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Synthesis and Characterization of Complexes of Transition Metal Ions with New Pentaazamacrocyclic Ligands

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New multidentate ligands 1,4,7,9,12-pentaaza-10,11-dioxo-8,9,12,13-bis-(1′,3′-dioxo-6,6-diethyl-2′-hydropyrimidine)-trideca-7,13-diene, (L^1) and 1,4,7,9,13-pentaaza-10,12-dioxo-8,9,13,14-bis-(1′,3′-dioxo-6,6-diethyl-2′-hydropyrimidine)-tetradeca-7,14-diene (L^2) have been prepared by the reaction of 5,5-diethylbarbituric acid, diethylenetriamine, diethyl oxalate and 5,5-diethylbarbituric acid, diethylenetriamine, diethyl malonate. Their coordination properties with the first row of transition metal ions have been explored. The macrocyclic complexes were characterized by elemental analysis, IR, ^{1}H NMR, UV-visible spectroscopy, magnetic moment measurements and molar conductance measurements. The electronic spectra and magnetic moment measurements are discussed with respect to assignment of square planar and tetrahedral structure except chromium(III), iron(III) ions. The chromium(III) and iron(III) complexes are considered to be octahedral. Molar conductance measurements suggest that the complexes of divalent metal ions are 1:1 electrolytes, while the trivalent metal ions are nonelectrolytes. The compounds have been tested against gram-positive bacteria *Staphylococcus aureus* and gram-negative bacteria *Escherichia coli.* The results show that all the compounds inhibit the growth of bacteria.

Key words: multidentate ligands, Cr(III) complexes, Fe(III) complexes, antibacterial activity

The synthesis and study of macrocycles have undergone tremendous growth in recent years [1–3] and their complexation chemistry with a wide variety of metal ions have been studied thoroughly. Macrocyclic ligands and their metal complexes are considered to be model of metalloporphyrins and metallocorrins, due to their intrinsic structural properties [4]. The metal ions and the ring play important roles on different counts, which direct the steric course of the reaction preferentially towards cyclic rather than oligomeric or polymeric products [5]. In 18-, 20-membered macrocycles, containing different transition metal ions, the metal center exhibits a hexacoordinate environment and the macrocyclic adopts a twisted helical topology [6]. Some new copper(II) complexes have been synthesized and characterized on the basis of analytical data, electronic and magnetic studies and their antifungal activities have been checked against phytopathogenic fungi [7]. Binuclear and trinuclear macrocyclic copper(II) complexes mimic the structure and properties of enzymes as ascorbate oxidase leccase and ceruplasmin [8]. Macrocycles have wide applications

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in medicine, cancer diagnosis and in treatment of tumors [9], while the pyrimidines have also been reported to be biologically active and are used as antimicrobial, antimalarial and anti-inflammantory agents [10].

In some closely related work, we have investigated the chemistry and complexation properties of pyrimidine based macrocycles [exo O_2]. In this study, we have prepared and characterized new 13- and 14-membered macrocycles, derived from 5,5-diethylbarbituric acid, diethylenetriamine, diethyl oxalate (L^1) and 5,5-diethylbarbituric acid, diethylenetriamine, diethyl malonate (L^2) and their complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have also been synthesized.

EXPERIMENTAL

5,5-Diethylbarbituric acid (Kotch light), diethylenetriamine, diethyl oxalate, diethyl malonate (BDH), transition metal(II) and metal(III) chlorides (s.d. fine-chem.) were used as received. Elemental analyses (CHN) were carried out with a Carlo Erba 1106 Thomas and Coleman analyzer. The metals were determined by complexometric titration [11] and chlorine and sulphur were determined gravimetrically [12]. IR spectra (4000–200 cm^{-1}) were recorded on a model 621 Perkin-Elmer spectrometer. The conductivity measurements were carried out on a CM-82T Elico conductivity bridge in DMSO. The UV-visible spectra were recorded on a Lambda EZ201 Perkin-Elmer spectrometer in DMSO, magnetic moment measurements were done with an Allied Research model 155 vibration sample magnetometer at room temperature. The ^1H NMR spectrum of macrocyclic ligands and their complexes were run in DMSO-d_6 on a JOEL-FX-100 spectrometer.

