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Synthesis, Characterization, Metal ion intake and Antibacterial Activity of Cardanol based Polymeric Schiff base Transition Metal Complexes using Ethylenediamine

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ABSTRACT

Cardanol, a naturally occurring C_{15} unsaturated aliphatic chain substituted phenol derived from cashew nut shell liquid (CNSL) was used for the preparation of polymeric Schiff base ligand using ethylenediamine. This preparation involved (a) the conversion of cardanol into bis(3-pentadecenylphenol) methane (BPPM) using formaldehyde. (b) bis(3-pentadecenylphenol) methane into di-α-formylmethoxy bis(3-pentadecenylphenyl)methane (DFMPM) on treatment with epichlorohydrin followed by the action of sodium periodate. (c) DFMPM to (2+2) macrocyclic Schiff base ligand with ethylene diamine and finally (d) Schiff base complexes with transition metal salts. The ligand and complexes were characterized by IR, UV-visible, ^{1}H NMR and elemental analysis, melting point, conductivity, metal ion intake and the antibacterial activity were studied. The conductance measurements indicate that all the complexes of non-electrolytes. The infrared spectra indicate the coordination of imino nitrogen and M-N bonds. UV-visible spectra provide structural details of these complexes. ^{1}H NMR data is also consistent with IR spectral data. The results indicate that the complexes of Cu(II), Ni(II) and Co(II) are hexacoordinated and have moderate antibacterial activity. The metal ion intake indicates the ligand can be used for the extraction of these metals from water.

Keywords: Cardanol, Formaldehyde, Epichlorohydrin, Ethylenediamine, Schiff base.

INTRODUCTION

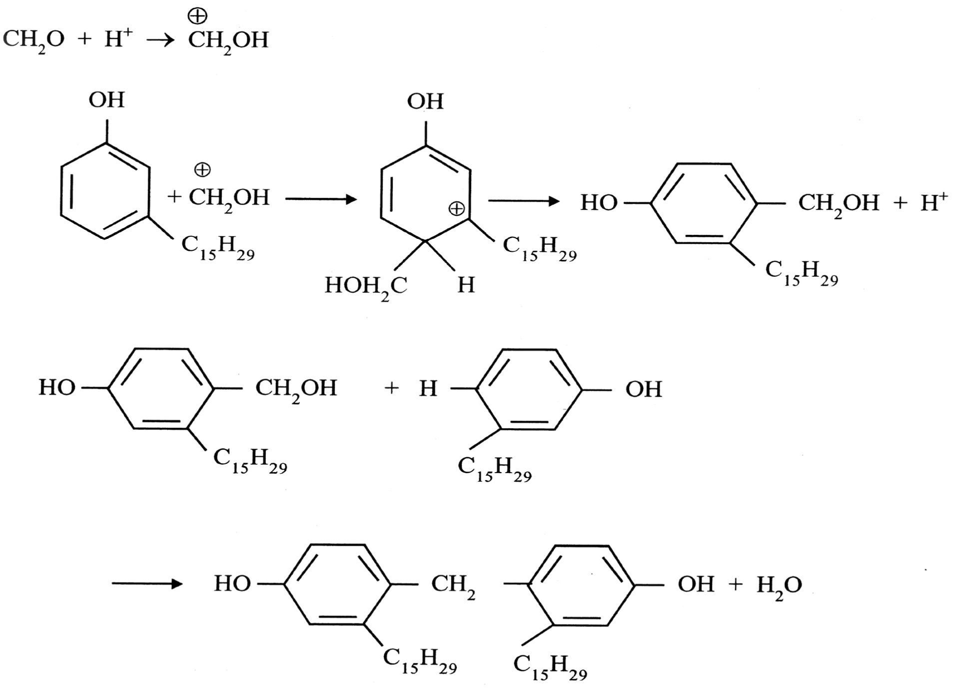
Cardanol, a distillate of cashew nut shell liquid (CNSL) differs in its reactivity with formaldehyde and is used for the development of substituted phenolic resins and various other valuable industrial products [1-4]. Bis(3-pentadecenylphenol) methane (BPPM) was prepared by the reaction between cardanol and formaldehyde in equimolar ratio in the presence of 3 % hydrochloric acid solution at 90-95 ^{0}C for 2hours. The phenolic group of BPPM was converted to diglycidylether with epichlorohydrin, which on treatment with sodium periodate, di-α-formylmethoxy bis(3-pentadecenylphenyl) methane (DFMPM) was obtained. DFMPM undergoes condensation reaction with ethylenediamine a (2+2) macro cyclic Schiff base ligand was obtained. Schiff base ligand formed Schiff base metal complexes with transition metal salts at their natural pH. The formation of Schiff base intermediate in reactions of biological importance is well documented. The present investigation involves the synthesis and characterization of Schiff base complexes of Cu(II), Ni(II) and Co(II) with the (2 + 2) macrocyclic Schiff base ligand. The result indicates all the complexes of Cu(II), Ni(II) and Co(II) are hexacoordinated having moderate and antibacterial activity. The ligand and complexes were characterized by IR, UV-visible, ^{1}H NMR and elemental analysis, melting point, conductivity; metal ion intake and antibacterial activity were studied.

