

Original Article

SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL INVESTIGATION OF NOVEL 17-MEMBERED DIOXADIAZA NAPHTHALDEHYDE BASED MACROCYCLIC LIGAND AND ITS COMPLEXES OF Co (III), Ni (II) AND Cu (II) PERCHLORATE IONS

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ABSTRACT

Objective: The objective of this research is to synthesis hitherto, novel unreported [17]-membered dioxadiazapentaldehyde based macrocyclic ligand (L) and to synthesize its Co (III), Ni (II) and Cu (II) metal ion complexes.

Methods: The synthesis of the ligand has been accomplished by two different synthetic routes each involving two stages. 2-Hydroxy-1-Naphthaldehyde in the presence of potassium carbonate was treated with α,α' -dibromo-m-xylene to yield the dial derivative (I). The dial derivative (I) was further made to undergo Schiff base condensation with 1,2-diaminobenzene to yield the bright yellow macrocycle (L) in good yield. In the second method the Schiff base condensed product Naphthaloph was synthesized and allowed to undergo Williamson's condensation with α,α' -dibromo-m-xylene to yield the ligand (L).

Results: The ligand and its complexes were characterized by elemental analysis, electronic spectroscopy, IR, Conductivity measurements, EPR, magnetic susceptibility, ¹H NMR and MS. The neutral seventeen membered tetradentate dioxadiazapentaldehyde ligand (L) readily complexes with Co(III), Ni(II) and Cu(II) perchlorate salts in 1:1 mole ratio to yield complexes of formulae [Co(L)X₂]ClO₄, [Ni(L)X₂], [Cu(L)X]ClO₄, (X = Cl, Br and NO₃). The complexes were also synthesized by the metal template method. The yield of the template procedure was found to be greater than the non-template method.

Conclusion: A hitherto 2, 10-dioxo-21,29-diazapentalheptacyclo-[29.4.2.1[4,8]0[1,32]0[11,20]0[14,19]0[23,28]0[32,37]]-tetraconta-4, 6, 8, 11, 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39-octatecaene. The [17]-membered tetradentate dioxadiazapentaldehyde macrocycle (L) was found to accommodate Co³⁺, Ni²⁺, and Cu²⁺ ions with ease due to the presence of flexible alkyl groups. Further studies with the inner-transition metal ions will be highly informative in understanding the coordinating capabilities of lanthanides and actinides.

Keywords: The synthesis and characterization of dioxadiazapentaldehyde macrocyclic ligand and its complexes of Co(III), Ni(II) and Cu(II) perchlorate complexes.

INTRODUCTION

The design and synthesis of macrocyclic complexes [1, 2] initially has lured many a scientist owing to their significance in serving as biological mimics [3-7]. The synthetic macrocyclic complexes mimic some natural occurring macrocyclic complexes [8] resemblance with natural macrocyclic like metalloproteins, porphyrins and cobalamine [9, 10]. The transition metal macrocyclic complexes are active part of metalloenzyme proteins and coenzymes like haemoglobin, myoglobin [11-14]. Lanthanide macrocyclic complexes involving Gd and Eu are extensively used as NMR shift reagents [15]. Identification and realization of the applications of macrocyclic ligands and their transition and inner-transition metal complexes as base transfer catalyst and in biological probe studies [16, 17] have opened up new avenues of exploring their potency in various other fields recently the Naphthaldehyde based Schiff bases are gaining significance due to their sequestering properties towards transition metals [18, 19]. The presence of azomethine group has been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities [20, 21]. In order to understand the involvement of azomethine groups in the above said properties, we have reported the synthesis and spectral characterization of hitherto unreported new 17-membered naphthaldehyde based dioxadiazapentaldentate macrocyclic ligand (L), and its Co (III), Ni (II) and Cu (II) perchlorate complexes.

MATERIALS AND METHODS

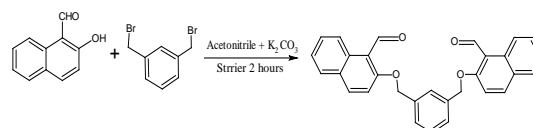
All the chemicals used in this study were of Analar grade. Metal salts were purchased from Merck and were used as such as received. Elemental analysis was carried out on Elementarvario EL III-Germany. ¹H NMR spectrum was recorded used to Bruker model 4276. FT IR spectra recorded on Perkin Elmer on KBr pellets in the range of 4000 to 400 cm⁻¹. The electronic spectrum recorded on

Lambda 35 in the range of 200 to 800 nm using 10⁻³M concentration solution in DMF. NMR spectrum was recorded using Bruker model 4276. The new dialdehyde was synthesis from 2-hydroxy-1-naphthaldehyde and α,α' -dibromo-m-xylene in basic medium using potassium carbonate under reported procedure [22].

