



ISSN 0973-3450

(Print)

JUC Vol. 13(5), 125-131 (2017). Periodicity 2-Monthly

(Online)



ISSN 2319-8036

9 772319 803009



Estd. 2005

JOURNAL OF ULTRA CHEMISTRY

An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering

website:- www.journalofchemistry.org

Biological Studies, Synthesis and Spectral Characterization of Nitrogen Donor Macrocylic Co(II) Complexes

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Acceptance Date 16th August, 2017,

Online Publication Date 2nd September, 2017

Abstract

New Co(II) complexes with macrocyclic ligands 2,7,9,14-tetrahydroxy phenyl-1,3,6,8,10,13-hexaazacyclooctadecane (L^1), 2,7,9,14-tetracyclohexane-1,3,6,8,10,13-hexaazacyclo octadecane (L^2) have been synthesized by template method. The structure of complexes was determined by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral studies. Based on the analytical analysis i.e. molar conductance the complexes were found to be non-electrolytic in nature except the complexes $[Co(L^{1,2})](NO_3)_2$ which is 1:2 electrolytic in nature. Thus, the complexes were found to have general compositions $[Co(L)X_2]$ and $[Co(L)]X_2$ (where $L = L^1$ and L^2 ligands, $X = Cl^-, NO_3^-, CH_3COO^-$). Magnetic moment and the electronic spectra of the complexes suggest that the ligands coordinate to metal ion via four donor sites to give six coordinate complexes having octahedral geometry except $[Co(L^{1,2})](NO_3)_2$ which is four coordinated tetrahedral geometry. Food Poison Technique was employed for screening the in vitro antifungal studies of the complexes. The complexes were also examined for antifungal studies against pathogenic strains like *Alternaria brassicae*, *Fusarium moniliformae*, *Rhizoctonia solani*.

Key words: Macrocylic complexes, Spectroscopic characterization, Transition metal, Biological activity.

Introduction

Template synthesis of one pot lies at the center of macrocyclic chemistry. The design and

synthesis of polyaza macrocycles have attracted increasing interest in recent years because of importance in bioinorganic chemistry, catalyst extraction of metal ions from solution¹⁻⁷. The lively

topic of coordination chemistry of synthetic macrocycles originated during the 1960s, in which the Co(II) ion was employed as a templating agent⁸. Condensation between carbonyl group with primary amine has played an important role in the development of synthetic macrocyclic ligands⁹⁻¹⁵. Due to the growing interest in macrocyclic ligands and their transition metal complexes we report here the synthesis, spectral characterization and antifungal studies of Co(II) complexes with macrocyclic ligands 2,7,9,14-tetrahydroxy phenyl-1, 3, 6, 8, 10, 13-hexaazacyclooctadecane (L¹) and 2, 7, 9, 14-tetracyclohexane-1,3,6,8, 10, 13-hexaazacyclo-octadecane (L²).

Experimental section

Materials and Methods

All chemicals used were of AR grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Other solvents and chemicals were of commercial product (Fluka, S.D. Fine, E. Merck and Thomas Backer).

Synthesis of metal complexes :

Co(II) complexes with 2,7,9,14-Tetrahydroxyphenyl-1,3,6,8, 10, 13-hexaazacyclooctadecane (L¹) :

All the complexes were prepared by template method. An ethanolic solution (20 mL) of diethylene triamine (2.0 mmol) was heated for 10 min. in the presence of one or two drop of dilute HCl. To this solution, a hot ethanolic solution (20 mL) of the corresponding metal salt like nitrate, chloride or acetate (1.0 mmol) and a hot ethanolic solution (20 mL) of salicyldehyde (2.0 mmol) were added with constant stirring. The resulting mixture was refluxed for 8-10 h at 75-80°C and then allowed to cool overnight at 0°C. The precipitated complex was filtered, washed with ethanol and dried under vacuum over P₄O₁₀.

Co(II) complexes with 2,7,9,14-Tetracyclohexane-1,3,6,8, 10, 13-hexaazacyclo octadecane(L²) :

All the complexes were prepared by template method. An ethanolic solution (20 mL) of diethylene triamine (2.0 mmol) was heated for 10 min. in the presence of one or two drop of dilute HCl. To this solution, a hot ethanolic solution (20 mL) of the corresponding metal salt like nitrate, chloride or acetate (1.0 mmol) and a hot ethanolic solution (20 mL) of cyclohexanone (2.0 mmol) were added with constant stirring. The resulting mixture was refluxed for 8-10 h at 75-80°C and then allowed to cool overnight at 0°C. The precipitated complex was filtered, washed with ethanol and dried under vacuum over P₄O₁₀.