EXPERIMENTAL SECTION

Materials and physical measurements

Cardanol was obtained from M/S. Satya Cashew, Chennai India, formaldehyde (37 % solution), hydrochloric acid, epichlorohydrin, ethylenediamine, sodiumhydroxide and other chemicals used were of GR/AR grade quality obtained from Merck chemicals. All the solvent used were purified by standard methods.

The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument. The metal ion intakes were estimated by standard methods [5]. IR spectra were obtained using PE IR spectrum instrument Model: System 2000. ^{1}H NMR spectrum was obtained using AMX-300MHz, FT NMR spectrometer.



Scheme 1 Synthesis of BPPM.

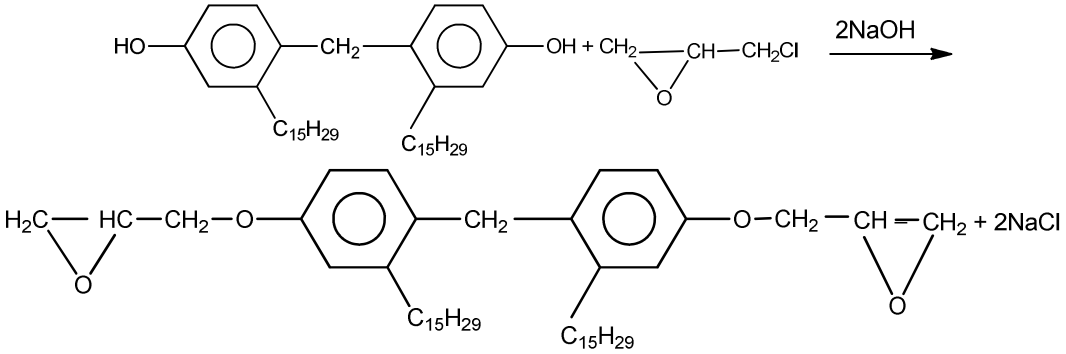
Preparation of bis (3-pentadecenylphenol)methane(BPPM)

BPPM was prepared by heating cardanol and formaldehyde in the molar ratio 2:1 in a three necked R.B. flask fitted with a Leibig's condenser and mechanical stirrer. Formaldehyde (37 %) solution was added to the cardanol through a dropping funnel along with hydrochloric acid. The heating was continued for two hours in between 90 ^{0}C to 95 ^{0}C [6-8]. The reaction product was cooled and purified by washing with 1:1:1 mixture of benzene, methanol and water and dried under vacuum (Scheme 1). Molecular formula = $C_{43}H_{68}O_2$. Molecular weight ≃ 614. Yield = 43 %.

Characteristic absorption were found around 3300 cm^{-1} (hydroxyl group, broad band), 3000 cm^{-1} (aromatic C-H$_{Str.}$ weak) 1500 cm^{-1} (phenyl ring) and 1475 cm^{-1} (–CH$_2$–bending). The two strong bands around 1230 cm^{-1} and 1010 cm^{-1} are characteristic of C–O stretching in phenol and alcohol groups respectively [9] (Fig. 1a).

Synthesis of diglycidylether of bis(3-pentadecenylphenol)methane (DEBPPM)

DEBPPM was synthesized by taking 1:2:2 molar ratio of BPPM, epichlorohydrin and sodium hydroxide in a three necked R.B Flask fitted with Leibig's condenser [10-12]. The reaction mixture was stirred continuously for 2 hours at a temperature of 75^0 C sodium hydroxide was added in drop by drop through a dropping funnel. Heating was stopped as the reaction mixture turned viscous. The excess epichlorohydrin was removed by vacuum distillation. The remaining mixture was extracted with 2-butanone and water in the ratio 1:1, the precipitated sodium chloride removed by filtration and dried under vacuum (Scheme 2). Molecular formula = $C_{49}H_{76}O_4$. Molecular weight ≃ 728. Yield = 48 %.