Synthesis of dialdehyde

To a solution of (1g, 5 mmol) of 2-hydroxy-1-naphthaldehyde in 15 mL of acetonitrile was added (0.345g, 2.5 mmol) of K₂CO₃ and the resulting solution was stirred for 30 min under thermostat condition at 60 °C wherein a bright yellow color solution was obtained. To this stirring solution was added a solution of (0.66g, 2.5 mmol) of α,α' -dibromo-m-xylene in 5 ml of acetonitrile in one lot. The resulting pale yellow solution was stirred until the solution decolorized and on addition of 20 ml of cold water it yielded a spongy white dialdehyde product. The spongy product was filtered using sintered crucible. Yield is 71%, m. pt 164 °C. Anal. Cal. (C₃₀H₂₄O₄), C(33.37), H(5.05), N(5.40), O(56.08) Found: C(33.31), H(5.02), N(5.37), O(56.04). IR (KBr Pellets) (C=O) 1665 cm⁻¹, (C=C)_{aro} 1581 cm⁻¹, (C-O) 1235 cm⁻¹. The synthesis of the dialdehyde is depicted in Scheme.1.

Scheme 1

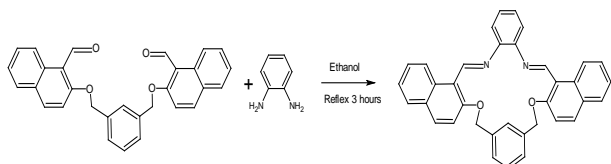


Synthesis of macrocyclic ligand (L)

To a ethanolic solution of (1g, 0.4 mmol) of the dialdehyde in 10 ml of ethanol was added a solution 1,2-diamino benzene (0.8g, 0.4

mmol) in 10 ml of ethanol solution under gradual addition in drops using a dropping funnel over 30 min. The resulting pale yellow turbid solution was refluxed for 4h wherein a clear bright yellow solution was obtained, on standing the solution to room temperature a bright yellow colored product separated out. Yield: 89% m. pt: 178 °C. Anal. Cal. (C₃₆H₂₆N₂O₂), C(83.37), H(5.05), N(5.40), O(6.17). IR (KBr Pellets) (C=N) 1602 cm⁻¹, (C=C)_{aro} 1510 cm⁻¹, (C-O) 1250 cm⁻¹. The synthesis of the overall ligand is depicted in Scheme 2.

Scheme 2



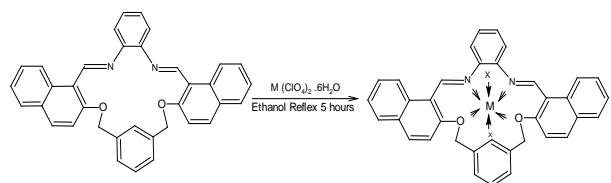
2,10-dioxa-21,29-diaza-heptacyclo-[29.4.2.1^{4,8}.0^{1,32}.0^{11,20}.0^{14,19}.0^{23,28}.0^{32,37}]-tetraconta-4,6,8,11, 13,15, 17, 19, 21, 23, 25, 27, 29, 31, 33, 35, 37, 39-octatecaene.

Synthesis of complexes

General procedure for the synthesis of metal complexes of ligand (L)

To a refluxing solution of a ligand (10 mmol) in 20 ml of absolute alcohol was added an equivalent mole ratio of the corresponding perchlorate salts M(ClO₄)₂·6H₂O (10 mmol) where in (M= Co, Ni, Cu). To this refluxing metal perchlorate solution of the ligand (L) was added the corresponding axial monoanionic ligand X in appropriate mole ratio, (X= Br⁻, Cl⁻ and NO₃⁻) on continuing the reflux for 30 min yielded macrocyclic complexes in good yield. The complexes of varying colour and nature were isolated from the mother liquor owing to the sparingly soluble nature. The complexes were filtered and washed repeatedly with diethyl ether and dried over anhydrous CaCl₂ under vacuum condition. No further purification carried out as the micro crystalline colored complexes separated readily, in pure condition. The Scheme 3 depicted the nature of bonding exhibited by the ligand.

