Synthesis and characterisation of the new zero generation dendrimer 1,3,5-tris{methyl(4,7,10-triaza-3,11-dimethyltrideca-3,10-diene-2,12-dione dioxime)}benzene and its transition metal complexes

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Abstract

The pseudo macroacyclic complexes formed from the dioxime based macroacyclic ligands with metal ions can be a promising approach to water softening, effluent treatment and metal ion estimations. In the present work, the Co(II), Ni(II) and Cu(II) complexes of the macroacyclic ligand appended zero generation-dendrimer,1,3,5-tris{methyl(4,7,10-triaza-3,11-dimethyltrideca-3,10-diene-2,12-dione dioxime)}benzene were synthesized and characterized by IR, NMR, UV, ESI Mass and molar conductance data. These complexes need to be subjected to further research in view of their varied applications.

Keywords: Macroacyclic ligand, dioxime, dendrimer, water softening, effluent treatment, metal ion estimations.

Introduction

The metallodendrimers formed from the macroacyclic dioxime[1-7] ligands attached to a dendritic core encapsulating the transition metal ions are stable and hence are used for various applications. The dioxime based macroacyclic ligands when treated with metal ions lead to the formation of complexes by the loss of proton which makes it more stable than normal macroacyclic complexes. The metal ions fit into the macroacyclic cavity formed by the hydrogen bonded dioxime ligands producing a pseudo macroacyclic complex (Scheme 1). When they are appended with water soluble entities, they can be used as metal ion scavengers for effluent-treatment, homogeneous catalysis or *in vitro* biological applications. They can be used as fluorescent markers when appended with fluorescing groups.[23,24]

Recently, Sarkar et al carried out the investigation of scavenging of nickel ion using PAMAM dendrimer from aqueous solutions. They synthesised the Schiff base ligand by condensation of diacetyl monoxime and diethylenetriamine in 1:1 molar ratio and two mononuclear nickel(II) complexes [Ni(L)Cl_2] and [Ni(L)$(NCS)_2$][21-23].

Motaleb and Selim synthesized a novel dioximederivative(2E,2′E,3E,3′E)-3,3′-(pyrimidine-4,5-diylbis(azanylylidene))bis(butan-one)dioxime. ^{99m}Tc-dioxime was radio-synthesized under the optimum conditions and it is a very good tumour imaging agent. They published a very interesting study on dioxime synthesis and their biomedical applications. It gives us an insight into the synthetic methodologies and various applications of dioxime based Schiff base complexes and paves way for further research in the respective fields. The transition metal complexes with vic-dioxime ligands have been investigated since many years and a subject of several reviews due to their applications in various fields.[12-17]

The synthesis of dioximes is relatively easier and on account of their unusual reactivity modes in coordination complexes, they are used as dyes, analytical and biochemical reagents, anti- fungal, anti- bacterial and anticancer agents. They are widely used in the synthesis of organic chemical manufacture like caprolactam. They are also used in nuclear medicine and they can be viewed as leading the pharmaceutical compounds in the upcoming years.[8-11] Synthesizing the suitable dendrimer ligands for investigating and understanding the applications of these molecules would be a desirable step for the research community.[18-20]

Material and Methods

Diacetylmonoxime (AR, SRL), diethylenetriamine (DETA) (TG, SRL) were used as such. Mesitylene (AR, Avra Synthesis) was purchased and brominated using N-bromo succinimide,(NBS) (AR, Loba Chemie). Diethylenetriamine (DETA) (TG, Sisco) was purchased and used as such. Cobalt(II) chloride dihydrate (AR, E. Merck), Nickel(II) nitrate hexahydrate (AR, E. Merck), Copper(II) chloride dihydrate (AR, E. Merck) and Zinc(II) nitrate hexahydrate (AR, E. Merck) were used as such.

Absolute ethanol was obtained by distillation of rectified spirit over lime. Carbon tetrachloride (LR, E. Merck), acetone (LR, SD's) and chloroform (LR, E. Merck) were distilled whenever necessary and used. Diethyl ether (LR, E. Merck) and dimethyl sulphoxide (DMSO) (LR, E. Merck) were used as such.

