concentration that inhibits the growth of the tested micro organism.

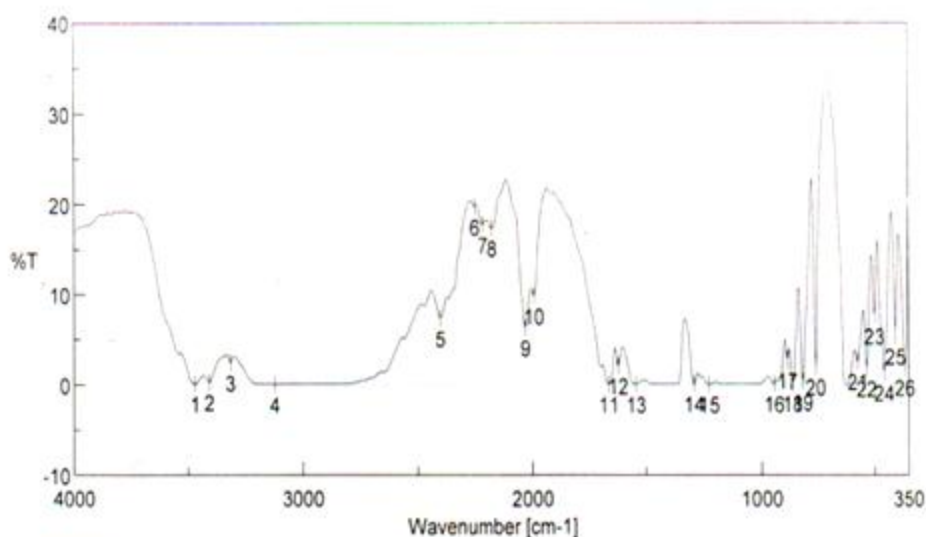
3. RESULTS AND DISCUSSION

3.1. Characterization of the Ligand

The 14-membered N₂O₂ demi-macrocyclic has been synthesized by mixed condensation of ethane-1,2-diamine with acetone as per the standard method. The addition of acid activates the amine group by protonation. The analytical results of the ligand and complexes are in conformity with their proposed compositions.

3.2. IR Spectra of N₂O₂

The IR Spectra of the ligand shows characteristic strong absorption band at 2960 cm⁻¹ primarily due the asymmetric stretching mode in which the two C–H bonds of the methyl group are extending while the third one is contracting at 2904 cm⁻¹ due to symmetrical stretching (v_sGHb) in which all three of the C–H bond extend and contract in phase. The peak at 2985 cm⁻¹ and 3007 are attributed to the asymmetrical stretching (v_{as}CH₂) and symmetrical stretching (v_sCH₂). The high energy shifting of these peaks reflect strain in the chain. The symmetrical bending vibration (5_sCH₃) causes peak at 1348 cm⁻¹, while the sharp peak at 1445 cm⁻¹ is attributed to asymmetrical bending (5_{as}CH₃). Strong absorption band at 1473 cm⁻¹ is the scissoring band (5_sCH₂) of methylene group. Absorption band between 1313 cm⁻¹ to 1156 cm⁻¹ is ascribed to twisting and wagging vibrations of methylene group. Strong absorption peak at 1685 cm⁻¹ is due to ketonic stretching vibration. Overlapping band peak at 3019, 3007, 3266 and 33701 are due to the N–H stretching vibration. Strong bands due to ionic perchlorate occur at 1105 cm⁻¹ and 655cm⁻¹ (Fig. 1).



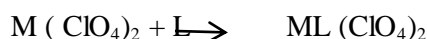
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[Measurement Information]
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 Detector TGS
 Accumulation Auto (162)
 Resolution 8 cm-1
 Zero Filling On
 Apodization Cosine
 Gain Auto (16)
 Aperture Auto (7.1 mm)
 Scanning Speed Auto (2 mm/sec)
 Filter Auto (30000 Hz)

Fig1.

3.3. Characterization of Complexes

The metal complexes have been synthesized by the reaction of the respective metal perchlorates with the demi-macrocyclic ligand according to the following reaction.



Where, M = Co(II), Ni(II) and Cu(II)

The molar conductance values ($\lambda_m = 5-15 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of the complexes in DMSO (10^{-3} M) indicate their non-electrolytic nature.

IR spectra the IR spectra of the complexes exhibit a strong sharp to medium intensity band at $500-457 \text{ cm}^{-1}$ region which may be assigned to metal oxygen stretching vibration. The $\nu(\text{M-O})$ stretching frequencies are in order of $\text{Co(II)} > \text{Cu(II)} > \text{Ni(II)}$. Upon complex formation, the intensities of some the vibrations are decreased which may be attributed to the hindered vibrations. The characteristic $\nu(\text{C-O})$ absorption frequencies undergo a negative shift by about 50 cm^{-1} in the complexes which may be ascribed to the relaxation effect caused to the lone pair donation by the oxygen atom to the metal ion. The $\nu(\text{M-ClO}_4)$ stretching frequency sharp band at $535-500 \text{ cm}^{-1}$ is assigned to the metal-nitrogen stretching frequency. The order of $\nu(\text{M-N})$ stretching frequencies is $\text{Co(II)} > \text{Cu(II)} > \text{Ni(II)}$. The non-appearance of $\nu_s(\text{N-H})$, $\nu_{as}(\text{N-H})$ and $\delta(\text{N-H})$ vibrations in the complexes confirm the co-ordination of the metal ion by the deprotonation of the internal protons.