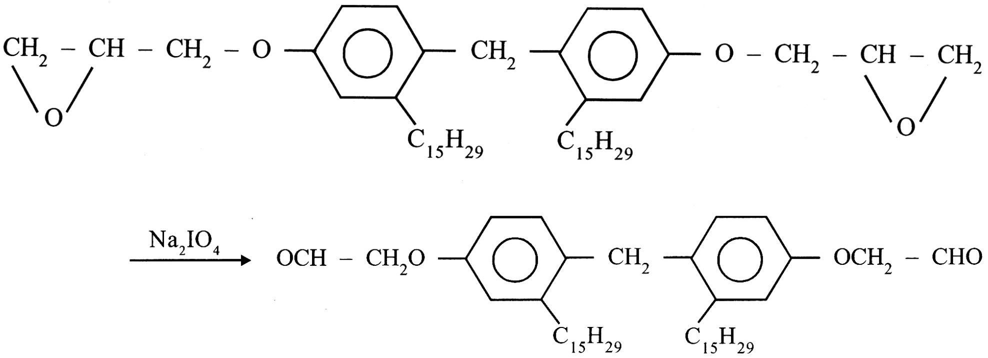


Scheme 2 Synthesis of DEBPPM.

The FT IR spectrum of DEBPPM is given in Fig.1b. The C–H stretching in epoxides is at 2929 cm^{-1}. Symmetrical stretching is observed at 1236 cm^{-1} is characteristic of the epoxy ring. Further bands at 915 cm^{-1}, 840 cm^{-1} and 760 cm^{-1} are also typical bands of epoxides.

Synthesis of di –α-formylmethoxy bis(3-pentadecenylphenyl)methane (DFMPM).

DFMPM was prepared by the action of DEBPPM and sodium periodate in the ratio 1:2 [13-15]. Sodiumperoidate is dissolved in water and taken in a Erlenmeyer flask. To this solution was added rapidly with stirring solutions DEBPPM in dioxane. The homogenous mixture was agitated below 50 ^{0}C for two hours and then was poured into water. The resulting mixture was extracted with petroleum ether, dried over sodium sulphate, filtered and evaporated on the steam bath and dried under vacuum (Scheme 3). Molecular formula = $C_{47}H_{72}O_4$. Molecular weight ≃ 700.
Yield = 46%.



Scheme 3 Synthesis of dialdehyde

The FT IR spectrum of the dialdehyde is given in Fig. 1c. The absorption at 1706 cm^{-1} is the characteristics of the aldehyde group. The strong band at 1067 cm^{-1} and 1595 cm^{-1} are due to ether linkage and non conjugated C = C bond respectively.

Synthesis of Schiff base ligand with ethylenediamine.

The Schiff base ligand was prepared by the reported methods [16-18]. Equimolar ethnolic solutions of DFMPM and ethylenediamine were mixed and refluxed for about an hour. Pour the reaction product in ice, (2+2) macro cyclic Schiff base ligand was obtained. The precipitated yellow compound was filtered, washed with water and dried over anhydrous calcium chloride. The crude sample was recrystalised from 50% absolute alcohol. Yield = 60%.

