ChemTech

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Design, Spectral Characterization and Biological Evaluation of Unsymmetrical 11-Membered Tetraaza Macrocyclic Complexes containing Thiourea

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Abstract: Unsymmetrical macrocyclic complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} have been synthesized by the template process using bis(benzil)ethylenediamine as precursor. The precursor and the metal complexes were characterized by elemental analysis, magnetic susceptibility, conductance measurement, IR, UV-Vis spectra, ^{1}HNMR, ^{13}C-NMR, EPR and antimicrobial assay. Macrocyclic complexes were prepared by the interaction of Bis(benzil)ethylenediamine with transition metal chlorides and thiourea. Based on analytical, spectral and magnetic moments, an octahedral geometry around the metal ion is suggested for the complexes. The shifts of the ν(C=N) (azomethine) stretches have been monitored in order to find out the donor sites of the ligands. Antimicrobial activities of the ligand and the complexes were screened against one gram positive and four gram negative bacteria. The activity data show that the metal complexes are more potent than the parent ligand.

Key words: Thiourea, Bis(benzil)ethylenediamine, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}.

1. INTRODUCTION:

Macrocyclic chemistry is a growing area of research in inorganic and bioinorganic chemistry in view of its biological significance. The studies of macrocycles have undergone tremendous growth in recent years and their complexation chemistry with a wide variety of metal ions has been extensively studied. Tetraazamacrocycles and their metal complexes have been studied extensively in connection with their resemblance to naturally occurring porphyrins. Macrocyclic compounds have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, catalysis and coordination chemistry (1-5). Transition metal macrocyclic complexes are of great significance on account of their unique coordination and structural properties, their utilities as bio-inorganic models. In this paper, we report the synthesis and characterization of new bivalent transition metal complexes from the reaction of bis(benzil)ethylenediamine

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with thiourea which show the marked effect of any build-up of ligand strain on the coordination geometry of the central metal. The possible biological application of these complexes was determined through antibacterial sensitivity assay.

2. EXPERIMENTAL:

2.1. Materials and methods:

All the chemicals used for the preparation of the ligands were of BDH quality, AR grade. The microelemental analysis was carried out using CHN-Rapid Analyzer. Conductivity was measured on a Toshniwals conductivity bridge using dip type platinised platinum electrode. Molecular weights were determined by the Rast camphor method. The magnetic susceptibilities were measured out by using guoy balance. Proton NMR spectra were recorded on an EM 300-30MHz NMR spectrometer in DMSO. IR spectra (KBr) of the samples were recorded on a shimadzce FTIR-8400s spectro-photometer. The electronic spectra (chloroform) were recorded on the Lamda 35 spectrometer.

2.2. Synthesis of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes of Ligand (L) with thiourea

Methanolic solution (25ml) of 1,2,7,8-Tetraphenyl-3,6-diazahexa-2,6-diene-1,8-dione (L) (2g, 4.3 mmol), thiourea (0.3273g, 4.3mmol) and methanolic solution (25ml) of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal chlorides (4.3mmol) are mixed together in 1:1:1 molar ratio with constant stirring. The mixture was refluxed for 5-7h at 70-90°C. On cooling, coloured complexes of $[Mn(C_{31}H_{24}N_4S)Cl_2]$, $[Co(C_{31}H_{24}N_4S)Cl_2]$, $[Ni(C_{31}H_{24}N_4S)Cl_2]$, $[Cu(C_{31}H_{24}N_4S)Cl_2]$ and $[Zn(C_{31}H_{24}N_4S)Cl_2]$ are isolated as crystals. These complexes are filtered, washed several times with hot water, then with cold methanol, dried in vacuum over anhydrous calcium chloride and recrystallised using methanol + benzene mixture (1/1).

2.3. Antimicrobial assay:

Anti microbial properties of the synthesized metal complexes have been evaluated as per the method described earlier(6). The test organisms were isolated from the clinical samples from patients attending Government Hospital, Kanchipuram. Tamilnadu, India. The organisms were isolated in nutrient agar medium and selectively cultured at 37^{0}C for 24 hrs. The bacterial strains were identified by biochemical and standard antibiogram tests as per the directions from Bergy's manual for determinative bacteriology. Circular disc of 6 mm diameter were made from the whatman no 1 filter paper. Discs were impregnated with equal volume (50 µl) of each metal complexes dissolved in DMSO at a concentration of 100 µg/ml. The discs were aseptically placed over plates of Muller Hinton agar (MHA ,Difco) seeded with each of test pathogens, and the inoculum was adjusted to 0.5 Mc Farland turbidometry. The plates were incubated in an upright position at 37^{0}C for 24 hours and the zone of inhibition was measured (in mm diameter). Inhibition zones with diameter less than 12 mm were considered as having low antibacterial activity. Diameters between 12 and 16 mm were considered moderately active, and these with > 16mm were considered highly active. The clinical strains were also tested for their sensitivity against the standard antibiotics, ciprofloxacin (5 mcg) and nalidixic acid (10 mcg) by the disc diffusion method. The solvent control (only DMSO) was also maintained throughout the experiment.