Synthesis of ligand 1,4,7,9,12-pentaaza-10,11-dioxo-8,9,12,13-bis-(1′,3′-dioxo-6,6-diethyl-2′-hydropyrimidine)-trideca-7,13-diene, (L^1): In a three necked round bottom flask, 5,5-diethyl barbituric acid (40 mmol, 7.4 g) was dissolved in ethanol (150 mL) by refluxing with strong stirring. In this solution diethyl oxalate (20 mmol, 2.7 mL) and diethylenetriamine (20 mmol, 2.2 ml) was added slowly and dropwise up to 2 h. The mixture was again refluxed with continuous stirring for 3 h and cooled at room temperature, then kept in refrigerator for 7 days. A light orange precipitate was filtered, washed with hexane and dry ether and dried *in vacuo*. Yield (64%).

Synthesis of ligand 1,4,7,9,13-pentaaza-10,12-dioxo-8,9,13,14-bis-(1′,3′-dioxo-6,6-diethyl-2′-hydropyrimidine)-tetradeca-7,14-diene, (L^2): 5,5-Diethyl barbituric acid (40 mmol, 7.4 g) was dissolved in refluxing ethanol (150 mL) taking in a three necked flask and were magnetically stirred with simultaneous addition of diethyl malonate (20 mmole, 3.0 mL) and diethylenetriamine (20 mmol, 2.2 mL) in 2:1:1 ratio and stirred for additional 4 h. It was kept in refrigerator for four days. Light orange product was collected by filtration, washed with hexane, acetone and dry ether and dried *in vacuo*. Yield (58%).

Synthesis of complexes of ligand (L^1): Nickel(II) chloride (10 mmol, 2.4 g) in 20 mL ethanol was mixed with ethanolic and conc. hydrochloric acid solution (40 mL and 1 mL) of L^1 (10 mmol, 4.9 g). The mixture was refluxed with stirring for 6 h. The dark orange precipitate that formed, was filtered, washed with acetone and dry ether and dried *in vacuo*. Yield (50%). The complexes of Mn(II), Co(II), Cu(II), Zn(II) were prepared by the similar procedure. The precipitates thus obtained were filtered, washed with acetone and dry ether and dried *in vacuo*. Yields (52–62%). The L^1 (10 mmol, 4.9 g) was dissolved in ethanol and conc. HCl (40 mL and 1 mL) solution, ferric(III) chloride (10 mmol, 1.6 g) in ethanol (25 mL) was added, the mixture was stirred for 8 h. The grey compound was filtered, washed with acetone and dry ether and dried *in vacuo*. Yield (56%).

$[CrL^1Cl_3]$ complex was synthesized by taking the ligand L^1 (10 mmol, 4.9 g) in ethanol and conc. HCl (50 mL and 1 mL) and Cr(III) chloride (10 mmol, 2.7 g) in ethanol (25 mL) in 250 mL round bottom flask. The mixture was stirred up to 7 h. The peacock blue precipitate that collected was filtered, washed with hexane and ether and dried *in vacuo*. Yield (60%).

Synthesis of the complexes of ligand (L^2): A solution of nickel(II) chloride (10 mmol, 2.4 g) in ethanol (25 mL) was added into the 250 mL round bottom flask containing an ethanolic and conc. hydrochloric acid solution (40 mL and 2 mL) of L^2 (10 mmol, 5.0 g). The resulting mixture was refluxed with stirring up to 10 h. The light red product that collected was filtered, washed with hexane and dry ether and dried *in vacuo*. Yield (55%). For the synthesis of $[MnL^2Cl]Cl$ $[CoL^2Cl]Cl$ and $[ZnL^2Cl]Cl$ complexes similar procedure was applied. The precipitates were filtered, washed with hexane and dry ether and dried *in vacuo*. Yields (49–61%).

The copper(II) complex was synthesized by the dissolution of Cu(II) chloride (10 mmol, 1.7 g) in ethanol (25 mL) which was added dropwise to the solution of L^2 (10 mmol, 5.0 g) in ethanol and conc. hydrochloric acid (50 mL and 2 mL) and the resulting solution was refluxed with stirring up to 7 h. The light green product thus obtained was filtered, washed with acetone and dry ether and dried *in vacuo*. Yield (48%).

Iron (III) complex was prepared by refluxing with stirring of L^2 (10 mmol, 5.0 g) in ethanol and conc. HCl (40 mL and 2 mL) with ferric(III) chloride (10 mmol, 1.6 g). The mixture was refluxed with stirring up to 12 h. The yellow product was filtered, washed with dry ether and dried *in vacuo*. Yield, (64%).