Scheme 3



RESULTS AND DISCUSSION

Synthesis and characterization of the ligand (L)

The dioxadiazanaphthaldehyde based tetradentate macrocyclic was synthesized by two different methods. The first method involves the Schiff's base condensation of the naphthaldehyde and *o*-phenylenediamine in 2:1 mole ratio in acetonitrile, to yield the Schiff's base condensed product (Naphthaloph). The azomethine derivative was further reacted with α,α' -dibromo-*m*-xylene under Williamsons condensation in 1:1 mole ratio to yield the 17-membered N₂O₂ macrocyclic ligand(L). The second method involves the Williamsons' condensation reaction of naphthaldehyde and α,α' -dibromo-*m*-xylene in 2:1 mole ratio to yield the dial derivative(I), further the dial derivative is made to undergo schiff's base condensation with 1,2-diamino benzene to yield the 17-membered macrocycle (L). The ligand isolated readily from the solution due to its sparingly soluble nature. The tetradentate dioxadiaza

macrocyclic ligand (L), was characterized by elemental analysis, electronic spectroscopy, IR, ¹H, ¹³C NMR, CIMS and Cyclic voltammetric studies. The elemental analysis was in good agreement with the experimental and theoretical value, which ensures the formation of the macrocyclic ligand. The presence of aldehyde peak at 1664 cm⁻¹ in the dial derivative(I) and the absence of the sharp ν (OH) peak at 3550 cm⁻¹ endures the formation of the dial intermediate(I) [23]. The disappearance of the ν (C=O) stretching frequency at 1664 cm⁻¹ and the appearance of the new peak at 1602 cm⁻¹ has been assigned to ν (C=N) stretching frequency [24]. This confirms the formation of the macrocyclic ligand. The ¹H NMR spectrum of the dial derivative(I) exhibits a sharp singlet at 11 ppm assigned to the aldehydic protons, the multiplet centered around 7.2 to 8.1 ppm has been attributed to the aromatic protons from both naphthalene and benzene moieties. The four proton sharp singlet appearing at 5.4 ppm has been assigned to the methylene protons. The ¹³C NMR of dial derivative (I) exhibits a sharp peak at 78 ppm with 70% intensity which has been assigned to the methylenic carbons, the sharp peak of weak intensity observed at 192 ppm has been assigned to aldehydic carbon and the medium intensity peaks centered around 112-138 ppm has been attributed to the aromatic carbon atoms pertaining to benzene and naphthalene moieties [25]. The mass spectrum of the dial derivative(I) exhibited the molecular base peak at 443 m/z of low intensity confirming the formation of the dioxadiaza tetra dentate macrocyclic ligand. The chemical ionization mass spectrum of the ligand exhibited a [M+H]⁺ molecular ion peak at 519 m/e value. The CHN analysis of the ligand is in good agreement of the observed value.

Characterization of the Co(III), Ni(II) and Cu(II) complexes of the ligand (L)

The perchlorate complexes of the macrocyclic ligand(L) were synthesized both by the reaction of the preformed ligand and metal perchlorate in 1:1 mole ratio in ethanol, and by the metal template method wherein the precursors and the corresponding metal perchlorates were made to react simultaneously in one pot synthesis method. The preformed ligand and metal perchlorate yielded better results than the template procedure. The varying coloured complexes obtained were characterized using elemental analysis, molar conductance, UV-vis spectroscopy, FAB-MS magnetic susceptibility and cyclic voltammetry. The infrared spectral data of the ligand and the complexes are tabulated in table-1. On complex formation the ν (C=N) peak which appears at 1602 cm⁻¹ in the pure ligand has been shifted towards lower frequencies which is in good agreement with the coordination of the azomethine group with the central metal ions. The occurrence of two types of ν (C-O) stretching frequencies corresponding to ν (C-O) aromatic and ν (C-O) aliphatic nature ensures the coordination of the two oxo groups with the central metal ions. The ligand is found to act as neutral dioxadiaza tetradentate ligand. The stretching due to ν (C=C) occurs within the range of 1508-1515 cm⁻¹ in all the complexes. All the perchlorate complexes exhibit ν (ClO₄) stretching pertaining to free ionic perchlorate groups around 1059-1085 cm⁻¹ in all the complexes [26-28]. The molar conductance values of the complexes reveal that the complexes exist as both neutral entities and 1:1 type of electrolytes. The electronic spectral data reveal that all the metal ions exist in their usual oxidation states, the cobalt (III) complexes in which cobalt acquires d⁶ state and is expected to exhibit an single electronic transition, and it is observed so indicating that the cobalt ion is in 3⁺oxidation state. [29-31] The ¹H NMR spectrum of the ligand (L) exhibits a multiplet around 7.1 ppm to 8.1 ppm assignable to the aromatic protons of Naphthaldehyde and benzene groups, the singlet of medium intensity occurring at 9.4 ppm has been assigned to azomethine protons in the macrocycle. The unsymmetrical triplet occurring around 1.6 to 2.4 has been assigned to methylene protons. The singlet peak of medium intensity occurring at 15.1 ppm may be assigned to the hydrogen bond that can be formed due to a transfer of proton from the macrocycle moiety that can form hydrogen bond between the two oxo donors in the macrocycle.