3. RESULTS AND DISCUSSION:

3.1. Molar conductance measurements

The molar conductance measurements of the complexes, $[Mn(C_{31}H_{24}N_4S)Cl_2]$, $[Co(C_{31}H_{24}N_4S)Cl_2]$, $[Ni(C_{31}H_{24}N_4S)Cl_2]$, $[Cu(C_{31}H_{24}N_4S)Cl_2]$ and $[Zn(C_{31}H_{24}N_4S)Cl_2]$ in acetonitrile are found to be 29.48, 22.63, 21.19, 25.94 and 22.33 mhocm^{2}mol^{-1} respectively. The values are shown in Table **1.2.** These values are less than 50mhocm^{2}mol^{-1} which corresponds to nonelectrolyte nature of these complexes.

Table 1.1. Physical and analytical data of the complexes (21-25)

Complex	Empirical Formula	Colour	Mol. Wt.	M.Pt. (^{o}C)	Yield (%)
[Mn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	C$_{31}$H$_{24}$MnN$_4$SCl$_2$	Light brown	610	105	50
[Co(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	C$_{31}$H$_{24}$CoN$_4$SCl$_2$	Bluish green	614	102	60
[Ni(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	C$_{31}$H$_{24}$NiN$_4$SCl$_2$	Dark blue	614	108	59
[Cu(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	C$_{31}$H$_{24}$CuN$_4$SCl$_2$	Light green	619	110	60
[Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	C$_{31}$H$_{24}$ZnN$_4$SCl$_2$	colourless	621	103	52

The predicted composition of the complexes are found to be [Mn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**21**), [Co(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**22**), [Ni(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**23**),[Cu(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**24**) and[Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**25**) which is in good agreement with the data obtained from molecular weight determination, elemental analysis, magnetic and conductance value.

Table 1.2. Elemental analysis, magnetic moment and molar conductance of the complexes (21-25)

Ligand/Complex	Elemental Analysis % Found (Calculated)				μ_{eff}. BM	Molar Conductance (Ω^{-1}cm^{2}mol^{-1})
	C	H	N	M		
C$_{31}$H$_{24}$MnN$_4$SCl$_2$	60.90 (60.98)	3.87 (3.93)	9.10 (9.18)	8.93 (9.01)	5.88	29.48
C$_{31}$H$_{24}$CoN$_4$SCl$_2$	60.51 (60.58)	3.86 (3.90)	9.08 (9.12)	9.56 (9.59)	4.93	22.63
C$_{31}$H$_{24}$NiN$_4$SCl$_2$	60.50 (60.58)	3.82 (3.90)	9.09 (9.12)	9.49 (9.56)	3.30	21.19
C$_{31}$H$_{24}$CuN$_4$SCl$_2$	60.05 (60.10)	3.82 (3.87)	8.99 (9.05)	10.20 (10.26)	1.93	25.94
C$_{31}$H$_{24}$ZnN$_4$SCl$_2$	59.86 (59.90)	3.82 (3.86)	8.97 (9.02)	10.53 (10.57)	Dia	22.33

3.2. Infrared spectral studies

The infrared spectra of the ligand (Fig. **1.1**) are compared with those of the complexes to determine the bonding mode of the ligand to the metal in the complexes. The infra red spectral data of the ligand and the complexes are shown in Table **1.3**. The ligand showed a strong absorption in 1772cm^{-1} which is assigned to C=O stretching mode of vibration(7). The band disappeared in the spectra of the metal complexes which suggest the involvement of the carbonyl groups in condensation with –NH$_2$ groups of thiourea. The coordination of azomethine nitrogen is confirmed by the presence of bands in the range 1628-1636 cm^{-1} which undergo a shift to a lower frequency after complexation due to the drift of the lone pair density of the azomethine nitrogen towards the central metal atoms(8). The complexes showed weak to medium intensity band in the regions 1113-1119cm^{-1} which is attributed to the >C=S group of amide. This band is not present in the ligand. The sharp band in the regions 1161-1179cm^{-1} are due to the ν(C-N) vibration. The medium intensity absorption band in the regions 3312-3319cm^{-1} is attributed to ν(C-H) vibration. The band characteristic of the benzil moiety appeared in the regions 1412-1423 cm^{-1} which corresponds to ν_{asym} C$_6$H$_5$ and in the regions 1328-1328 cm^{-1} which corresponds to ν_{sym} C$_6$H$_5$. The presence of new bands in the spectra of metal complexes in the regions 456-457 cm^{-1} is due to the ν (M-N) vibration. This supports the coordination of the imines nitrogen to the metal ion. The infrared spectrum of [Co(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] (**22**) is shown in Figure **1.2**. And also, bands observed in the

region 332cm^{-1} which is assigned to γ M-Cl vibrations which substantiate the participation of chloride in coordination (Fig. **1.3**).