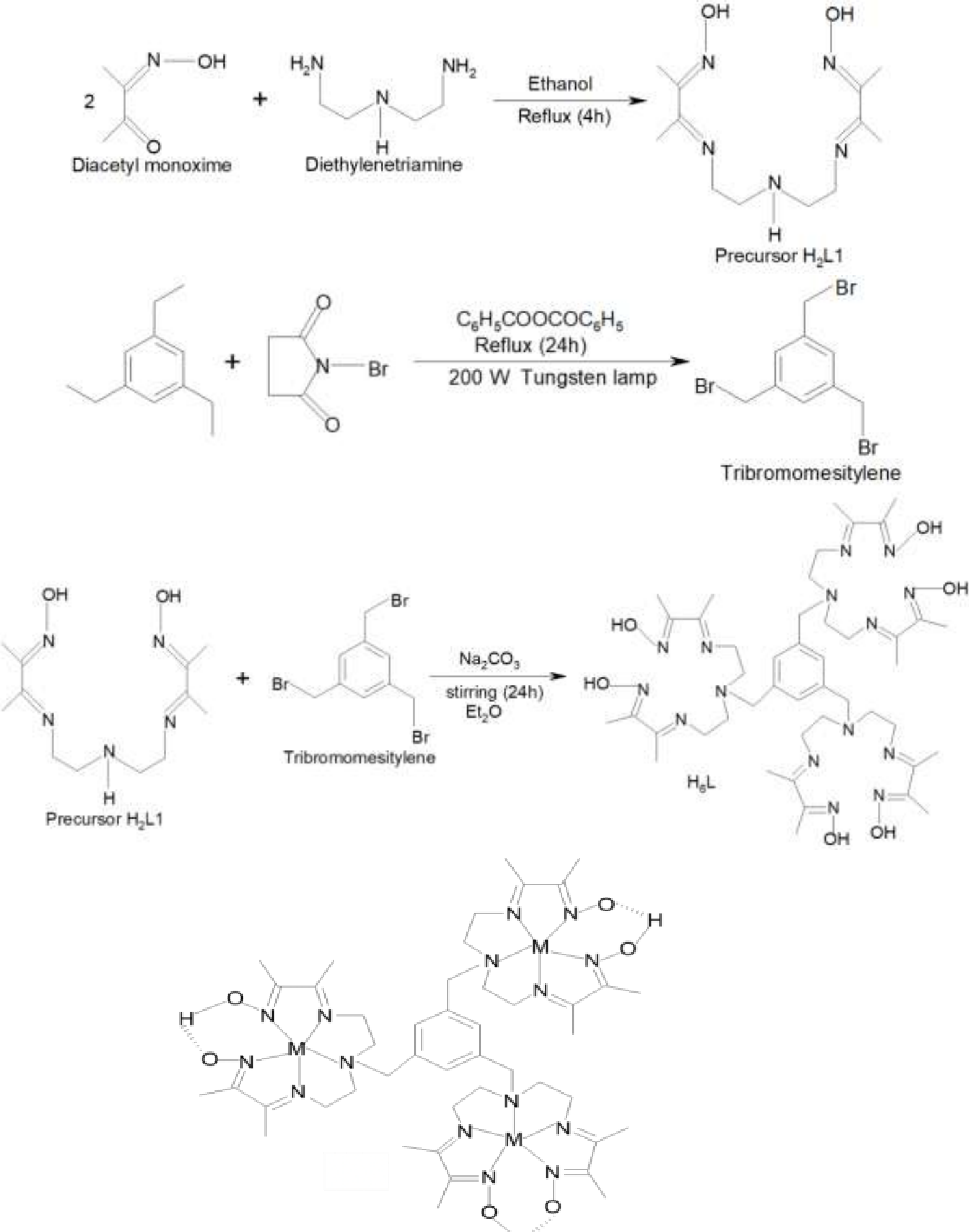
Infrared Spectra: The infrared spectra of the ligand and its complexes were recorded on a Perkin Elmer FT-Spectrometer in the range 4000 – 400 cm^{-1} using KBr pellets.

UV – Visible Spectra: UV-Visible spectra of the ligand and its complexes were recorded on Perkin Elmer Lambda 3B UV-Visible Spectrophotometer in the range 200-900 nm. The spectra of the complexes were recorded in DMSO at 25

°C using matched pair of Teflon stoppered quartz cell of path length 1 cm.

NMR Spectra: The ^{1}H and ^{13}C NMR spectra of the ligand were recorded in Joel 500 MHz NMR spectrometer using $(CD_3)_2SO$.

Mass Spectra: The mass spectrum of the ligand was recorded by JEOL GCmate Mass Spectrophotometer. The inlet of the sample was done by Direct Probe. Electron ionization mode was used for the fragmentation.



[M_3 (H_3L)]X_3

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

X= Cl^- , NO_3^-

Scheme 1:

Molar Conductivity Measurements: The molar conductance of the Co(II) and Cu(II) complexes was measured using 10^{-4} M solution of acetonitrile and Ni (II) complex in 10^{-4} solution of $CHCl_3$ at 25°C using an Elico CM-180 Conductivity meter and Elico type CC-03 Conductivity cell of cell constant 0.8 cm^{-1}.

Synthesis of Zero Generation Dendrimer

Synthesis of precursor H_2L1: A hot solution of diacetylmonoxime (3 g, 29.7 mmol) in ethanol and diethylene triamine (1.5 ml, 13.8 mmol) was mixed and then refluxed for 4 hours. The resultant dark yellow solution was cooled and poured in water to get white crystals. It was filtered, washed with water and dried. Yield - 40%; Colour: White.

Synthesis of 1,3,5- tris(bromomethyl)benzene: To a hot solution of mesitylene (1.4 ml, 1 mmol) in CCl_4, N-bromo succinimide (6.2 g, 3.5 mmol) was added along with benzoyl peroxide (1 g) and was refluxed for 24 h under photochemical condition (200 W Tungsten lamp). The crystals of succinimide formed on cooling of the solution were filtered off. The filtrate was evaporated to near dryness to form oily gel which on recrystallization in chloroform using charcoal yielded white crystals. Yield - 45%; Colour: White.