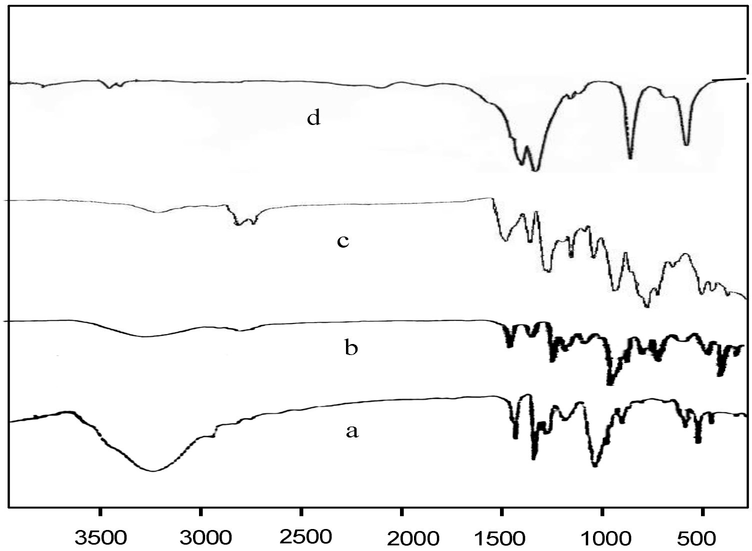


Fig.1 FTIR spectrum of (a) BPPM (b) DEBPPM (c) DFMPM (d) ligand

Preparation of Schiff base metal complexes

The metal complexes were prepared by adding ethanolic solution of Cu(II) nitrate, Ni(II) nitrate and Co(II) nitrate to the ligand in 1:1 molar ratio and refluxed for about twelve hours at 80 ^{0}C [19]. The resulting product was collected by filtration, washed with ethanol, diethylether and hot water, and finally dried under vacuum at 90 ^{0}C. Yield = 55-59%.

Estimation of metal ion intake

The filtrates obtained in the above methods were collected. The collections were used for the estimation of the transition metal ions used for complexation by using standard methods [5].

RESULTS AND DISCUSSION

All the metal complexes are coloured solids, stable towards air and have high melting points (above 250 ^{0}C). The complexes are insoluble in water and common organic solvents but are soluble in DMF, $CDCl_3$ and DMSO. Analytical data suggest that the metal to ligand ratio in all the complexes to be 1:1 (Table 1). Conductivities of solutions of the complexes in DMF are also shown in Table 1. All the complexes are non-electrolytes because their conductivity values were in the range 14-17 ohm^{-1} cm^{2} mol^{-1}. The low conductivity value indicated that the nitrate groups are present in the coordination sphere.

Table 1. Physical characteristics and analytical data of the complexes

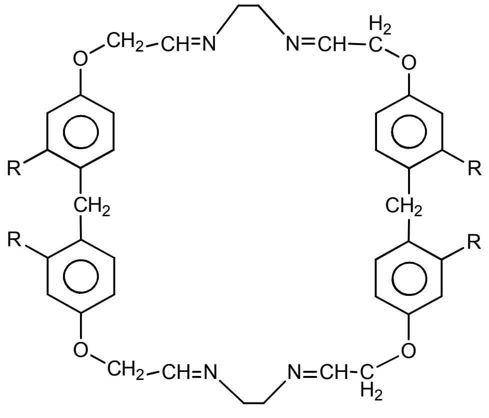
Compound	Yield %	Colour	Mol. formula	Mol. weight	Melting point ^{o}C	Elemental analysis, found (calcd) %			Molar conductance Ohm^{-1} cm^{2} mol^{-1}	Metal ion intake meq/g
						C	H	N		
Ligand (L) ($C_{94}H_{156}N_4O_4$)	60	Brown	$C_{94}H_{156}N_4O_4$	1404	217	80.12 (80.34)	10.99 (11.11)	4.01 (3.98)	–	–
[Cu L$(NO_3)_2$]	57	Light green	$C_{94}H_{156}N_6O_{10}$ Cu	1591	> 250	70.00 (70.89)	9.91 (9.80)	4.00 (3.95)	17	0.6820
[Co L$(NO_3)_2$]	59	Brown	$C_{94}H_{156}N_6O_{10}$ Co	1586.93	> 250	70.90 (71.08)	9.72 (9.82)	5.26 (5.29)	16	0.5507
[Ni L$(NO_3)_2$]	55	Brown	$C_{94}H_{156}N_6O_{10}$ Ni	1586.69	> 250	70.99 (71.04)	9.78 (9.83)	5.30 (5.29)	14	0.4892

IR Spectra

Selected IR spectral bands for the ligand and its complexes are given in Table 2. The IR spectrum of the free ligand is characterized mainly by the strong bands at 2851.2 cm^{-1}, 2919.8 cm^{-1} and 1642 cm^{-1} which are attributed the stretching frequencies of O–C, C–H and C = N (azomethine) respectively [17] (Fig. 1d). Hence the probable structure of the ligand is given in Fig. 2. The IR Spectrum of the free ligand was compared with the spectra of metal complexes. The characteristic absorption bands 3200-3435.1 cm^{-1} range were attributed to –OH group of the coordinated water or lattice water [20]. The absorption bands in the range 2852 – 2854.5 cm^{-1}, 2926-2928.4 cm^{-1} and 1600–1631.6 cm^{-1} were assigned to O–C, C–H and C = N respectively [21-22]. The imine peak in the metal complexes showed change in shifts compared to the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination. Another absorption bands at 991.41 cm^{-1} – 1050.9 cm^{-1} is assigned to the coordinated nitrate group with the central metal atom and 491 cm^{-1} – 781.3 cm^{-1} is assigned to M-N bond and 459 cm^{-1} is assigned to M-O bond [23-24] Fig. 3 and 4.