Chromium(III) complex was prepared by the same method. The bluish green precipitate was filtered, washed with acetone and dry ether and dried *in vacuo*. Yield (57%).

Inhibitory activity of microorganisms: The preliminary screening on the antibacterial activity of the macrocyclic ligands L^1 and L^2 and their complexes in DMSO was performed *in vitro* by agar diffusion method [13]. The ligands and their complexes were prepared by dissolving 0.5 mg and 1.0 mg of each compound in 1 mL DMSO. The bacteria were grown in nutrient broth at 37°C for 48 h. Whatman No. 4 filter paper discs (6 mm diameter) were impregnated with stock solution of the compound (0.5–1.0 mg/mL) and dried under sterile condition. The plates of bacteria were incubated at 37°C for 24 h. At the end of incubation period, the inhibition around the walls were measured in mm. DMSO was used as control and gentamicin were also screened under similar condition for comparison as a reference standard. Antimicrobial activity was indicated by presence of inhibition zone around the discs.

RESULTS AND DISCUSSION

The new macrocycles L^1 and L^2 were synthesized by condensation reaction of 5,5-diethyl barbituric acid, diethylenetriamine, diethyl oxalate and 5,5-diethyl barbituric acid, diethylenetriamine, diethyl malonate in ethanol (2:1:1 molar ratio).

The reactions are represented as:

$$2C_8H_{12}N_2O_2 + NH(CH_2CH_2NH_2)_2 + (C_2H_5CO_2)_2 \xrightarrow{\text{EtOH, Stir, Reflux}} \underset{L^1}{C_{22}H_{31}N_7O_6}$$

$$2C_8H_{12}N_2O_2 + NH(CH_2CH_2NH_2)_2 + (C_2H_5CO_2)_2CH_2 \xrightarrow{\text{EtOH, Stir, Reflux}} \underset{L^2}{C_{23}H_{33}N_7O_6}$$

$$L^1 + MCl_2 \xrightarrow{\text{HCl, Reflux}} [ML^1Cl]Cl;\ L^1 + M'Cl_3 \xrightarrow{\text{HCl, Reflux}} [M'L^1Cl_3];$$

$$L^2 + MCl_2 \xrightarrow{\text{HCl, Reflux}} [ML^2Cl]Cl;\ L^2 + M'Cl_3 \xrightarrow{\text{HCl, Reflux}} [M'L^2Cl_3]:$$

where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), M′ = Cr(III), Fe(III).

The melting points, colour and molar conductance of the two ligands and their complexes are given in Table 1. Elemental analysis correspond to the composition $[ML^1Cl]Cl$, $[ML^2Cl]Cl$, where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and $[M'L^1Cl_3]$

[M′L^{2}Cl$_3$], where M′ = Cr(III), Fe(III). All the complexes are soluble in DMSO and CH_3CN. The molar conductance of 10^{-3} M solution of the complexes in DMSO (57–70 Ω^{-1}cm^{2}mole^{-1}) suggest that 1:1 electrolytic [14] for divalent metal complexes, while for chromium(II) and iron(III) complexes the values fall in (18–27 Ω^{-1}cm^{2}mole^{-1}) range revealing the nonelectrolytic behavior for trivalent metal complexes.

Table 1. Colour, m.p., yield, percentage and molar conductances of ligands and their complexes.