Synthesis of Zero Generation Dendrimer H_6L: Sodium carbonate (0.4 g, 3.77 mmol) was added to the precursor H_2L1 (1 g, 3.71 mmol) dissolved in diethyl ether. Tribromomesitylene (0.5 g, 1.23 mmol) was added to it and stirred for 4 hours. White precipitate was obtained which was filtered. Crystals were formed on evaporation of ether and it was washed with hot water 5 to 6 times and dried. Yield - 50%; Colour: White.

Synthesis of complexes of H_6L

Synthesis of $[Co_3(H_3L)(H_2O)_3]Cl_3$: To a solution of H_6L (0.15 g, 0.162 mmol) in ethanol was added a solution of cobalt chloride hexahydrate (0.114 g, 0.479 mmol) in ethanol and refluxed for one hour. The dark brown precipitate which separated out was filtered, washed with ethanol and dried over anhydrous calcium chloride. Yield - 40%;Colour: Dark brown.

Synthesis of $[Ni_3(H_3L)](NO_3)_3$: To a solution of H_6L (0.15 g, 0.162 mmol) in ethanol was added a solution of nickel(II) nitrate dihydrate (0.105 g, 0.480 mmol) in ethanol and refluxed for one hour. The resultant reddish brown precipitate was filtered, washed with ethanol and dried over anhydrous calcium chloride. Yield -70%; Colour: Reddish brown.

Synthesis of $[Cu_3(H_3L)]Cl_3$: To a solution of H_6L (0.15 g, 0.162 mmol) in ethanol was added a solution of copper(II) chloride dihydrate (0.081 g, 0.475 mmol) in ethanol and the resultant green solution was refluxed for one hour. The dark green precipitate which separated out was filtered, washed with ethanol and dried over anhydrous calcium chloride. Yield - 50%; Colour: Dark green.

Synthesis of $[Zn_3(H_3L)(H_2O)_3](NO_3)_3$: To a solution of H_6L (0.15 g, 0.162 mmol) in ethanol was added a solution of zinc(II) nitrate hexahydrate (0.107 g, 0.487 mmol) in ethanol and refluxed for one hour. The dirty white precipitate which separated out was filtered, washed with ethanol and dried over anhydrous calcium chloride. Yield - 30%; Colour: Dirty white.

Results and Discussion

The trimacroacycles appended zero generation dendrimer is synthesized by stepwise condensation reaction. The first step is the Schiff base condensation of diacetyl monoxime and diethylenetriamine (DETA) in 2:1 mole ratio in ethanol to obtain 4,7,10-triaza-3,11-dimethyltrideca-3,10-diene-2,12-dione dioxime, I, the ligand. In the second step 1,3,5-tris(bromomethyl)benzene is prepared by bromination of mesitylene in CCl_4 with NBS and benzoyl peroxide. Zero generation dendrimer ligand, 1,3,5-tris{methyl(4,7,10-triaza-3,11-dimethyltrideca-3,10-diene-2,12-dionedioxime) }benzene, H_6L is prepared in the third step by treating the I with 1,3,5-tris(bromomethyl)benzene in 3:1 mole ratio in the presence of a base in diethyl ether.

The ligand obtained is soluble in ether, ethanol, acetonitrile and DMSO but insoluble in $CHCl_3$ and water. The precursor I is characterized by IR which shows peaks at 3208 cm^{-1} for the oxime –OH stretching and at 1694cm^{-1} for C=N stretching. The peak at 3400cm^{-1} is due to N-H stretching.

Characterization of ligand

The ligand is characterized by UV, IR, ^1H ,^{13}C NMR and ESI Mass spectrometry.

IR Spectrum: The IR spectrum of the ligand H_6L shows absorbance at 1637 cm^{-1} which is due to C=N stretching and at 3450 cm^{-1} due to ν(OH). The absorbance at 2929 cm^{-1} is attributed to ν(C-H) of the aliphatic unit. The medium absorption at 1547 cm^{-1} is due to C=C stretching vibration of benzene ring. The absorption at 1388 cm^{-1} is due to N-O group. The IR spectrum of the ligand is shown in figure 1 and the IR spectral data are presented in table 1.

^1H NMR spectrum: The 500 MHz ^1H NMR spectra of the ligand H_6L was recorded in DMSO. The ligand shows signals corresponding to 7 types of protons. Two types of –CH_3 protons of diacetylmonoxime are observed as a singlet at 1.05 and 1.31 ppm and the –CH_2 protons of diethylenetriamine are observed as triplets in the range of 2.21 – 2.52 ppm respectively. The –CH_2 protons of the mesitylene are observed as singlet at 7.95 ppm and the aromatic protons are observed as multiplet in the range 7.15-7.85 ppm. The –OH proton of diacetylmonoxime is observed as a singlet at 11.33 ppm. The 500 MHz NMR spectra of H_6L are shown in figure 2.

^{13}C NMR Spectrum: The ^{13}C NMR Spectrum of the ligand shows 9 types of carbon atoms. Two types of $–CH_3$ carbon atoms of the diacetylmonoxime are observed as 2 lines at 9 and 10 ppm. The $–CH_2$ carbon of mesitylene is observed at 11ppm. The $–CH_2$ groups of diethylenetriamine is observed as 2 lines at around 25 ppm. Two types of aromatic carbons are observed as multiple lines at around 129-155 ppm. C=N carbon atoms of diacetylmonooxime are observed as 2 lines at 167 ppm and that of oxime group is observed at 197 ppm. The ^{13}C NMR spectrum of ligand is shown in figure 3.