Antifungal Screening :

The antifungal activities of the complexes were tested against the pathogenic fungi *Alternaria brassicae*, *Fusarium moniliformae* and *Rhizoctonia solani* in vitro using the food poison technique¹⁶⁻¹⁸. The stock solution of the compound was directly mixed to the PDA (Potato Dextrose Agar) medium according to the tested 500, 250, 125 ppm concentration. A disc of 5 mm of test fungal culture of a specific age growing on solid medium is then cut with a sterile cork borer and was placed at the center of the solid PDA plate with the help of inoculums' needle. The plates were sealed by parafilm and incubated at 292°C for 7 days. Radial growth of colonies was measured at two points along the diameter of the plate and average of these two readings was taken as the diameter of the fungal colony. DMSO was used as a control and Captan as a standard fungicide. The inhibition of the fungal growth expressed in percentage terms was determined from the growth in the test plate to the respective control plate as given i.e. Inhibition (%) = (C-T) 100 / C Where C = diameter of fungal growth in the control plate, T = diameter of fungal growth in the test plate. The results have shown that complexes used for the experiment exhibited noble activities than the ligand towards the inhibition of test fungi under the test conditions. MIC (Minimum Inhibitory Concentration) of test compounds against both the fungus was 500 ppm and have shown 100% inhibition.

Physical Measurements :

The C, H, and N were analyzed on carlo-Erba

1106 elemental analyzer. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. The magnetic susceptibility was measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. Infra-red spectra were recorded on a Perkin Elmer 137 instrument in the region $4000\text{--}200\text{ cm}^{-1}$ as KBr pellets. EPR spectra of complexes were recorded on JEOL, JES, FE3XG, EPR spectrometer. The spectra were recorded in solid as polycrystalline sample at liquid nitrogen temperature on E-EPR spectrometer operating at with 100 KHz modulation frequency, 10 mW microwave power and 2.5 G modulation amplitude using the DPPH as the marker.

Results and Discussion

Based on analytical data of the complexes were found to have the composition listed in Table 1. The magnetic moments of the complexes account for their nature suggest six coordinated octahedral geometry. The molar conductance values of complexes in DMSO were found to be $11\text{--}18\ \Omega^1\text{cm}^2\text{mol}^{-1}$ corresponding to their non-electrolytic nature¹⁹ while 1:2 electrolyte for $[\text{Co}(\text{L}^{1,2})](\text{NO}_3)_2$. Thus, these complexes may be formulated as $[\text{Co}(\text{L})\text{X}_2]$ and $[\text{Co}(\text{L})]\text{X}_2$ (where $\text{L} = \text{L}^1$ and L^2 ligands, $\text{X} = \text{Cl}^-, \text{NO}_3^-, \text{CH}_3\text{COO}^-$).

Table 1. Elemental analysis data and molar conductance of Complexes

Complexes	Color	Molar Conductance ($\Omega^1\text{cm}^2\text{mol}^{-1}$)	% Yield	Elemental Analysis Data Calculated (Found) %				M. Pt ($^\circ\text{C}$)
				C	H	N	M	
$[\text{Co}(\text{L}^1)\text{Cl}_2]$	Brown	17.2	59	56.12 (56.10)	7.80 (7.79)	10.97 (10.90)	7.55 (7.53)	246
$[\text{Co}(\text{L}^1)](\text{NO}_3)_2$	Brown	12.8	58	52.55 (52.53)	7.29 (7.28)	13.60 (13.58)	7.05 (7.04)	217
$[\text{Co}(\text{L}^1)(\text{CH}_3\text{COO})_2]$	Brown	15.2	65	58.88 (58.82)	8.15 (8.08)	10.40 (10.29)	7.16 (7.10)	276
$[\text{Co}(\text{L}^2)\text{Cl}_2]$	Light Brown	11.8	69	58.70 (58.62)	8.90 (8.85)	12.95 (12.82)	8.92 (8.85)	240
$[\text{Co}(\text{L}^2)](\text{NO}_3)_2$	Brownish black	12.3	68	54.32 (54.23)	8.22 (8.19)	15.99 (15.81)	8.21 (8.19)	217
$[\text{Co}(\text{L}^2)(\text{CH}_3\text{COO})_2]$	Brown	16.3	67	61.56 (61.53)	9.2 (9.1)	11.98 (11.96)	8.37 (8.26)	287