Table. 1.3. Characteristic IR bands (cm^{-1}) of the ligand and its complexes (21, 22, 23 & 25)

Ligand/ Complex	ν(C=O)	ν(C=N)	ν (C=S) of amide	ν(C-H)	ν(C-N)	ν$_s$ C$_6$H$_5$	ν$_a$ C$_6$H$_5$	γ M-N
L(C$_{30}$H$_{24}$N$_2$O$_2$)	1772	1667	-	3317	1169	1312	1439	-
[Mn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	-	1636	1119	3317	1179	1328	1412	457
[Co(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	-	1633	1114	3319	1174	1328	1422	457
[Ni(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	-	1628	1113	3312	1161	1329	1423	456
[Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	-	1632	1114	3318	1162	1328	1420	456
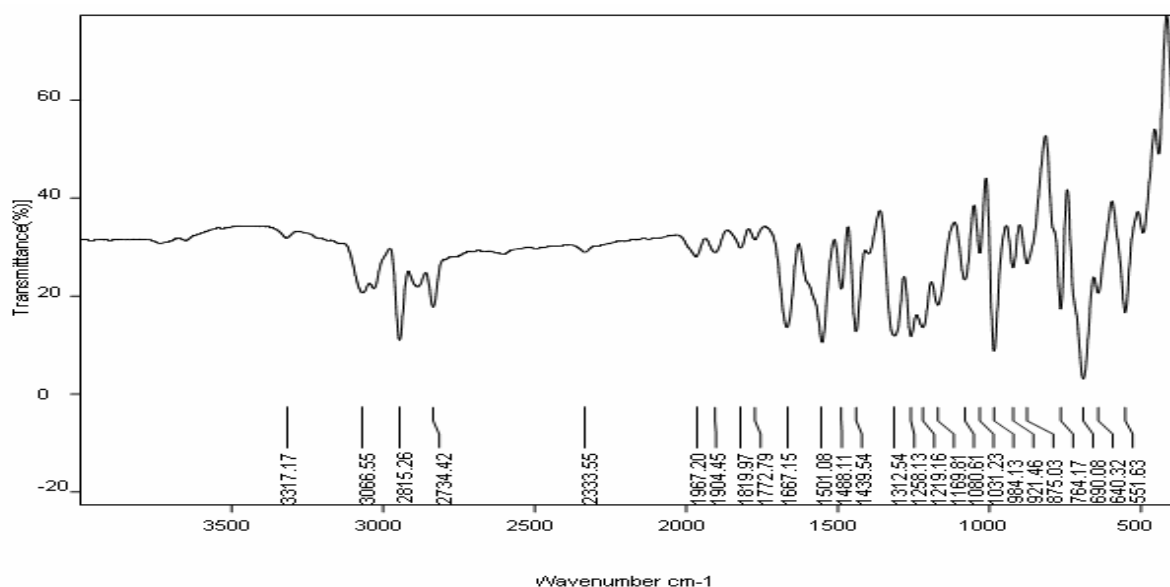
Fig. 1.1. FT-IR spectrum of ligand