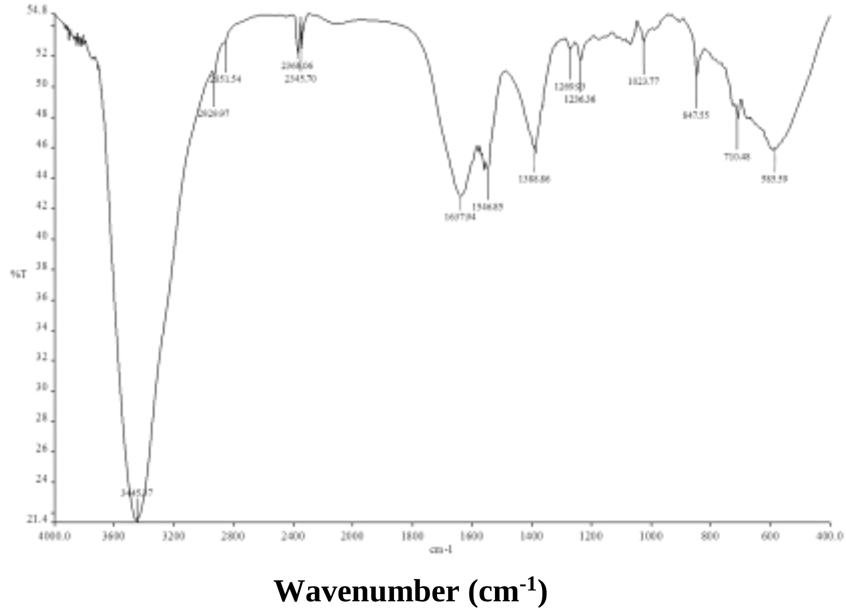


Figure 1: Infrared spectrum of the ligand

Table 1
Infrared spectral data of the ligand and the complexes

Compound	ν (O-H)	ν(C-H)	ν(C=N)	δ(C-H)	δ(N-O)	δ(O-H)
H_6L	3450	2918	1637	1388	1228	710
$[Co_3 (H_3L) (H_2O)_3] Cl_3$	3445	2918	1636	1364	1223	707
$[Ni_3(H_3L)](NO_3)_3$	3445	2929	1637	1364	1239	770
$[Cu_3(H_3L)]Cl_3$	3445	2924	1735	1364	1217	751
$[Zn_3 (H_3L)](NO_3)_3$	3439	3014	1735	1364	1217	701