Compounds	Colour	M.p. (°C)	Yield (%)	Λ_M (Ω^{-1} cm^2 mole^{-1})
$C_{22}H_{31}N_7O_6$, (L^1)	Light orange	158	60	–
[CrL^{1}Cl$_3$] [$C_{22}H_{31}N_7O_6CrCl_3$]	Peacock blue	310 d	64	22
[MnL^{1}Cl]Cl [$C_{22}H_{31}N_7O_6MnCl$]Cl	Light brown	295 d	60	70
[FeL^{1}Cl$_3$] [$C_{22}H_{31}N_7O_6FeCl_3$]	Grey	330 d	56	18
[CoL^{1}Cl]Cl [$C_{22}H_{31}N_7O_6CoCl$]Cl	Blue	315 d	58	58
[NiL^{1}Cl]Cl [$C_{22}H_{31}N_7O_6NiCl$]Cl	Dark orange	270 d	50	63
[CuL^{1}Cl]Cl [$C_{22}H_{31}N_7O_6CuCl$]Cl	Light green	290 d	52	69
[ZnL^{1}Cl]Cl [$C_{22}H_{31}N_7O_6ZnCl$]Cl	White	345 d	62	57
$C_{23}H_{33}N_7O_6$, (L^2)	Light orange	178	58	–
[CrL^{2}Cl$_3$] [$C_{23}H_{33}N_7O_6CrCl_3$]	Bluish green	300 d	57	20
[MnL^{2}Cl]Cl [$C_{23}H_{33}N_7O_6MnCl$]Cl	Light brown	263 d	61	58
[FeL^{2}Cl$_3$] [$C_{23}H_{33}N_7O_6FeCl_3$]	Yellow	325 d	64	27
[CoL^{2}Cl]Cl [$C_{23}H_{33}N_7O_6CoCl$]Cl	Brown	294 d	58	60
[NiL^{2}Cl]Cl [$C_{23}H_{33}N_7O_6NiCl$]Cl	Light red	262 d	55	66
[CuL^{2}Cl]Cl [$C_{23}H_{33}N_7O_6CuCl$]Cl	Light green	254 d	48	62
[ZnL^{2}Cl]Cl [$C_{23}H_{33}N_7O_6ZnCl$]Cl	White	331 d	49	68

IR spectra: The IR spectral bands and their assignments are depicted in Table 2. The interaction of 5,5-diethyl barbituric acid, diethylenetriamine and diethyl oxalate gives the ligand (L^1), while the ligand (L^2) was formed by the reaction of 5,5-diethyl barbituric acid, diethylenetriamine and diethyl malonate. In the ligands L^1 and L^2 one weak N–H band of 5,5-diethyl barbituric acid (3190 cm^{-1}) disappears, while the other

Table 2. IR spectra of the ligands and their complexes (cm^{-1}).

Compounds	ν(N-H)	ν(N-H) (secondary amine)	ν(C=O)	ν(C=O) (oxalate or malonate group)	ν(C=N)	ν(C-N) & δ(N-H)	Ring stretching mode	ν(M-N)	ν(M-Cl)
Ligand L^1	3190 m	3230 m	1630 m	1620 m	1648 m	1440	1322, 1404, 1455 – –	–	–
[CrL^1Cl_3]	3186 m	3210 m	1630 m	1616 m	1628 m	1434	1330, 1405, 1460 1464, 1534,	490 s	295 m
[MnL^1Cl]Cl	3192 m	3200 m	1624 m	1618 m	1618 m	1438	1322, 1400, 1454 1560, 1550	395 s	300 m
[FeL^1Cl_3]	3196 m	3185 m	1632 m	1622 m	1608 m	1430	1320, 1402, 1458 1562, 1540	470 s	275 m
[CoL^1Cl]Cl	3182 m	3195 m	1628 m	1616 m	1615 m	1432	1318, 1402, 1462 1560, 1535	390 s	330 m
[NiL^1Cl]Cl	3192 m	3205 m	1634 m	1610 m	1620 m	1438	1320, 1400, 1456 1568, 1546	445 s	315 m
[CuL^1Cl]Cl	3188 m	3200 m	1630 m	1608 m	1610 m	1428	1322, 1404, 1462 1566, 1538	405 s	310 m
[ZnL^1Cl]Cl	3180 m	3189 m	1636 m	1612 m	1603 m	1432	1316, 1406,1464 1575, 1542	440 s	305 m
Ligand L^2	3190 m	3230 m	1630 m	1624 m	1632 m	1440	1324, 1408, 1460 – –	–	–
[CrL^2Cl_3]	3196 m	3200 m	1622 m	1620 m	1607 m	1446	1322, 1405, 1456 1460, 1540,	490 s	280 m
[MnL^2Cl]Cl	3188 m	3185 m	1634 m	1618 m	1612 m	1434	1324, 1405, 1462 1555, 1538	380 s	295 m
[FeL^2Cl_3]	3180 m	3195 m	1626 m	1616 m	1600 m	1432	1326, 1402, 1455 1568, 1540	485 s	230 m
[CoL^2Cl]Cl	3192 m	3205 m	1638 m	1622 m	1590 m	1435	1312, 1410, 1458 1558, 1540	385 s	310 m
[NiL^2Cl]Cl	3190 m	3210 m	1632 m	1626 m	1597 m	1436	1315, 1415, 1460 1562, 1540	440 s	305 m
[CuL^2Cl]Cl	3184 m	3198 m	1628 m	1617 m	1592 m	1444	1318, 1404, 1452 1562, 1540	415 s	306 m
[ZnL^2Cl]Cl	3182 m	3192 m	1626 m	1628 m	1604 m	1441	1317, 1400,1458 1560, 1538	485s	385 m