FTIR SPECTRUM
Date: 10/1/2011

Spectrum Name: L1+TU+CoCl2
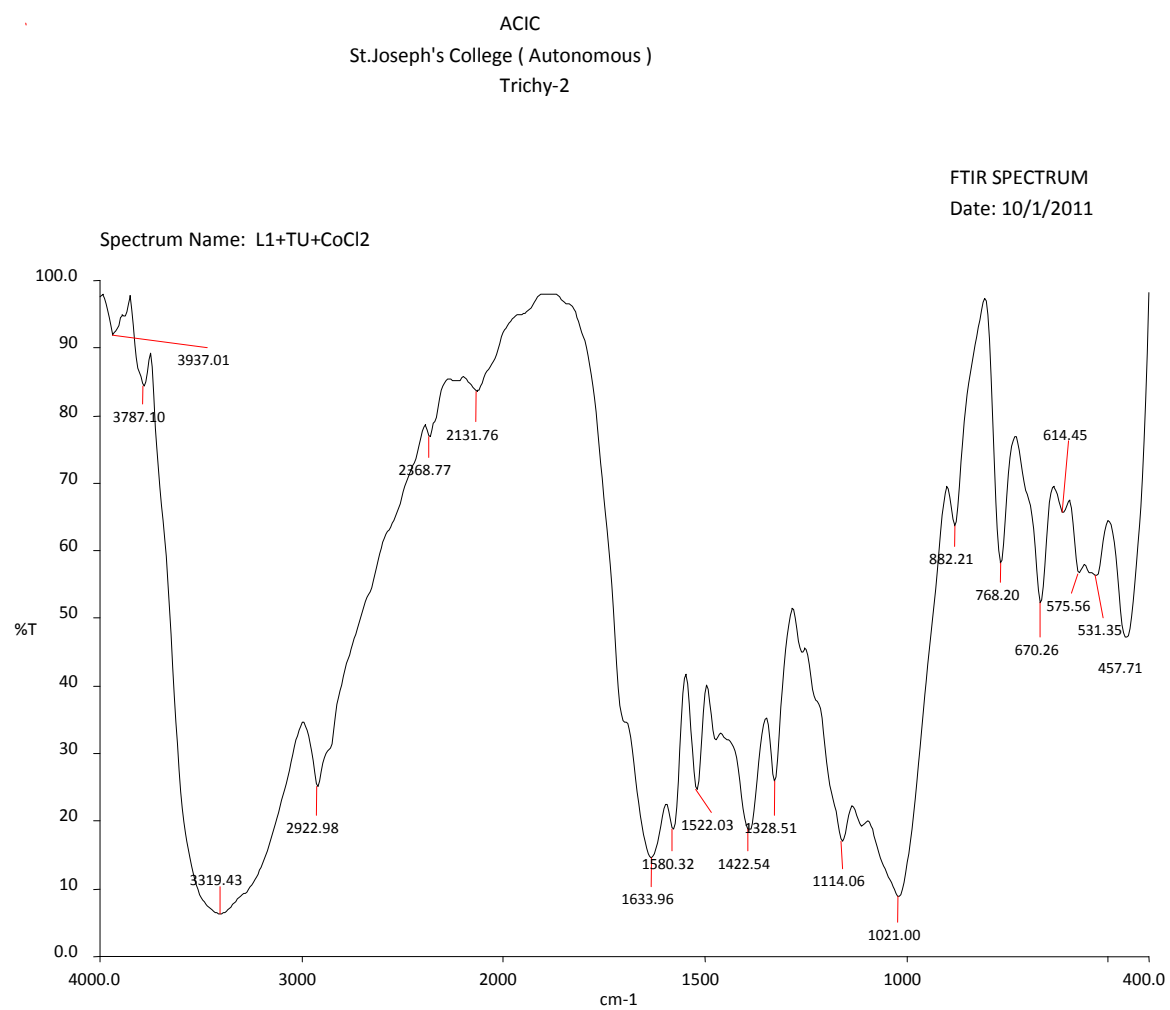
Fig. 1.2. FT-IR spectrum of [Co(C$_{31}$H$_{24}$N$_{4}$S)Cl$_{2}$] complex
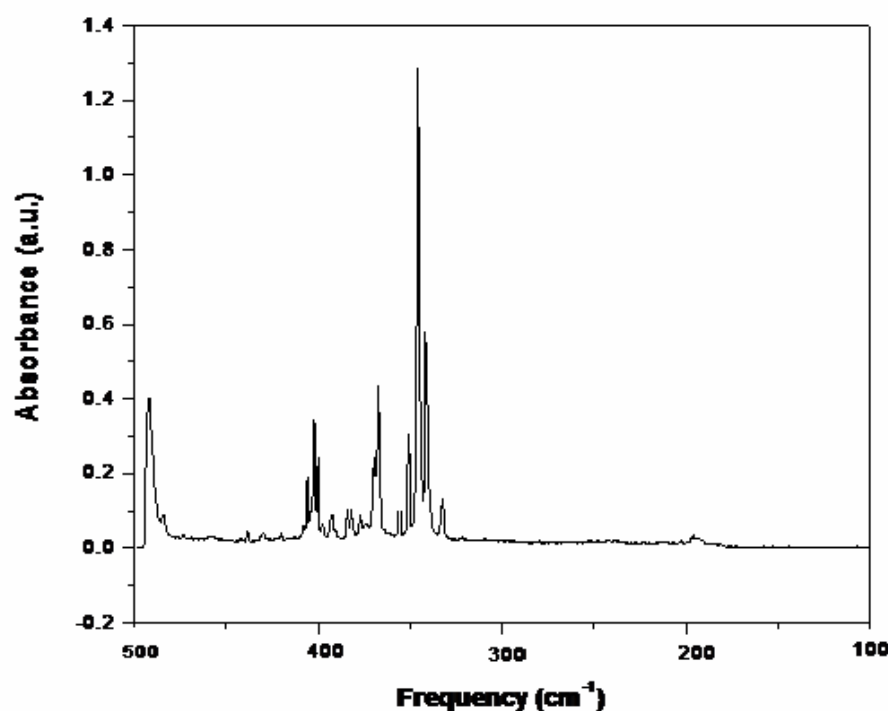
Fig. 1.3. Far-IR spectrum of $[Co(C_{31}H_{24}N_4S)Cl_2]$ complex

3.3. Magnetic moment and Electronic spectral analysis

The magnetic moment values of cobalt(II), nickel(II) and copper(II) complexes are shown in Table **1.2.**

The Co^{II} complex showed a magnetic moment value of 4.93 B.M., while Ni^{II} complex show magnetic moment value of 3.30 B.M. at room temperature. The magnetic moment of Cu^{II} complex is 1.93 B.M. corresponding to one unpaired electron. The values are in tune with a high spin configuration and show the presence of an octahedral environment around the Co^{II} and Ni^{II} ion. The Cu^{II} complex is considered to have distorted octahedral geometry around Cu^{2+} ion and anions occupied the axial positions. The possible geometry of the complexes is assumed from IR, UV-Visible and EPR spectral studies(9-11).

The electronic spectrum of this complex shows two main d-d bands of medium intensity at 681nm ($14684cm^{-1}$) and 559nm ($17889cm^{-1}$) characteristic to an octahedral geometry.

The bands may be assigned to $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) (v_2) and $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) (v_3) transitions respectively.

The electronic spectrum of nickel (II) chloride complex exhibits main d-d band at 398nm ($25126cm^{-1}$) characteristic to an octahedral geometry and thus may be assigned to $^3A_{2g}$(F) $\rightarrow$ $^3T_{1g}$ (P) transition. The value of the magnetic moment (3.30 B.M) also confirms the octahedral environment around the Ni (II) ion.

The observed electronic spectrum of copper(II) chloride complex shows a broad band in the range 14599 cm^{-1} in the visible region is due to $^2E_g \rightarrow$ $^2T_{2g}$ transition, which is in good agreement with a distorted octahedral geometry for copper(II) ion(12) .