Table 2. IR spectral bands of the complexes

S. No.	Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	Anion bands
1	$[\text{Co}(\text{L}^1)(\text{Cl})_2]$	1627	3225	329
2	$[\text{Co}(\text{L}^1)](\text{NO}_3)_2$	1632	2949	1389
3	$[\text{Co}(\text{L}^1)(\text{CH}_3\text{COO})_2]$	1629	2960	1456, 1297
4	$[\text{Co}(\text{L}^2)(\text{Cl})_2]$	1635	3228	324
5	$[\text{Co}(\text{L}^2)](\text{NO}_3)_2$	1638	2956	1397
6	$[\text{Co}(\text{L}^2)(\text{CH}_3\text{COO})_2]$	1630	3010	1445, 1259

IR spectra :

The IR data of the complexes are given in Table 2. IR spectra of the complexes do not show any band corresponding to aldehyde and primary amine which suggests the condensation between aldehyde and primary amine groups. The absence of absorptions around 3400 cm^{-1} show that amino group of the diamine have reacted with the di ketone. IR spectra give the bands in the range 1627-1638 cm^{-1} due to coordinated azomethine group²⁰. Additionally, the spectra also give the bands at 380-440 cm^{-1} due to (Co-N) which supports the coordination through nitrogen atom²¹. However, nitrate complex of Co(II) displays a sharp and strong band at 1389-1397 cm^{-1} which suggests

that the nitrate group is uncoordinated. The acetato complexes show the IR bands in the region 1445-1456 and 1259-1297 cm^{-1} due to $\text{as}(\text{OAc})$ and $\text{s}(\text{OAc})$ stretching vibrations. The chloro complexes give IR bands at 324-329 cm^{-1} due to (M-Cl)²².

Magnetic Moments :

In literature²³⁻²⁵ experimental magnetic moment lie in the range 4.42 to 4.7 B.M. At room temperature, magnetic moment of the complexes under study have been determined and lie in the range of 4.69-4.81 B.M. indicating a spin quartet six coordinate octahedral Co(II) complexes and 4.57-4.64 B.M. for nitrate complexes indicating four coordinate geometry (Table 3).

Table 3. Electronic spectral and magnetic moments of the complexes

Complexes	$\lambda_{\text{max}}(\text{cm}^{-1})$	$\mu_{\text{eff}}(\text{at room temperature})$
$[\text{Co}(\text{L}^1)\text{Cl}_2]$	9480, 14410, 20145	4.81
$[\text{Co}(\text{L}^1)(\text{NO}_3)_2]$	21250, 25839	4.57
$[\text{Co}(\text{L}^1)(\text{CH}_3\text{COO})_2]$	9584, 14738, 20120	4.69
$[\text{Co}(\text{L}^2)\text{Cl}_2]$	9638, 14652, 20237	4.85
$[\text{Co}(\text{L}^2)(\text{NO}_3)_2]$	21739, 27624,	4.64
$[\text{Co}(\text{L}^2)(\text{CH}_3\text{COO})_2]$	8895, 20878, 26738	4.74

Electronic spectra

The electronic spectra of Co(II) complexes under study display d-d transition band in the range 8895-9638 cm^{-1} , 14410-14738 cm^{-1} and 20120-20878 cm^{-1} . These bands may assigned to the ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F})$, ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F})$ and ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P})$ and fourth band due to charge-transfer transition²⁶. The position of these bands suggests an octahedral environment around the Co(II) ion²⁷. In case of the electronic spectra of $[\text{Co}(\text{L}^{1,2})(\text{NO}_3)_2]$, the three electronic transitions occur from the ground state. ${}^4\text{A}_2$ and the first ν_1 is rarely observed while ν_2 is usually

wide and appears in the near IR region and ν_3 is intense and broad occurring in the region 21250–21740 cm^{-1} . The electronic spectral data of the complexes are given in Table 3.