band persists at the same wave number region. The free ligands L^1 and L^2 exhibit the ν(N–H) of secondary amine vibration at 3230 cm^{-1}, ν(C=O) bands at 1630 cm^{-1}, at 1620 cm^{-1} (oxalate group) and at 1624 cm^{-1} (malonate group). The strong band at 1648 cm^{-1} for L^1 and 1632 cm^{-1} for L^2 ligands is assignable to ν(C=N) vibration [15–16]. The absorption bands occurring at 1440 cm^{-1} indicate the coupling band of ν(C–N) and δ(N–H) vibration. The ν(C=N) vibration as a strong band is observed in 1590–1628 cm^{-1} region in all the complexes indicating the bathochromic shift relative to the free ligands. The lowering of ν(C=N) and ν(N–H) (20–45 cm^{-1}) in all the complexes suggests the involvement of these groups in coordination of metal ion *via* nitrogen atom.

The far infrared spectra of the complexes show absorption bands in 390–490 cm^{-1} range, which may be assigned to ν(M–N) stretches. ν(M–Cl) vibration can be distinguished from ν(M–N) vibration as it appears in the low frequency far infrared region and are quite useful to determine the stereochemistry of the coordination compounds. In all the complexes with ligands L^1 and L^2 the ν(M–Cl) vibration has been found to be in 275–330 cm^{-1} wave number regions.

Electronic spectra and magnetic moments: The observed electronic spectral bands of macrocyclic complexes have been recorded in DMSO and the magnetic moment values are given in Table 3.

Table 3. Electronic spectral bands, magnetic moments and ligand field parameters of the macrocyclic complexes.

Compounds	Magnetic moment (B.M.)	Electronic bands (cm^{-1})	Possible assignment	10 Dq (cm^{-1})	(B) (cm^{-1})	β
$[CrL^1Cl_3]$	3.28	31760	$^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$	14157	1089	1.05
		25640	$^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$			
		19600	$^4T_{2g}(P) \leftarrow {}^4A_{2g}(F)$			
$[MnL^1Cl]Cl$	5.68	22990	$^4A_1(G) \leftarrow {}^6A_1$	–	–	–
		20200	$^4A_1(G) \leftarrow {}^6A_1$			
$[FeL^1Cl_3]$	5.80	28570	$^4E_g(D) \leftarrow {}^6A_{1g}$	9898	707	0.642
		27027	$^4T_{2g}(D) \leftarrow {}^6A_{1g}$			
		19230	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$			
$[CoL^1Cl]Cl$	3.55	25640	Charge Transfer	–	–	–
		10930	$^4T_1(F) \leftarrow {}^4A_2(F)$			
$[NiL^1Cl]Cl$	Diamagnetic	22430	$^1B_{1g} \leftarrow {}^1A_{1g}$	–	–	–
		21505	$^1A_{2g} \leftarrow {}^1A_{1g}$			
$[CuL^1Cl]Cl$	1.84	14710	$^2A_{1g} \leftarrow {}^2B_{1g}$	–	–	–
		13690	$^2E_g \leftarrow {}^2B_{1g}$			
$[ZnL^1Cl]Cl$	Diamagnetic	–	–	–	–	–

Table 3 (continuation)