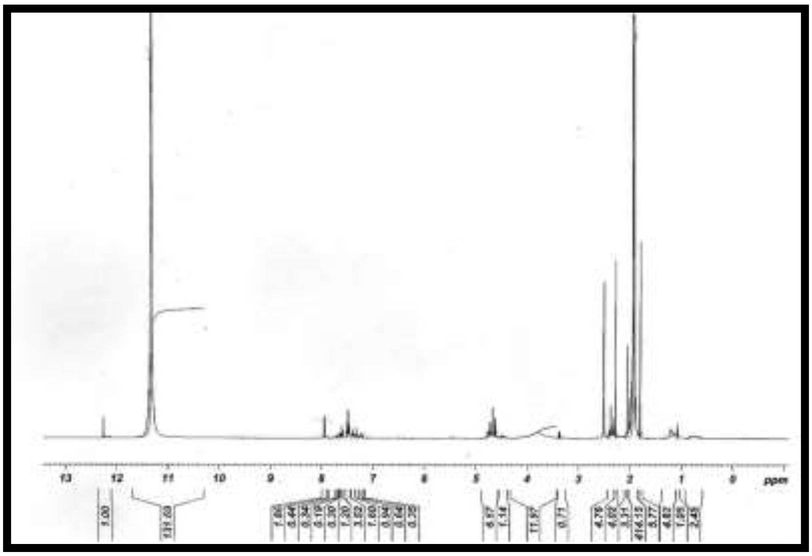


Figure 2: 500 M Hz ^{1}H NMR Spectrum of H_6L

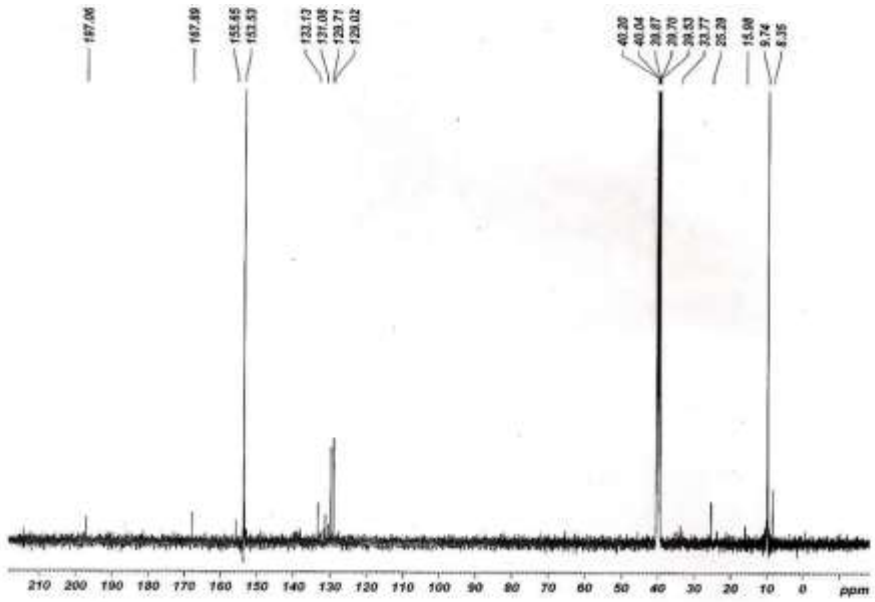


Figure 3: 125MHz ^{13}C NMR Spectrum of H_6L

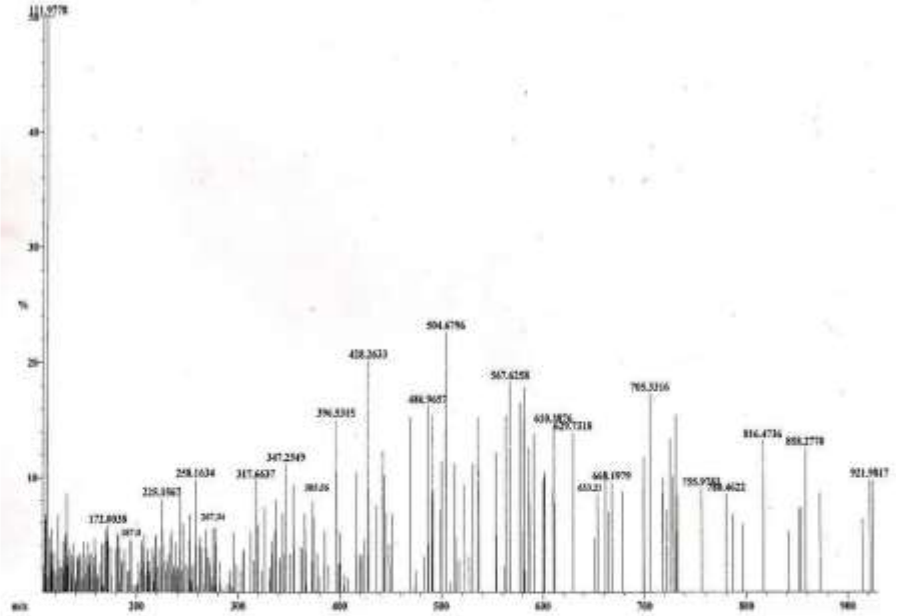


Figure 4: Mass Spectrum of H_6L

Mass Spectrum: The molecular ion peak at m/z 921.9 confirms the molecular formula of the compound whose theoretical mass is found to be 922 g/mol. The base peak at m/z 111.9 corresponds to the formation of the fragment $[C_{40}N_{13}O_5H_{67}]^+$ which is the dioxime ligand. The peak at m/z 653 corresponds to the fragment $[C_{12}N_5O_2H_{23}]^+$ and the peak at m/z 385 is due to the fragment formed after cleavage of two appended dioxime ligands from parent ion which is $[M\text{-}C_{24}N_{10}O_4H_{46}]^+$. The peak at m/z 588 is due to the formation of the fragment $[C_{24}N_4O_6H_{42}]^+$. The ESI mass spectrum of the ligand is shown in figure 4.

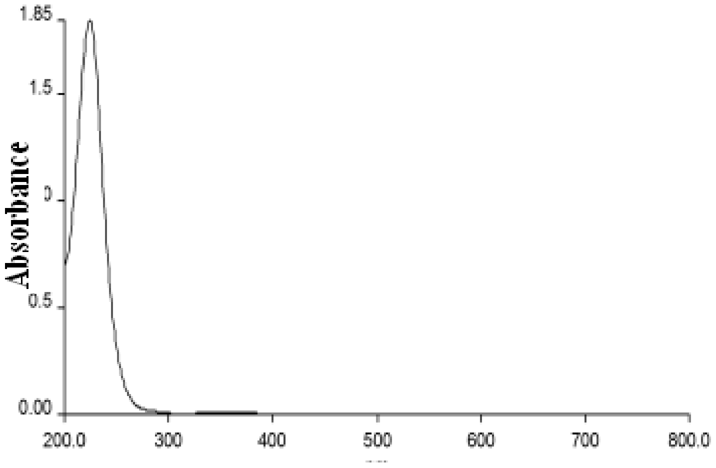
Electronic absorption spectrum of H_6L: The electronic absorption spectrum of H_6L was recorded using 10^{-4} M solution in acetonitrile. The absorption at 220 nm is due to $\pi \rightarrow \pi^*$ transition. The electronic absorption spectrum of H_6L is shown in figure 5.

Characterization of complexes

The complexes are characterized by IR and electronic absorption spectroscopies and molar conductivity measurements.