3.4. NMR spectral analysis

The ^1H NMR spectrum of Zinc(II) complex is recorded and is shown in Fig **1.4**. In the precursor, 1,2,7,8-tetraphenyl-3,6-diazahexa-2,6-diene-1,8-dione, the α-CH_2 protons is reported to appear as a singlet at δ 3.58 ppm. As compared to the precursor, in Zn^{II} complex of the macrocycle, this peak is observed at higher field. This highfield shift of these protons confirms the coordination of the nitrogen atoms of the macrocycle to the zinc atom. A complicated pattern is observed in the aromatic region. They are observed at δ 7.24 – 7.92 ppm in the spectra of the precursor and the metal complex of the macrocycles (Table **1.4**).

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Table 1.4. ^{1}H NMR Spectral Data (δ, ppm) of the Precursor and [Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] complex

Compound	-NCH$_2$ (s)	Aromatic Protons		
		2	3	4
L(C$_{30}$H$_{24}$N$_2$O$_2$)	3.58	7.80 (d)	7.40 (dd)	7.60 (d)
[Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	3.65	7.92 (d)	7.24 (dd)	7.61 (d)
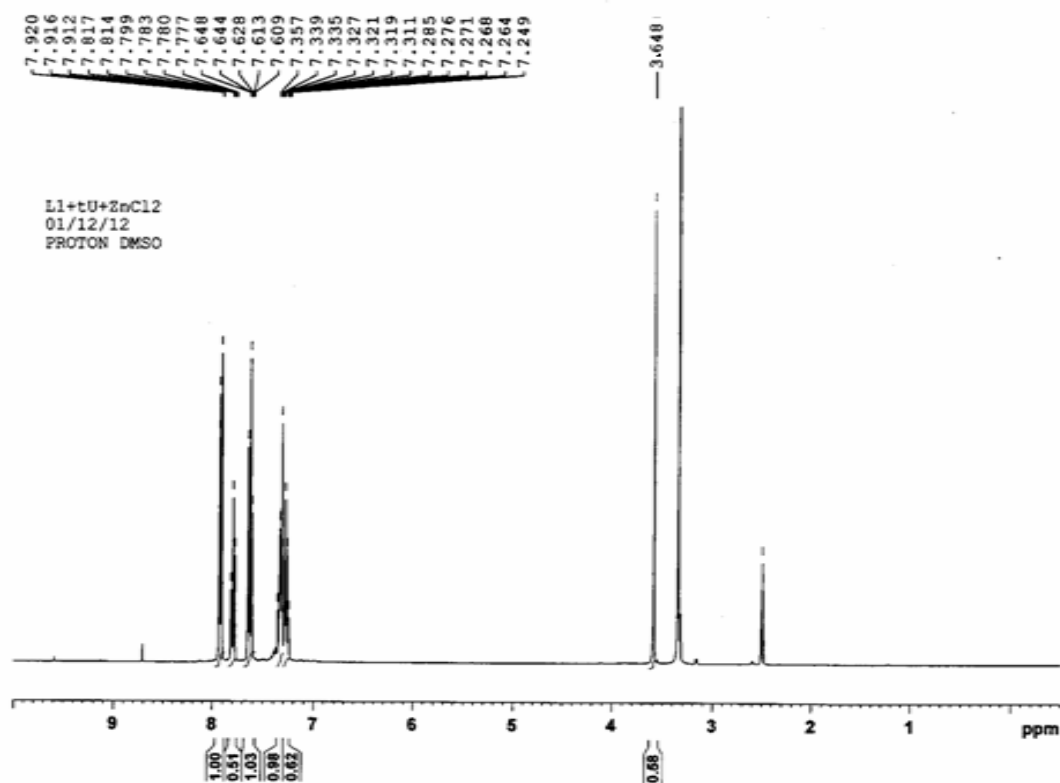
Fig. 1.4. ^{1}H NMR spectrum of [Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] complex

The ^{13}C NMR spectrum of [Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] complex is shown in Fig **1.5**. The spectral data of the precursor and the metal complex of the macrocycle (Table **1.5**) also support the formation of this complex and the formation of the macrocyclic ring structure. There is no peak corresponding to the keto group. But there is a peak at δ 194.78ppm corresponding to C=S group. A singlet is observed at δ 159.26 and δ 32.20ppm which shows the presence of groups >C=N and –CH. The presence of a multiplet in the range of δ 127-132ppm indicates the presence of aromatic carbons.

Table 1.5. ^{13}C NMR Spectral Data (δ, ppm) of the Precursor and [Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] complex