Table 1: Infrared Spectral data of the ligand (L) and its transition metal Complexes

Compound	ν (C=N) (cm^{-1})	ν (C=C) (cm^{-1})	ν (C-O) _{Aro} (cm^{-1})	ν (C-O) _{AlI} (cm^{-1})	ClO_4^-
Ligand	1602	1510	1250	1080	1071
[Co(L)Cl ₂] ClO ₄	1586	1510	1239	1071	1073
[Co(L)Br ₂] ClO ₄	1588	1510	1240	1064	1064
[Co(L)(NO ₃) ₂]ClO ₄	1582	1510	1238	1076	1076
[Ni(L)Cl ₂]	1186	1515	1240	1078	1078
[Ni(L)Br ₂]	1585	1508	1241	1061	1061
[Ni(L)(NO ₃) ₂]	1586	1511	1240	1065	1084
[Cu(L)Cl] ClO ₄	1599	1515	1245	1060	1085
[Cu(L)Br] ClO ₄	1595	1512	1240	1070	1083
[Cu(L)NO ₃] ClO ₄	1588	1514	1239	1059	1059

Table 2: Physical properties of M-Dial perchlorate complexes

Name of the complexes	Color	Molecular weight	Yield %	Molar conductance ($\text{mho cm}^2 \text{mol}^{-1}$) mho	Nature of the electrolyte
[Co(L)Cl ₂] ClO ₄	Light Brown	725.63	71	67	1:1
[Co(L)Br ₂] ClO ₄	Black	814.53	73	72	1:1
[Co(L)(NO ₃) ₂] ClO ₄	Dark Brown	776.73	74	76	1:1
[Ni(L)Cl ₂]	Grey Color	725.39	81	37	Neutral
[Ni(L)Br ₂]	Grey Color	746.19	83	35	Neutral
[Ni(L)(NO ₃) ₂]	Grey Color	846.29	80	39	Neutral
[Cu(L)Cl] ClO ₄	Light Brown	679.75	77	72	1:1
[Cu(L)Br] ClO ₄	Brown	724.20	78	67	1:1
[Cu(L)NO ₃] ClO ₄	Dirty White	737.34	74	76	1:1

Table 3: Electronic spectral data of the ligands and its complexes

Complexes	Frequency Range (cm^{-1})
[Co(L)Cl ₂] ClO ₄	25641
[Co(L)Br ₂] ClO ₄	22172
[Co(L)(NO ₃) ₂] ClO ₄	23529
[Ni(L)Cl ₂]	24271, 27027, 29411
[Ni(L)Br ₂]	21739, 24390, 29411
[Ni(L)(NO ₃) ₂]	22075, 22727, 30581
[Cu(L)Cl] ClO ₄	23419
[Cu(L)Br] ClO ₄	23474
[Cu(L)NO ₃] ClO ₄	23443

Table 4: CHN analysis

Ligand	% of C		% of H		% of N	
	Cal value	Obs value	Cal value	Obs value	Cal value	Obsvalue
	80.5658	80.378	3.9675	3.934	15.2452	15.0243

CONCLUSION

The pre-designed [17]-membered neutral dioxadiaza tetradentate macrocyclic ligand (L), has been achieved through two step, synthetic strategy, the conventional method and microwave assisted synthetic methods yield the ligand in good yields. The microwave assisted synthetic method, provided high yields of pure macrocycle. No further purification was required, to attain the sharp melting point. The sharp melting point the good agreement of the elemental analysis along with the spectroscopic evidences confirms the formation the [17]-membered neutral dioxadiaza tetradentate macrocyclic ligand (L). The dioxadiaza tetradentate macrocyclic ligand, readily complexes with the transition metal ions such as Cobalt (III), Nickel (II) and Copper (II) metal salts in ethanolic medium. The fine microcrystalline coloured complexes separated out of the reaction mixture due to its sparingly soluble nature. The complexes were characterized, without any further purification. The preformed ligand reacted with the corresponding metal salts in 1:1 mole ratio to yield complexes, the metal template method gave instant complexation but with relatively lower yields. The investigation of spectroscopic data of the metal complexes of the macrocycle revealed the formation of mononuclear complexes of molecular formula $M(\text{C}_{41}\text{H}_{43}\text{N}_2\text{O}_2)\text{X}_2$. The electronic

spectral data along with the molar conductivity studies are in the favor of octahedral geometry of Co (III) and Ni (II) complexes and square pyramidal geometry of Cu(II) complexes. The macrocyclic cavity provided by the [17]-membered tetradentate dioxadiaza macrocycle is tunable enough with the chosen metal ions to form stable complexes. The ligand has proven a good vehicle to study the physico chemical properties of the varying metal ions in an identical frame work.

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CONFLICT OF INTERESTS

The authors do not have any conflict of interest to declare.

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