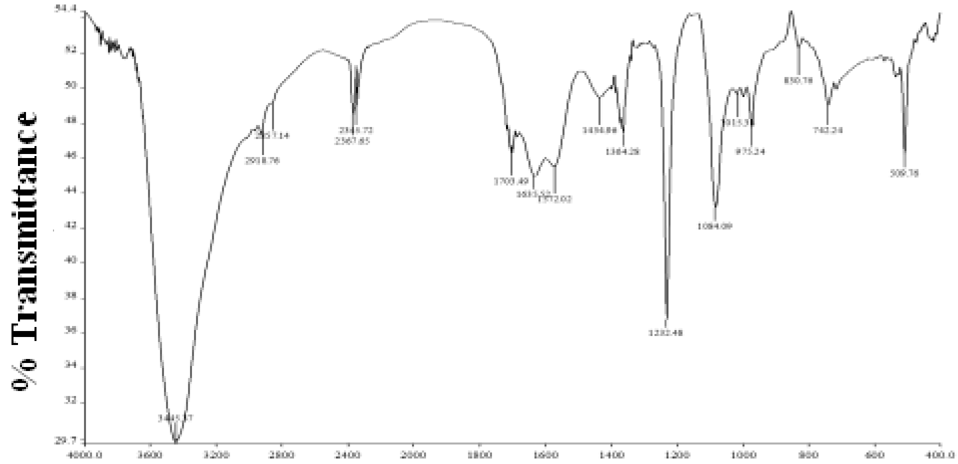
Infrared Spectra: The infrared spectra of Co(II), Ni(II), Cu(II) and Zn(II) complexes were recorded using KBr pellets. The infrared spectrum of the nickel(II) complex shows a strong absorption at 3445cm^{-1} due to OH stretching of oxime OH. The absorption at 1637cm^{-1} is attributed to C=N stretching of the imine group involved in coordination. Similar observation is noticed in Cu(II), Zn(II) and Co(II) complexes of H_6L also. Co(II) complex shows absorption at

1635cm^{-1}, Zn(II) complex at 1735cm^{-1} and Cu(II) complex at 1638cm^{-1}, due to C=N stretching. The infrared spectra of Co(II), Ni(II), Cu(II) and Zn(II) complexes of H_6L are shown in figures 6, 7, 8 and 9 respectively. The infrared spectral data of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of H_6L are shown in table 1.



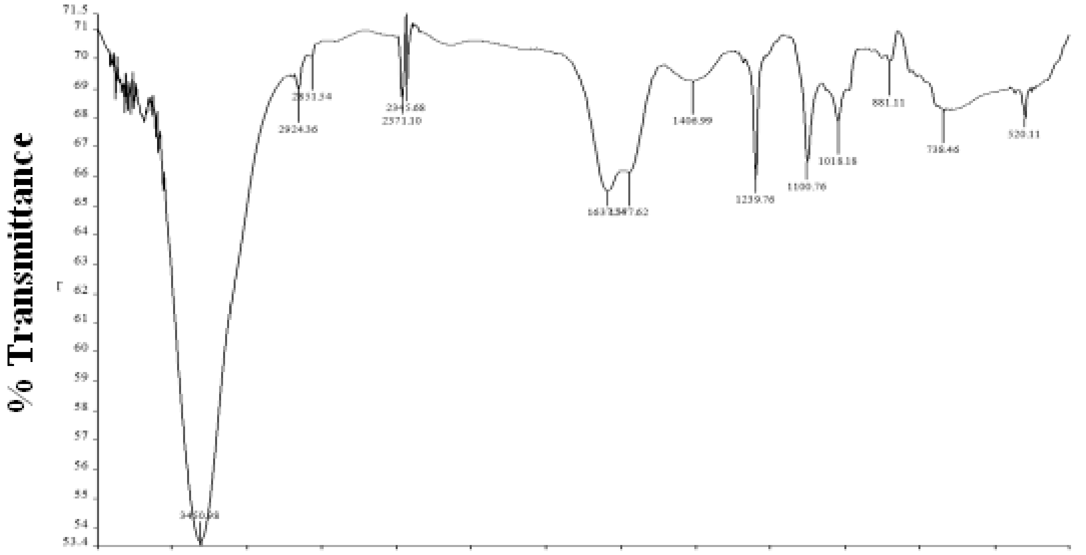
Wavelength (nm)

Figure 5: Electronic absorption spectrum of H_6L.



Wavenumber (cm^{-1})

Figure 6: Infrared Spectrum of $[Co_3(H_3L)(H_2O)_3]Cl_3$



Wavenumber (cm^{-1})