Compound	Chemical Shift Values				
	>C=O	>C=N	-CH	C=S	Aromatic Carbons
L(C$_{30}$H$_{24}$N$_2$O$_2$)	177.07	159.26	32.21	-	C$_1$, 128.61; C$_2$, 127.20; C$_3$, 126.77; C$_4$, 126.12
[Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$]	-	159.26	32.20	194.78	C$_1$, 132.20; C$_2$,; 129.55 C$_3$,127.59; C$_4$,129.36
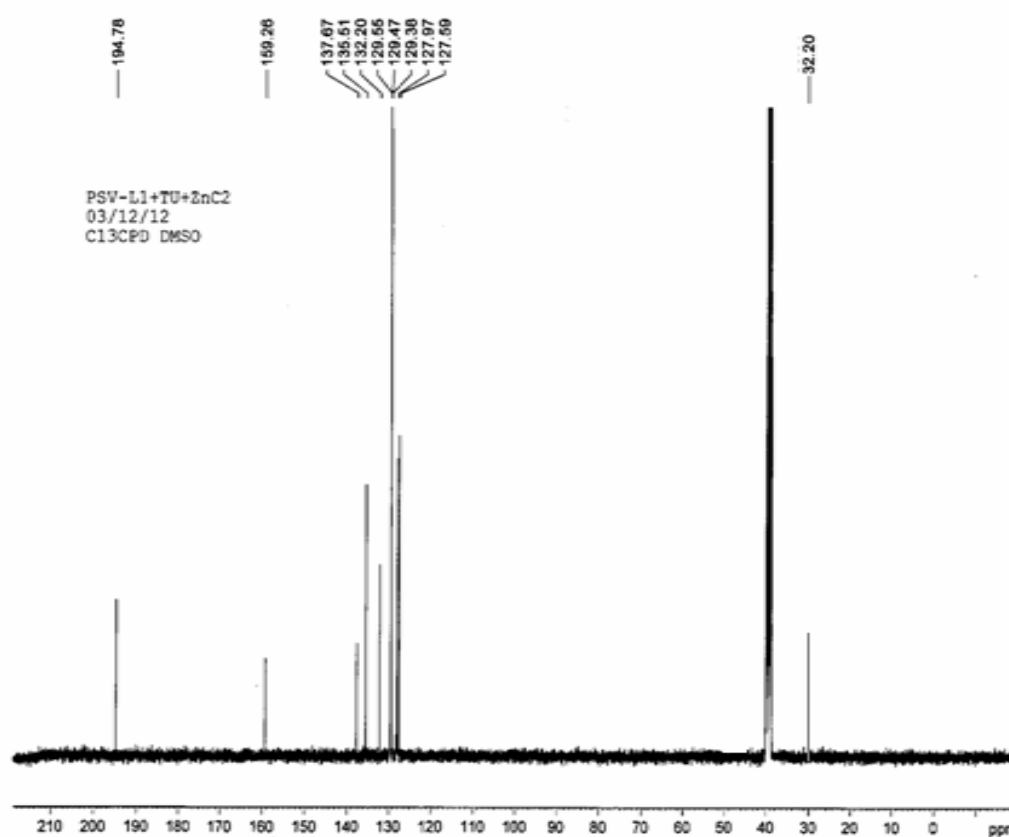
Fig. 1.5. ^{13}C NMR spectrum of [Zn(C$_{31}$H$_{24}$N$_4$S)Cl$_2$] complex

3.5. EPR spectral analysis

The EPR spectrum of Cu(II) complex (Fig **1.6**), recorded as a polycrystalline matrix at 300K (Room temperature) provides positive information which are significant in studying the metal ion environment. The spectrum indicates one intense absorption band in the high field region and it is isotropic, due to tumbling motion of the molecules. The magnetic moment of the copper complex is 1.93 B.M. which corresponds to one unpaired electron, indicating that the complex is mononuclear. For the present Cu(II) complex, the observed g values are $g_∥$ (2.278) > $g_⊥$ (2.091) > g_e (2.0023), suggesting the unpaired electron to be in the $d_{x^2-y^2}$ orbital and the complex is octahedral(13).

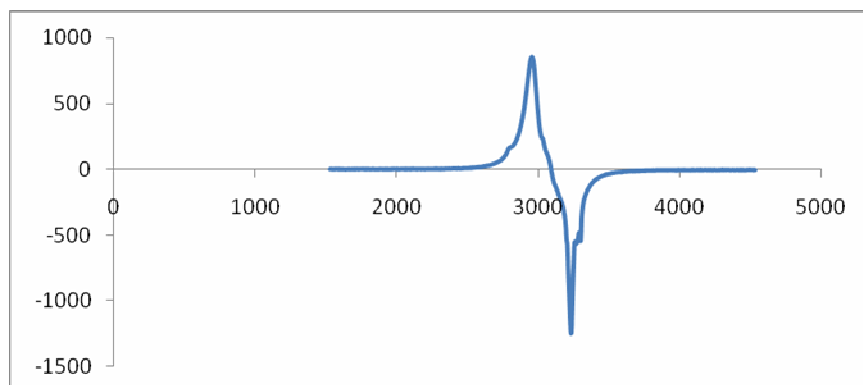**Fig. 1.6. EPR spectrum of [Cu($C_{31}H_{24}N_4S$)Cl_2] complex**

The exchange interaction coupling constant G is calculated from the equation **(1.1),** which is the measurement of the exchange interaction between the metal centers in a solid sample of the complex.

$$G = g_\parallel - 2/g_\perp - 2 \quad \rightarrow \quad (1.1)$$

According to Hathaway(14), if the value of G is larger than four, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. If the value of G is less than four, the exchange interaction is considerable and the local tetragonal axes are misaligned. For the present copper complex, the G value is 3.1 which suggest that the local tetragonal axes are misaligned and the exchange interaction is considerable.