UV-vis spectra the cobalt complex displays three absorption bands at $7940-7890$, $15,620-15523$ and $19260-19120 \text{ cm}^{-1}$. These bands are assigned to ${}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$, ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{A}_2(\text{F})$ and ${}^4\text{T}_1(\text{P}) \rightarrow {}^4\text{T}_1(\text{P})$ transition respectively. The ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{A}_2(\text{F})$ transition is assigned to the weak band present towards low energy side of the strongest band. The calculation of Dq and $E({}^4\text{P})$ values is based on the assumption that the most intense band at $7950-7871 \text{ cm}^{-1}$ is due to ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition. The values of ligand field parameters are in good agreement with those reported for other Co(II) complexes, which indicated that the Dq values of the Co(II) ^[7-10] complex are always slightly higher than that for the Ni(II) complexes for the same ligand (Fig. 2).

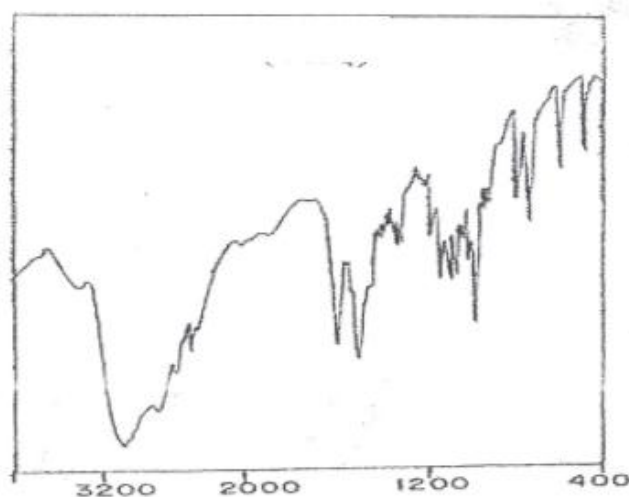


Fig2. Wave number (cm^{-1}) UV Spectra of Co(II)

UV-visible spectra the electronic spectra of the complexes were recorded in various solvents. The electronic spectral data of the complexes indicate an octahedral geometry around entire metal ion. The electronic spectra of the copper complex shows a band at $10,869-10,752 \text{ cm}^{-1}$ corresponding to ${}^2\text{E} \rightarrow {}^2\text{T}_2$ transition, which is characteristic of the octahedral Cu(II) complex. The Ni(II) complex exhibits three absorption bands at $8,200-8,140$, $13,531-13,477$ and $24,096-24,000 \text{ cm}^{-1}$ which can be attributed to the three allowed d-d transitions arising from ${}^2\text{A}_2(\text{F})$ ground state to ${}^3\text{T}_2(\text{F})$ (ν_1), ${}^3\text{T}_2(\text{F})$ (ν_2), and ${}^3\text{T}_2(\text{F})$ (ν_3) excited states respectively indicating an octahedral environment around Ni(II). These assignments are further supported by a close agreement between the observed and calculated values of A_{max} for the ν_2 transition and also by the constant value of the intensity ratio of ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ to ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_2(\text{F})$ transitions.

3.4. Magnetic Moment

The observed magnetic moment^[11] of 2.08 BM of copper complex are higher than the expected values, probably due to octahedral geometry around Cu(II) ion. The observed magnetic moment of Cobalt complex Co(II) has magnetic moment value 4.21 BM, which is diagnostic of the high spin state of the metal ion in an octahedral field. The Ni(II) complex exhibited 3.01 BM indicating octahedral the Cu(II) complex exhibit magnetic moment in the range 2.01 BM' suggested octahedral nature electronic spectra of the metal complex also supports the octahedral geometry.

3.5. Antimicrobial Activity of the Complex Compound

In this study, all chemically synthesized complexes were evaluated against Iron positive and Iron negative bacteria. The minimum inhibitory concentrations (mic.) of these synthetic complexes were determined. The standard antibiogram^[12-17] namely streptomycin and chloramphenicol were used for comparison with the antibacterial activity against gram positive bacteria and gram-negative bacteria (Table 5) complexes of $[Co(C_{14}H_{30}N_2O_2)(ClO_4)_2]$ and $[Cu(C_{14}H_{30}H_2O_2)(ClO_4)_2]$ exhibit good activities against all the tested bacterial strains complex $[Ni(C_{14}H_{30}N_2O_2)(ClO_4)]$ showed highest zone of inhibition. In vitro-antibacterial activity of the complexes obtained by the diffusion method for a concentration 100 $\mu\text{g/ml}$.

Table5.

S. No.	Complex	The zone of is with inhibition mm	
		E. Coli. (M T C C 51)	Pseudomonas (M T C C 507)
1	$[Co(C_{14}H_{30}N_2O_2)ClO_4]$	32	29
2	$[Cu(C_{14}H_{30}N_2O_2)ClO_4]$	13	10
3	$[Ni(C_{14}H_{30}N_2O_2)ClO_4]$	47	9

4. CONCLUSION

The demi-macrocyclic complexes have been characterized by various physico-chemical methods. The antimicrobial activities of synthesized complex compounds were screened against few bacteria using vitro-disc diffusion method, the result revealed that the most of the synthesized complex compounds exhibited antimicrobial activities. In present study, demi-macrocyclic complexes play vital role in therapeutic use.

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