[CrL^{2}Cl$_3$]	3.35	31440	$^4T_{1g}(P) \leftarrow {}^4A_{2g}$ (F)	13526	1017	0.987
		25450	$^4T_{1g}$ (F) $\leftarrow {}^4A_{2g}$ (F)			
		19120	$^4T_{2g}$ (P) $\leftarrow {}^4A_{2g}$ (F)			
[MnL^{2}Cl]Cl	5.45	22570	$^4A_1$ (G) $\leftarrow {}^6A_1$	–	–	–
		20490	$^4A_1$ (G) $\leftarrow {}^6A_1$			
[FeL^{2}Cl$_3$]	5.86	28250	^4E_g (D) $\leftarrow {}^6A_{1g}$	9561	664	0.603
		26810	$^4T_{2g}$ (D) $\leftarrow {}^6A_{1g}$			
		18590	$^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$			
[CoL^{2}Cl]Cl	3.61	24510	Charge Transfer	–	–	–
		11050	$^4T_1$ (F) $\leftarrow {}^4A_2$ (F)			
[NiL^{2}Cl]Cl	Diamagnetic	21190	$^1B_{1g} \leftarrow {}^1A_{1g}$	–	–	–
		20080	$^1A_{2g} \leftarrow {}^1A_{1g}$			
[CuL^{2}Cl]Cl	1.78	14880	$^2A_{1g} \leftarrow {}^2B_{1g}$	–	–	–
		13680	$^2E_g \leftarrow {}^2B_{1g}$			
[ZnL^{2}Cl]Cl	Diamagnetic	–	–	–	–	–

Three bands are observed in the [CrL^{1}Cl$_3$] and [CrL^{2}Cl$_3$] complexes assigned to $^4T_{1g}(P) \leftarrow {}^4A_{2g}(F)$, $^4T_{1g}(F) \leftarrow {}^4A_{2g}(F)$ and $^4T_{2g}(P) \leftarrow {}^4A_{2g}(F)$ transitions, respectively. The magnetic moment values are 3. 28–3.35 B.M., which are well within the range for three unpaired electrons. These studies suggest an octahedral geometry around the chromium(III) ion.

Most of Mn(II) complexes are high-spin, which have d^5 configuration and have (spin) only magnetic moment of 5.8 B.M. This value is slightly lower than that calculated for five unpaired electrons. In these cases two bands have been observed at 22990 cm^{-1}, 20200 cm^{-1} for L^1 and 22570 cm^{-1}, 20490 cm^{-1} for L^2, which may be assigned to $^4A_1(G) \leftarrow {}^6A_1$ and $^4A_1(G) \leftarrow {}^6A_1$ transitions, respectively. These values reveal tetrahedral geometry around Mn(II) ion.

In the high-spin octahedrally coordinated iron(III) complexes the three bands (Table 3) have been assigned to ^4E_g (D) $\leftarrow {}^6A_{1g}$, $^4T_{2g}$ (D) $\leftarrow {}^6A_{1g}$ and $^4T_{1g}$ (G) $\leftarrow {}^6A_{1g}$ transitions, respectively. Since this is the only sextet level present, all the d-d transitions must be spin forbidden. The μ_{eff} value is slightly different than the calculated value. The observed magnetic moment values (5.80 B.M. for L^1 and 5.86 B.M. for L^2) suggest an octahedral [17–18] geometry around iron(III).

Electronic absorption spectra of the cobalt(II) complexes with L^1 and L^2 show two d-d transition bands at 25640 cm^{-1}, 10930 cm^{-1} and 24510 cm^{-1}, 11050 cm^{-1}, respectively. The former is due to the charge transfer while the latter is assigned to $^4T_1$ (F) $\leftarrow {}^4A_2$ (F) transition. The μ_{eff} values have been observed in the [CoL^{1}Cl]Cl and [CoL^{2}Cl]Cl complexes in 3.55–3.61 B.M. range, which indicates the tetrahedral [19] geometry around cobalt(II) ion.

The UV-visible spectra of Ni(II) and Cu(II) complexes with ligands L^1 and L^2 show two absorption bands at 22430 cm^{-1}, 21505 cm^{-1}, 21190 cm^{-1}, 20080 cm^{-1} and 14710 cm^{-1}, 13690 cm^{-1}, 14880 cm^{-1}, 13680 cm^{-1}, respectively, which are similar to those of square planar nickel(II) and copper(II) ions. The magnetic moment values are 1.84 B.M. for $[CuL^1Cl]Cl$ and 1.78 B.M. for $[CuL^2Cl]Cl$ complexes, respectively. On the basis of these studies nickel(II) and copper(II) complexes are proposed to have square planar [20–21] geometry.