The EPR spectra of [Mn($C_{31}H_{24}N_4S$)Cl_2] complex are recorded at room temperature as polycrystalline sample (Fig.**1.7**). The polycrystalline spectrum is isotropic and exhibits the 'g' value as 2.0046. The broadening of the spectra is probably due to spin relaxation (15).
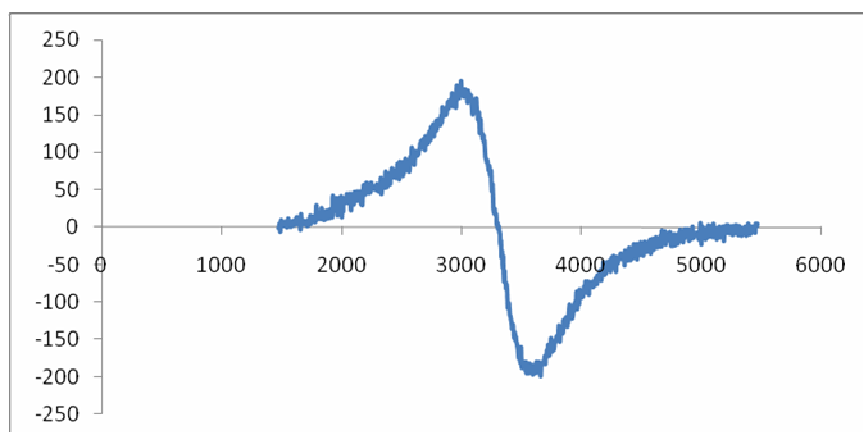

**Fig. 1.7. EPR spectrum of [Mn($C_{31}H_{24}N_4S$)Cl_2] complex**

3.6. Structure of the complexes (21-25)

1) The elemental analyses correspond to the metal: ligand stoichiometry of 1:1.

2) The conductance measurement shows that the metal (II) chloride macrocyclic complexes are non-electrolytes.

3) The magnetic moments, μ_{eff} of the macrocyclic complexes of L reveal that they are all of high spin type with paramagnetic nature (except zinc) and hence Mn, Co, Ni, Cu and Zn are in the +2 oxidation state.

4) The electronic spectral data are in conformity with the transitions for octahedral metal (II) chloride

complexes.

5) The infrared spectral data show that the ligand coordinates to the metal ion through the four imines nitrogen atoms of the macrocyclic ring.

6) The far infrared spectral data confirm the presence of γM-N and γ M-Cl bonds and proving the 'N' coordination with metals.

7) The structures of complexes are assigned on the basis of electronic spectra, magnetic moments and analytical data.

Thus from the above observations, the following structure is tentatively proposed for the complexes **(21-25)** (Fig.**1.8**)
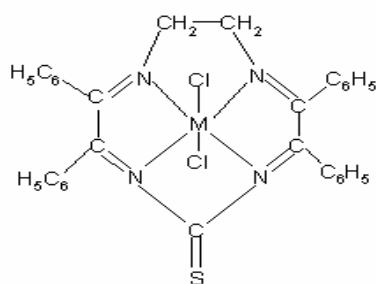
$M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}$ and Zn^{II}

Figure 1.8. Proposed structure of the complexes (**21-25**)

3.7. Antibacterial Activity

In the present study, antibacterial activity of the newly synthesized metal complexes is evaluated by disc diffusion method and minimum inhibition concentration. The macrocyclic multidenate Schiff-base ligand metal complexes were synthesized and evaluated against four Gram-negative and one Gram-positive bacteria includes, *Vibrio cholerae, Shigella flexneri, Pseudomonas aeruginosa, Staphylococcus aureus* and *E. coli*. The zone of inhibition values of synthesized ligand and macrocyclic metal complexes are depicted in Table **1.6** and the corresponding graph is given in Fig **1.9**.

From the results of disc diffusion assay, the synthesized complex **22** exhibited antibacterial activity against *S. flexneri* (18mm) and *V. cholerae* (12 mm), also they are moderately active against *P. aeruginosa* (8 mm) and *E. coli* (8 mm each). The extensive analysis by minimum inhibitor concentration assay also exhibits 2.5 mg/ml as final MIC value. Furthermore, the complex **24** expresses antimicrobial activity against four microbes namely, *V. cholerae , S. flexneri , P.aeruginosa* and *E. coli* .among all the four pathogenic cultures the *Vibrio cholerae* alone exhibit better activity. The maximum activity of 9 mm for *V. cholera* species, while all the other bacterial strains except *staphylococcus aureus* shows activity of 7 mm as zone of inhibition.

The Complex **21** showed better antibacterial activity against only microorganism of tested was *S. flexneri* with maximum zone of inhibition of 16mm.

Among the tested metal complexes, the complex **23** and complex **25** do not showed any potent antimicrobial activity against any of five human pathogenic organisms.

Similarly, the MIC assay of all the complexes except the metal complex of $CoCl_2$ doesn't showed any MIC value against all the tested pathogens. The minimum inhibitory concentration values of synthesized ligand and macrocyclic metal complexes are depicted in Table **1.7** and the corresponding graph is given in Fig **1.10**.