Table 2. Selected FT IR frequencies (cm^{-1}) and UV-visible spectral data (nm) of the ligand and complexes

Ligand/ Complex	$\nu_{O-H\,(H2O)}$	ν_{O-C}	ν_{C-H}	$\nu_{C=N}$	ν_{M-N}	ν_{M-O}	$\lambda_{max\,(nm)}$		
$C_{94}H_{156}N_4O_4$(L)	-	2851.2	2919.8	1642	-	-	276	360	385
[Cu L $(NO_3)_2$]	3400	2852	2926	1600	491	459	760	615	380
[Co L $(NO_3)_2$]	3435.1	2853.2	2928.4	1631.6	781.3	-	780	621	512
[Ni L $(NO_3)_2$]	3419.7	2854.5	2926.4	1611	695.2	-	772	590	402



R = –C_{15} H_{29}

Fig. 2 Structure of ligand

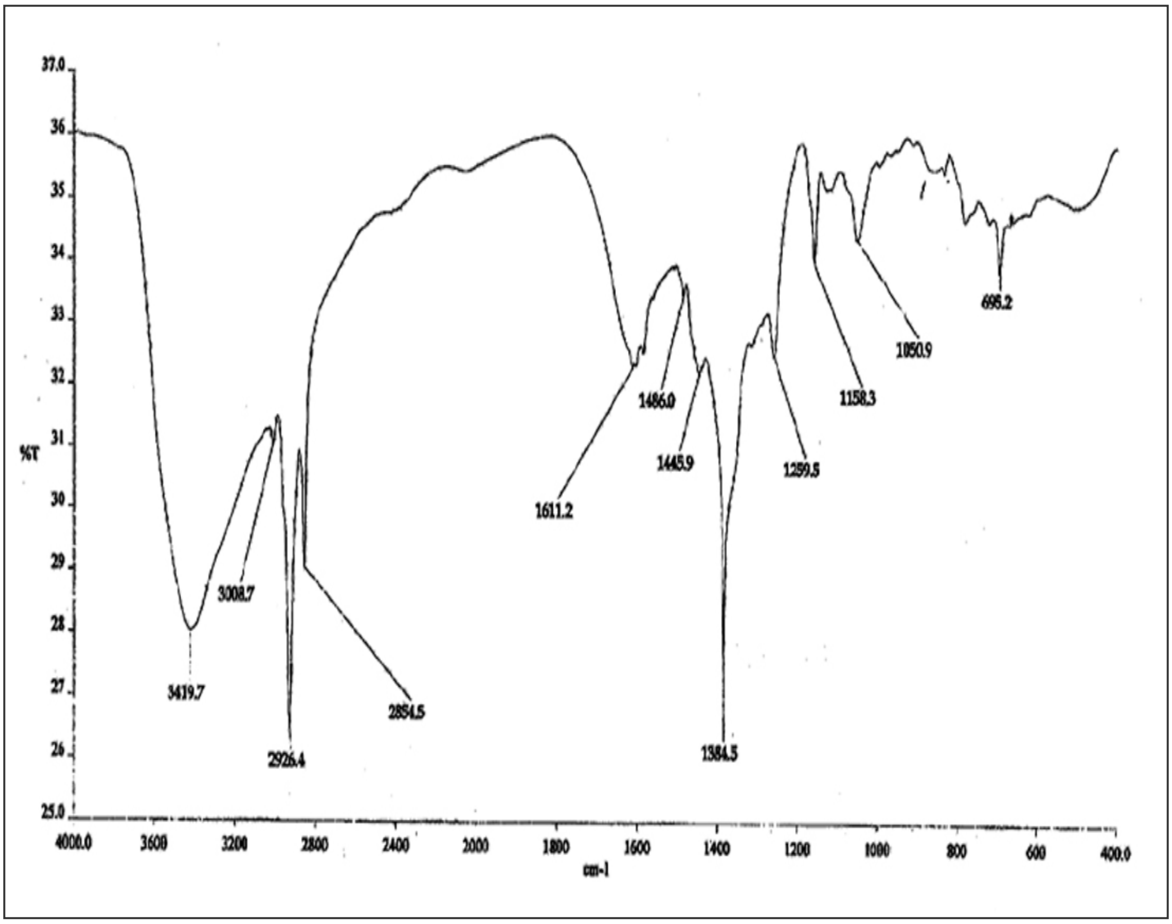