Figure 7: Infrared Spectrum of $[Ni_3(H_3L)](NO)_3$

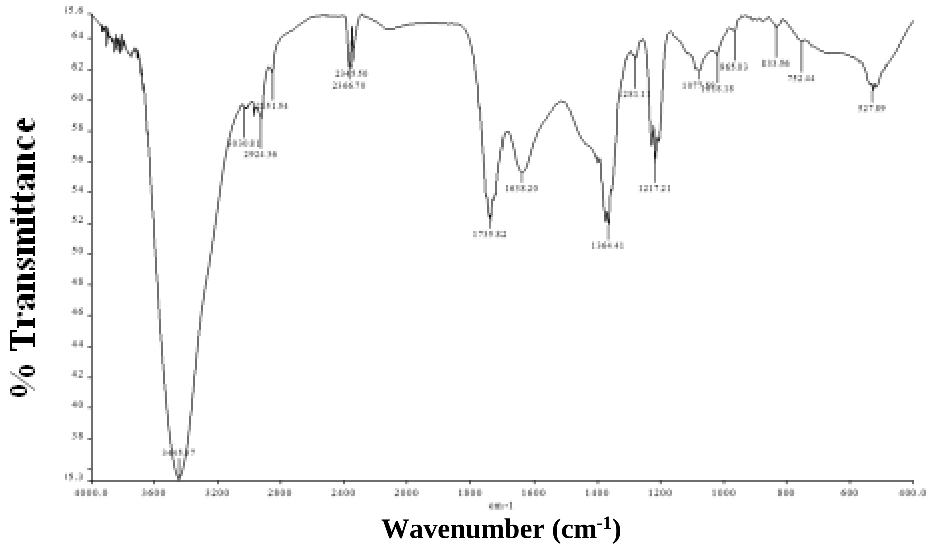


Figure 8: Infrared Spectrum of $[Cu_3(H_3L)]Cl_3$

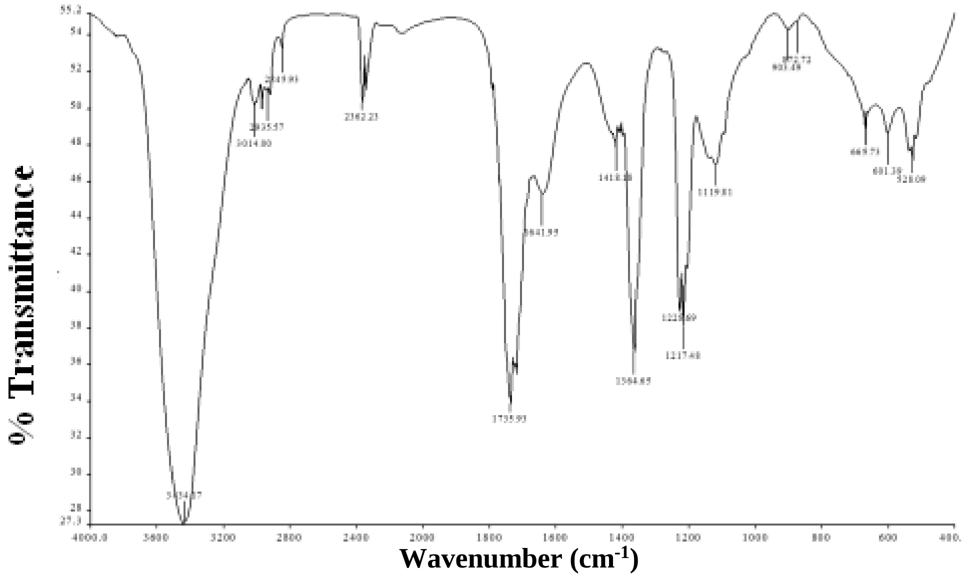


Figure 9: Infrared Spectrum of $[Zn_3(H_3L)](NO_3)$

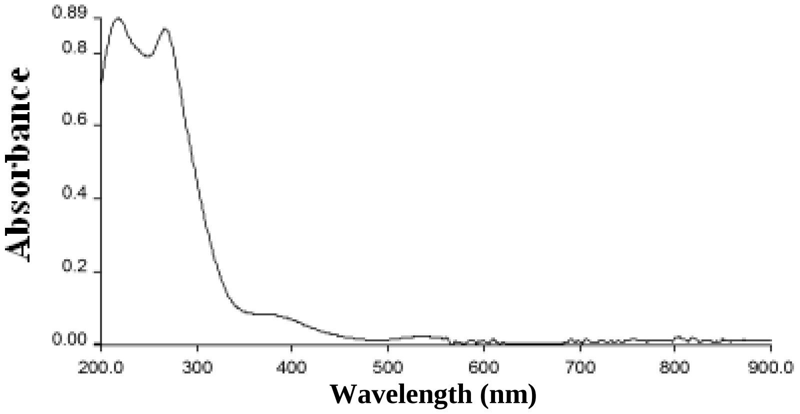


Figure 10: Electronic absorption spectrum of $[Cu_3(H_3L)]Cl_3$

Electronic Absorption spectra: The electronic absorption spectra of the Cu(II) and Co(II) complexes of H_6L were recorded using 10^{-4} M solutions in acetonitrile and Ni(II) complex were recorded using 10^{-4} M solution in $CHCl_3$. The electronic spectrum of Co complex shows 4 absorptions at 252, 275, 585 and 680 nm. The absorption maximum at 252 nm is due to $\pi \rightarrow \pi^*$ transition and at 275 nm due to $n \rightarrow \pi^*$ transition. The absorption maximum at 585 nm is due to charge transfer transitions. The absorption at 680nm is due to $d \rightarrow d$ transitions. The spectral data are shown in table 2.

The electronic absorption spectrum of the Co(II) complex is shown in figure 10. The electronic absorption spectrum of the nickel complex shows six absorptions at 275, 362, 425, 494, 545 and 624 nm. The absorption maximum at 275 may be due to π → π* transition and at 362 nm due to n → π* transition. The absorption at 425 nm is due to charge transfer transition of ligand to metal ion. The d → d transition is observed at 494, 545 and 624 nm. The electronic absorption spectrum of the Ni(II) complex is shown in figure 11.

The electronic absorption spectrum of Cu(II) complex of H_6L shows peaks at 215, 267, 388 and 538 nm. The absorption maximum at 215nm is due to π → π* transition of the ligand and at 267 nm due to n → π* transition. The absorption at 388 nm is due to charge transfer transition of ligand to metal ion. The d → d transition is observed at 538 nm. The electronic absorption spectrum of the Cu(II) complex is shown in figure 12.