Table 1.6. Zone of Inhibition (mm) of ligand and macrocyclic complexes (21-25)

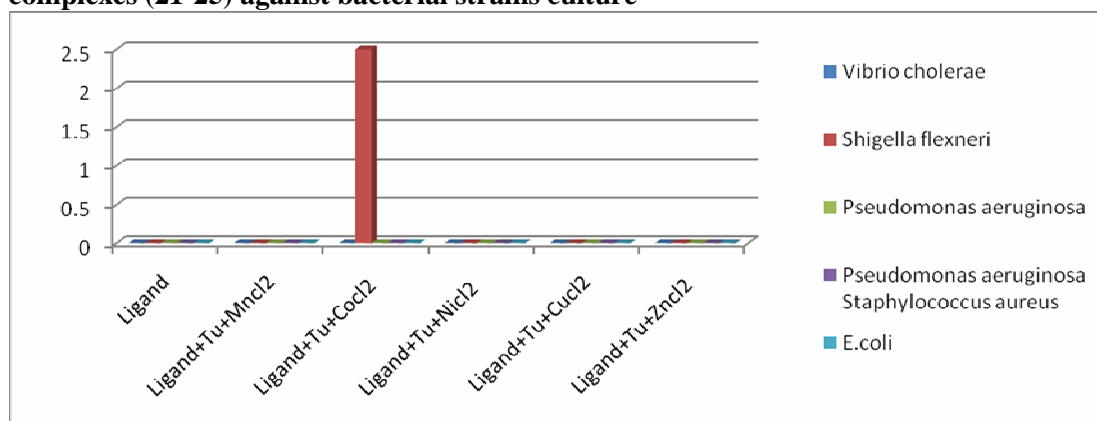| Ligand/Complex	Zone of inhibition in mm				
	Vibrio cholerae	*Shigella flexneri*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*E.coli*
Ligand	--	--	--	--	--
$[Mn(C_{31}H_{24}N_4S)Cl_2]$ (**21**)	--	16	--	--	--
$[Co(C_{31}H_{24}N_4S)Cl_2]$ (**22**)	12	18	8	--	8
$[Ni(C_{31}H_{24}N_4S)Cl_2]$ (**23**)	--	--	--	--	--
$[Cu(C_{31}H_{24}N_4S)Cl_2]$ (**24**)	9	7	7	--	7
$[Zn(C_{31}H_{24}N_4S)Cl_2]$ (**25**)	--	--	--	--	--
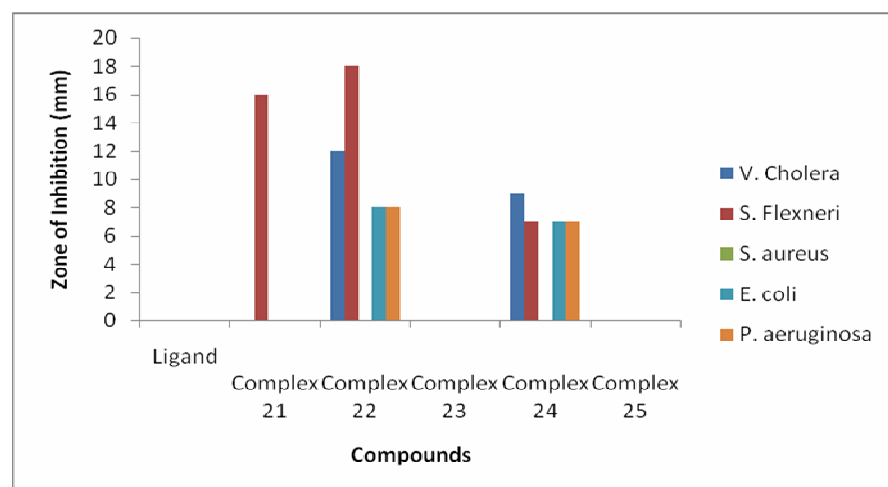
Fig. 1.9. Graph showing the Zone of inhibition (mm) for ligand and the complexes (21-25)

The obtained results indicated that the complexes are more effective against some microbes under identical experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane(16) and can be explained by Tweedy's chelation theory(17). Chelation will enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of the cell membrane(18) and blocking the metal binding sites on enzymes of microorganisms.

In a similar study, the metal complexes have observable antimicrobial activity against gram negative species only compared with free ligand, by which the complexation increases the antimicrobial activity and such increased activity of metal complexes were explained on the basis of chelation theory(19).

Table 1.7. **Minimum Inhibitory concentrations for the ligand and the complexes (21-25)**

Ligand complex	MIC at mg/ml				
	Vibrio cholera	*Shigella flexneri*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*E.coli*
Ligand	--	--	--	--	--
$[Mn(C_{31}H_{24}N_4S)Cl_2]$ (**21**)	NA	NA	NA	NA	NA
$[Co(C_{31}H_{24}N_4S)Cl_2]$ (**22**)	NA	2.5	NA	NA	NA
$[Ni(C_{31}H_{24}N_4S)Cl_2]$ (**23**)	NA	NA	NA	NA	NA
$[Cu(C_{31}H_{24}N_4S)Cl_2]$ (**24**)	NA	NA	NA	NA	NA
$[Zn(C_{31}H_{24}N_4S)Cl_2]$ (**25**)	NA	NA	NA	NA	NA

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Fig. 1.10. Graph showing Minimum Inhibitory Concentration of ligand and complexes (21-25) against bacterial strains culture

Among the synthesized complexes, complex **21** and **22** exhibited better antibacterial activity against the microbe *Shigella flexneri* with a zone of inhibition value of 18mm and 16 mm respectively. The MIC assay of all the complexes showed that only complex **22** showed the value of 2.5mg/ml for *Shigella flexneri* but the other complexes doesn't showed MIC value for any of the tested pathogens.

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