Fig. 3 FTIR spectrum of Ni(II) complex

^{1}H NMR Spectra

The NMR spectrum of Schiff base ligand exhibit a multiplet signal at δ 7.142 – 7.66 ppm is due to substituted aromatic ring protons. The singlet at δ 8.8 ppm is due to the proton of H – C = N–. A signal at δ 1.3938 ppm, δ 2.35 ppm and δ 3.78 ppm were due to $–CH_2$ – protons. The multiple at δ 6.17 – 6.7 ppm and δ 3.36 – 3.78 ppm were due to the olifinic protons of the side chain and – $O–CH_2$ – group of the ligand respectively [25].

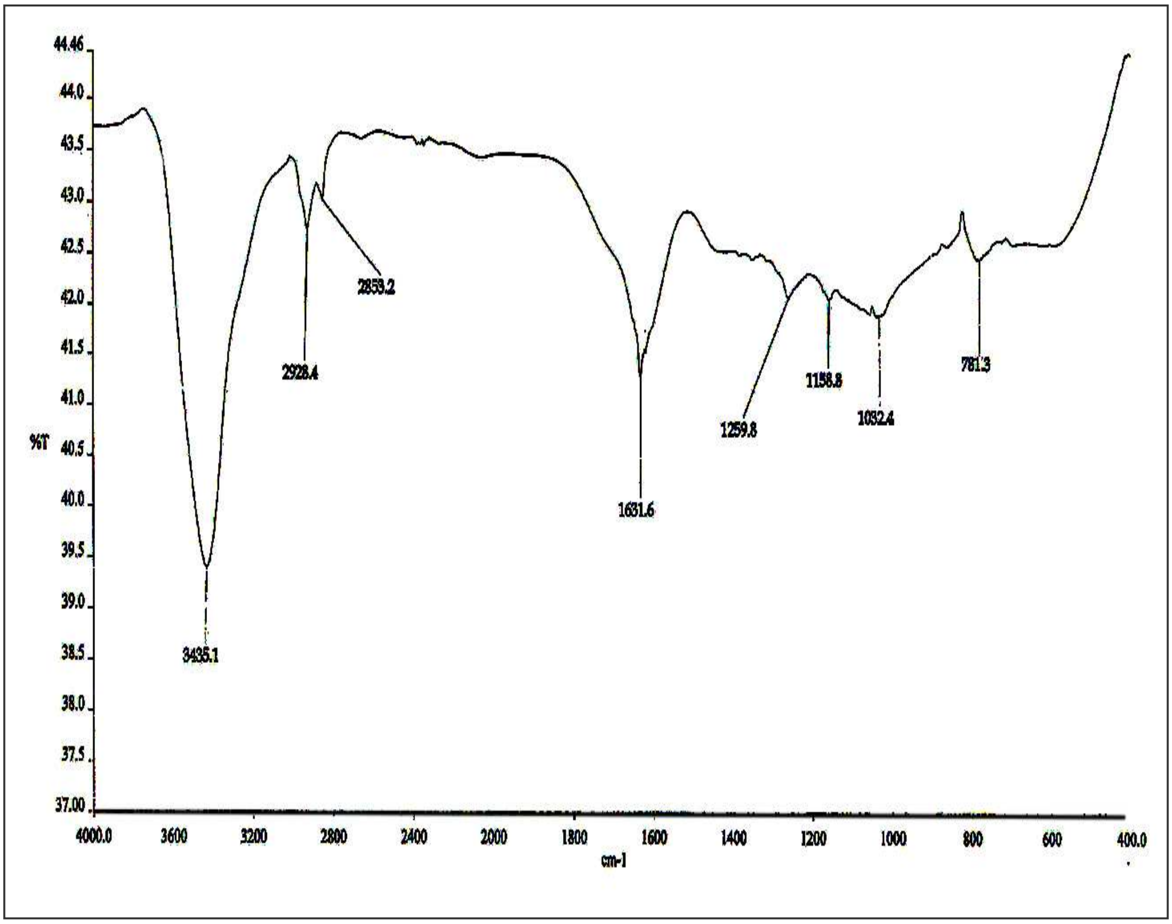
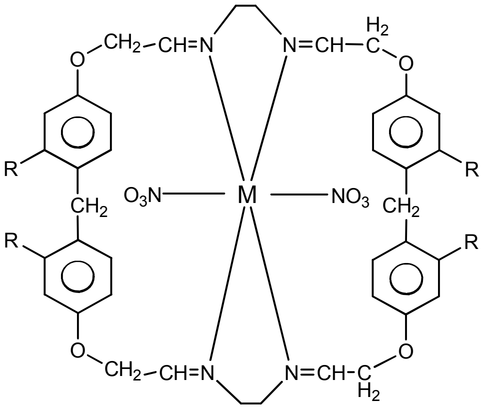