EPR :

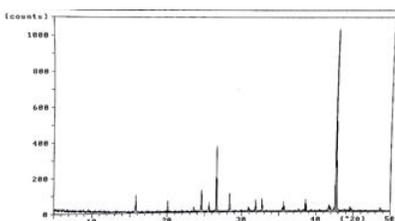
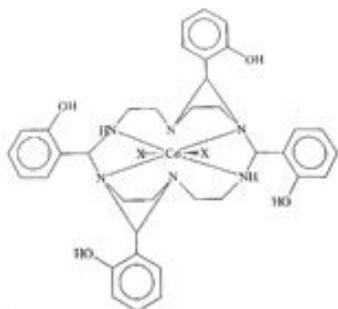
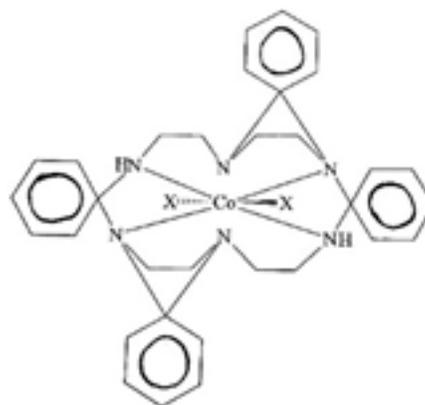
The g-values are presented in Table 4. The e.p.r spectra of the polycrystalline complexes under study²⁸ were recorded at liquid nitrogen temperature (LNT). The rapid spin lattice relaxation of Co^{2+} broadens the lines at higher temperatures. The large deviation of the g values from the spin only value ($g = 2.0023$) is due to the large angular momentum contribution.

Table 4. EPR spectral data of the complexes

Complexes	Temperature	g_{\parallel}	g_{\perp}
$[\text{Co}(\text{L}^1)\text{Cl}_2]$	LNT	1.912	1.504
$[\text{Co}(\text{L}^1)(\text{CH}_3\text{COO})_2]$	LNT	1.925	1.508
$[\text{Co}(\text{L}^2)\text{Cl}_2]$	LNT	1.918	1.501

XRD :

The XRD spectra have been recorded for all the complexes as shown in Figure 1. Bragg's Law i.e. $n\lambda = 2d \sin\theta$ to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta, θ). The variable d is the distance between atomic layers in a crystal, and the variable λ is the wavelength of the incident X-ray beam, n is an integer. For all the complexes, the value of d is found to be same. This indicates that the complexes have same geometry as shown in the Figure 2 and Figure 3

Figure 1: $[\text{Co}(\text{L}^1)\text{Cl}_2]$ Figure 2 : $[\text{Co}(\text{L}^1)\text{X}_2], \text{X}=\text{Cl}^-$ Figure 3 : $[\text{Co}(\text{L}^2)\text{X}_2], \text{X}=\text{Cl}^-$ **Antifungal studies :**

The studies reveal that the coordination compound have moderate antipathogenic activities. The result of antifungal screening showed that complexes have the higher activities than the reactants towards the inhibition of test fungi. The data of the antifungal activities of ligand and complexes are given in Table 5. This modified activity of compounds on complexation can be explained by Overtone's Concept and Chelation Theory²⁹⁻³⁰. The theory states that chelation reduces the polarity of the metal atom by the partial sharing of its positive charge with donor groups and possible π -electron delocalization over the whole ring.

Table 5. Fungicidal screening data of the ligand and complexes

Complexes	Alternaria Brassicae			Fusarium moniliformae			Rhizoctonia Solani		
	500	250	125	500	250	125	500	250	125
Cyclohexanone	100	49	32	100	45	35	100	42	33
Salicylaldehyde	100	58	34	100	47	37	100	44	35
Diethylene triamine	100	51	35	100	49	39	100	48	38
$[\text{Co}(\text{L}^1)\text{Cl}_2]$	100	72	54	100	68	53	100	70	62
$[\text{Co}(\text{L}^2)\text{Cl}_2]$	100	77	66	100	81	69	100	73	65
$[\text{Co}(\text{L}^1)(\text{CH}_3\text{COO})_2]$	100	80	68	100	83	70	100	79	69
$[\text{Co}(\text{L}^2)(\text{CH}_3\text{COO})_2]$	100	82	69	100	84	72	100	83	71

This results with increasing of the lipophilic character of the complex and favor the permeation of the complex through the lipid layer of cell membrane. Finally, the compound prevents the metabolic functions of the cell and acts as antipathogen. The experimental findings reveal that the antipathogenic capacity of the compounds increases with concentration.

Conclusion

The present study revealed octahedral and tetrahedral geometry for Co(II) complexes. The studies support that the ligands have four donor sites and coordinate to metal ion in NNNN fashion. The synthesized macrocyclic complexes are characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR and UV, EPR analysis. On the other hand, the *in vitro* antifungal screening to the compounds revealed that the compounds have the considerable act as antifungal agents. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

Acknowledgement

We are thankful to I.I.T Chennai for recording EPR spectra.

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