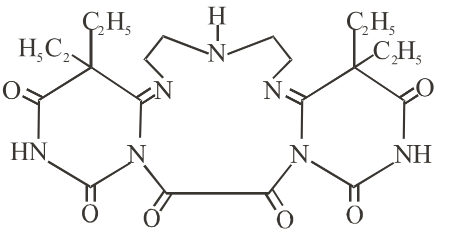
^{1}H NMR spectra: The ^{1}H NMR spectra of ligand L^1 and L^2 and their nickel(II) complexes in DMSO-d_6 exhibit two triplets at δ (2.22–2.70 ppm) and δ (2.87–3.15 ppm) due to two types of -CH_2- protons of secondary amine and two triplets at (1.41–2.29 ppm) for pyrimidine groups (CH_3CH_2-), respectively. The broad band of N–H proton appears at δ (7.2–8.85 ppm) for pyrimidine and for the secondary amine at δ (4.56 ppm). However, in the case of ligand L^2 an additional triplet of -CH_2- appears at δ (3.73 ppm). The above values broadly confirmed the structure of ligands L^1 and L^2. Other characteristic peaks are represented in Table 4.

Table 4. ^{1}H NMR spectra of the ligands and complexes δ (ppm).

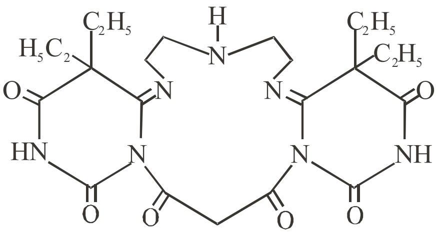
Compounds	N–H (1H)	N–H (2° amine), (1H)	CH_3CH_2- (10H), (10H)	-CH_2- (4H), (4H)	CH_2- (malonate group), (2H)
L^1	7.2–8.85 b	4.56 b	1.41–2.29 t	(2.22–2.70) t, (2.87–3.10) t	–
L^2	7.2–8.80 b	4.56 b	1.42–1.26 t	(2.22–2.68) t, (3.88–3.15) t	3.73 t
$[NiL^1Cl]Cl$	7.2–9.0 b	4.89 b	1.41–1.27 t	(2.26–2.83) t, (3.10–3.15) t	–
$[NiL^2Cl]Cl$	7.2–9.0 b	4.75 b	1.42–1.27 t	(2.26–2.27) t, (2.87–3.10) t	3.76 t

The characteristic peaks for the -CH_2- and N–H groups for secondary amine in Ni(II) complex formation are shifted towards low field (high δ values) due to the decrease in electron density after complex formation. This is attributed to the coordination of metal ion with these groups.

The stability of the complexes of each metal decreases as the cavity size of the macrocycle is increased. In all the complexes with the ligands L^1 and L^2, the metal center exhibits a pentacoordinate environment. Both the ligands have enough flexibility to encapsulate all the metal ions. The 10 Dq value also depends on the ring size. The ligand L^1 has greater 10 Dq value than that of L^2, although it is clear that ligand L^2 is more flexible than ligand L^1. From the above studies, the structures of the ligands L^1 and L^2 have been proposed.



L^1



L^2

Antimicrobial activity: Antibacterial activities of the stock solutions of all the compounds were performed qualitatively using the disc diffusion assay (Table 5).

Table 5. Antibacterial activity of ligands and complexes (Zone formation in mm).

Compounds	*S. aureus*		*E. coli*	
	0.5 mg cm^{-3}	1.0 mg cm^{-3}	0.5 mg cm^{-3}	1.0 mg cm^{-3}
Control	7	8	6	9
Ligand L^1	8	14	10	13
Ligand L^2	12	15	11	13
CrL^1	14	19	12	20
MnL^1	16	23	14	19
FeL^1	18	29	17	22
CoL^1	14	26	12	23
NiL^1	15	22	13	25
CuL^1	13	19	17	29
ZnL^1	17	26	13	25
CrL^2	14	23	15	26
MnL^2	18	27	17	22
FeL^2	15	22	14	23
CoL^2	17	20	11	17
NiL^2	12	18	15	24
CuL^2	11	25	17	27
ZnL^2	14	21	13	21

All the compounds yielded clear inhibition zone around the discs. These showed significant bioactivity against *Staphylococcus aureus* (gram positive bacteria) and *Escherichia coli* (gram negative bacteria). The results revealed that the metal complexes inhibit higher antibacterial activity than that of the free ligands and the control. The increase in concentration of the metal complexes with increase the antibacterial activity is due to the effect of metal ion on the normal cell process.

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