Fig. 4 FTIR spectrum of Co(II) complex



R = $C_{15}H_{29}$

Fig. 5 Structure of Schiff base complexes, M = Cu(II) Ni(II) and Co(II)

UV – Visible Spectra

The UV – visible spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The ligand showed a broad band at 360 nm which is assigned to π- π* transition of the C = N chromophore [26]. On complexation this bond was shifted to lower wave length suggesting the coordination of imine nitrogen with central metal ion. The UV absorption of the Cu(II) complex showed three absorption bands at 760 nm, 615 nm and 380 nm arising octahedral field transitions $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_{2g}$ respectively. This indicates octahedral geometry for the Cu(II) complex. The UV spectra of Co(II) complex and Ni(II) complex were also showed absorption bands at 780 nm, 621 nm and 512 nm and 772 nm, 590 nm and 402 nm respectively indicating octahedral geometry. On the basis of above studies the probable structure of the M(II) Schiff base complexes of Cu(II), Ni(II) and Co(II) may be presented as in (Fig. 5).

Metal ion intake

The complexation behaviour of cardanol based Schiff base was affected by structural parameters [27]. This study indicated that the metal ion intake decreased from $Cu^{II} > Co^{II} > Ni^{II}$ at their natural pH (Table 1). This order can be explained by Pearson's proposal [28-30], hard acids prefer to combine with hard base and soft acids prefer to combine with soft base. It was found that the interaction of Cu^{II} is normally more intense than any other divalent metal ions with Schiff base ligands [31]. Nature of the ligand and the chelate effect were the factors involved in complexation. Hence the ligand have been used as metal ion acceptor in the environmental chemistry and technological interest [31]. It can be also used for the removal of Cu(II), Ni(II) and Co (II) ions from waters.

Antibacterial activity

Antibacterial activities of the ligand, complexes and standard drugs were screened by agar cup method in DMF solvent at a concentration of 1mg/mL and were checked against gram positive bacteria *B. subtilis* and *S.aureus* also are is and gram negative bacteria *E.coli* and *S.typhi* using ampicillin and tetracycline as standards. The results of antibacterial study are given in Table 3. In the typical procedure a well was made on the agar medium, inoculated with micro organisms. The well was filled with the test solution using a micropipette and the plate was incubated at room temperature for two days. During this period the test solution was diffused and growth of micro organisms was affected. The antibacterial activity was estimated based on the size of inhibition zone in the cups [32-35]. Under identical conditions the Table 3 shows that the Schiff base complex copper had moderate antibacterial activities against these bacteria.

Table 3. Antibacterial activity data of ligand and complexes

Ligand/ Complex	*B. subtilis*	*S. aerus*	*E-coli*	*S.typhi*
$C_{94}H_{156}N_4O_4$(L)	++	++	++	++
[Cu L $(NO_3)_2$]	+++	+++	+++	+++
[Co L $(NO_3)_2$]	++	++	++	++
[Ni L $(NO_3)_2$]	++	++	++	++

1-5 mm (++) = less active, 6-10 mm (+++) = moderately active

CONCLUSION

Schiff base transition metal complexes Cu(II), Ni(II) and Co(II) were synthesised from cardanol using ethylenediamine were clearly described and characterized on the basis of analytical and spectral data. Metal ion take explained that the ligand can be effectively used for extraction of metal ion from waters. Antibacterial study showed that the copper complexes have effective antibacterial activity.

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