Table 2
Electronic Absorption Spectral data and Molar conductance data of Co(II), Ni(II) and Cu(II) complexes.

Compound	Assignment					
	π → π*	n → π*	CT	d → d	Λo Ω^{-1} cm^2 mol^{-1}	Electrolytic Nature
H_6L	220	-	-	-	55	Neutral
$[Ni_3(H_3L)](NO_3)_3$	210	362	425	494,545,624	184	1:3
$[Cu_3(H_3L)]Cl_3$	215	267	388	538	194	1:3
$[Co_3(H_3L)(H_2O)_3]Cl_3$	275	252	585	680	225	1:3

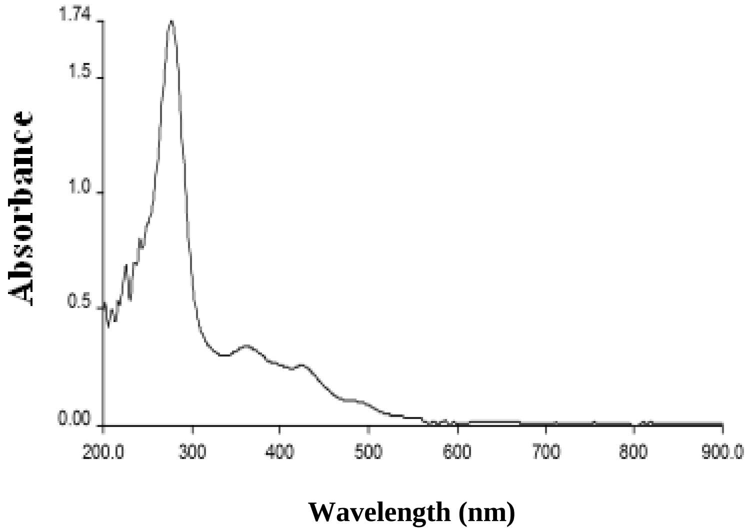


Figure 11: Electronic absorption spectrum of $[Ni_3(H_3L)](NO_3)_3$

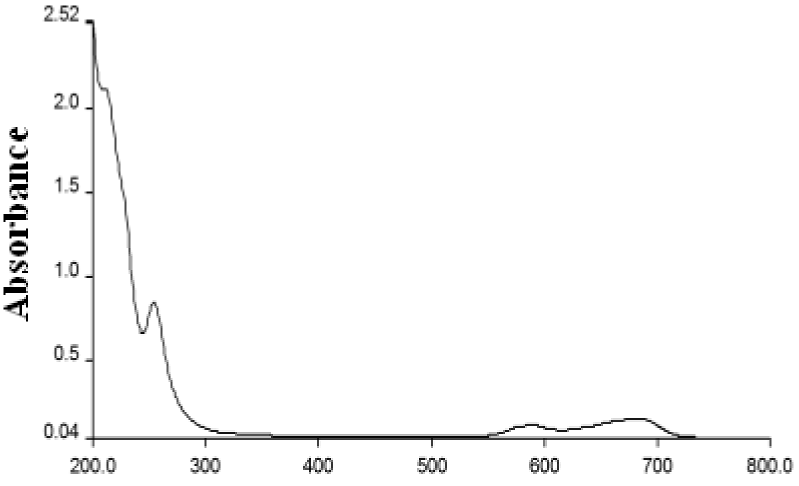


Figure 12: Electronic absorption Spectrum of $[Co_3(H_3L)(H_2O)_3]Cl_3$

Molar Conductivity Measurements: The molar conductances of the Co(II) and Cu(II) complexes were measured using 10^{-4} M in acetonitrile and for Ni(II) measured using 10^{-4} M in chloroform. The molar conductance of Co(II), Ni(II) and Cu(II) complexes are measured as 225, 184 and 194 ohm^{-1} cm^2 mol^{-1} which suggest that they correspond to 1:3 electrolyte. Hence the molecular composition of the Ni(II) complex is assigned to $[Ni_3(H_3L)]\ (NO_3)_3$. Similarly molecular composition for Cu(II) complex is $[Cu_3(H_3L)]Cl_3$ and that of Co(II) complex is $[Co_3(H_3L)(H_2O)_3]\ Cl_3$. The ligand is capable of undergoing deprotonation so that during complexation it loses one oxime proton and forms pseudo macroacyclic complexes.

Conclusion

The dioxime functionlized zero generation dendrimer 1,3,5-tris{methyl(4,7,10-triaza-3,11-dimethyltrideca-3,10-diene-2,12-dione dioxime)}is synthesized. It forms stable complexes with transition metal ions. The structure of the ligand is confirmed by IR, UV, NMR and mass spectroscopic techniques. The ligand and the complexes are stable at room temperature both in the solid state and in solution. The complexes are soluble only in DMSO and acetonitrile.

Suitable modifications like incorporating water soluble groups can make these ligands very good metal ion scavengers in effluent-treatment, water-softening and as complexing agents in quantitative metal ion estimations. Further studies can be done in their redox behaviour, fluorescent properties and antimicrobial properties which is a welcoming step in the field of dendrimer chemistry and its applications.

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