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Synthesis And Characterization Of Lignocaine Associated Sn(IV)-Cd(II), Sn(IV)-Fe(III) And Sn(IV)-Ni(II) Heterobimetal Complexes

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ABSTRACT

The hetero bimetal ion-pair complexes involving chloro complex anions of Sn(IV)-Cd(II), Sn(IV)-Fe(III) and Sn(IV)-Ni(II) associated with lignocaine as counter cation were synthesized. The synthetic routes for all the complexes were similar. The complexes were characterized by elemental analyses, molar conductance, magnetic susceptibility, UV-Visible, IR, ^{1}HNMR, ^{13}CNMR, ESR and Mass spectral measurements. Tentative schemes for mass spectral fragmentation patterns of Sn(IV)-Fe(III) complex was proposed. Based on these studies, the complexes were represented by the general formulae, $[SnCl_6][FeCl_4][LH]_3$, $[CdCl_6][MCl_4][LH]_4$, where M=Cd(II) or Ni(II) and LH= lignocaine.

KEYWORDS

Lignocaine cation;
Ion-pair complexes;
ESR;
Heterobimetal;
IR.

INTRODUCTION

Introducing the concept of ion-pair in 1926by Bjerrum[1], increasing interest has been given to the ion-pair complexes due to their wide variety of stereochemical features and their applications in organic[2-5], inorganic[6,7], analytical[8-10] pharmaceutical analyses [11-14]. The development of new approaches to the preparation of mono and hetero bimetal complexes plays an important role in synthetic coordination chemistry. Heterobimetal complexes behave differently than those of mononuclear and homobinuclear complexes for example; since there are two different metal atoms in a single entity, there may be change in magnetic[15] electronic and structural behavior compared to the mononuclear complexes[14,16,17] through the spin-orbital coupling and electron–electron interaction[18]. Heterobimetal complexes and complex hetero bimetallic salts possessing metal ions with diverse electronic properties in a single entity often display interesting reactivity patterns and solid-state properties[19]. This unique combination of properties makes them potential candidates for application in both biological[20,21] material sciences and in several homogeneous catalytic reactions[22-26]. Considerable effort has thus been directed in recent years towards the synthesis of ligands capable of holding two metal ions[27]. Though tin is well known to form complexes, which are diamagnetic, and spectrally uninteresting, but the literature survey on the complexes of tin are found to be extremely interesting, possessing various physico-chemical behavior account for their applications in medicine[28,29], nutrition[30], several homogeneous catalytic reactions[22,23,31]. Lignocaine, 2-(diethylamino)-N-

(2,6-dimethylphenyl) acetamide is an antiarrythmic drug[32] having inherent potentiality to form cation and also in preparing a variety of metal anionic complexes of structural, analytical and biological importance[33-36]. Literature survey reports a very few lignocaine associated mono[10,14] and bimetal transition metal complexes[36,37]. However, through literature survey reveals no hetero bimetallic complexes involving chloro complex anions of Sn(IV)-Cd(II), Sn(IV)-Ni(II) and Sn(IV)-Fe(III) associated with lignocaine as counter cation. In the present work lignocaine associated Sn(IV)-Cd(II), Sn(IV)-Fe(III) and Sn(IV)-Ni(II) heterobimetal complexes were synthesized and characterized for their structure by various physico-chemical techniques.

EXPERIMENTAL

Materials and physical measurements

Lignocaine(sigma, USA), cadmium chloride hemi penta hydrate, nickel chloride hexa hydrate, ferric chloride hexa hydrate, tin metal(BDH) ethanol and concentrated hydrochloric acid were used without further purification. Elemental analysis and mass spectra of complexes were carried out at Central Drug Research Institute(CDRI), Lucknow. IR spectra were recorded in KBr(4500-500cm^{-1}) using a Perkin-Emler-FT-IR spectrophotometer. UV-Vis spectra were recorded with UV Pharmaspec-1700, Shimadzu, Japan, NMR spectra were recorded with FT-NMR-600, HITACHI, JAPAN and ^{13}C-NMR spectra were recorded with DRX500 and Jeol GSX400 spectrometer. Molar conductances were measured with digital conductivity meter model DT909. Magnetic susceptibility measurements at room temperature were carried out by Gouy's method using $Hg[Co(SCN)_4]$ as calibrant and Keroy semimicro balance. ESR spectrum was recorded at Indian Institute of Technology, Chennai.

General procedure for preparation of the complexes

All the complexes reported here were prepared by a similar experimental procedure. To a 25ml of 0.1M ethanolic solution of required metal salt, [nickel chloride hexa hydrate, ferric chloride hexa hydrate or cadmium chloride hemi penta hydrate], 25ml of 0.1M ethanolic solution of tin metal was added at room temperature. To this, about 3 to 4 ml of concentrated hydrochloric acid and 25ml of 0.5M ethanolic solution of lignocaine were added. The resulting solution was mixed well and the pH of the solution was adjusted to about 4 with 2M hydrochloric acid. The solution was evaporated to a small volume on a steam bath. The resulting colored solution [pale yellow for nickel or iron and colorless for cadmium salts] was kept at room temperature. After 3-4 days colored crystals were separated out. Crystals were filtered off, washed with diethyl ether and were dried in a desiccator over anhydrous silica gel.

RESULTS AND DISCUSSION

Elemental analysis

Tin content of the complexes was brought into solution by repeated decomposition of the complexes with concentrated hydrochloric acid. Later tin content was determined with cupferron and weighed as tin(IV) oxide, SnO_2[38]. The solution containing cadmium was neutralized with sodium carbonate and metal was precipitated with sodium anthranilite solution. The precipitate was washed with alcohol, dried and weighed as $Cd[C_7H_6O_2N]_2$[39]. Iron(III) was estimated gravimetrically as Fe_2O_3[39], and nickel was estimated by dimethylgloximate method[39]. Chloride content of the complexes was estimated by gravimetric method using $AgNO_3$ as a precipitating agent[39,40] The nitrogen content of the complexes was estimated by Kjeldahl's method[39]. The complexes were also analyzed for C, H and N by micro analytical methods. The elemental analysis data of the prepared complexes are presented in TABLE 1 suggest that, in all the complexes except Fe(III) complex, Sn: LH: M were found to be in 1:4:1 ratio, whereas that for Fe(III) complex it was found to be in 1:3:1 ratio. Therefore, they may be represented by the formulae $[SnCl_6][FeCl_4]$ $[LH]_3$,

TABLE 1: Analytical data of hetero bimetal complexes of Sn(IV) with lignocaine and Cd(II), Ni(II) and Fe(III)

Complex	Color	% Yield	%Sn(Cal)	% M(Cal)	%C(Cal)	%N(Cal)	%H(Cal)	%X(Cal)	Molar conductance (Ohm $^{-1}$cm^{2}mol^{-1})
$[SnCl_6][NiCl_4][LH]_4$	Pale yellow	52	7.12(7.34)	3.78(3.63)	41.97(41.62)	7.02(6.93)	5.93(5.73)	30.98(30.76)	196.2
$[SnCl_6][CdCl_4][LH]_4$	White	56	7.35(7.11)	6.94(6.73)	41.25(40.29)	6.64(6.71)	5.48(5.55)	29.47(29.77)	201.7
$[SnCl_6][FeCl_4][LH]_3$	Pale yellow	47	8.75(8.84)	4.38(4.16)	37.88(37.59)	6.38(6.26)	5.24(5.18)	29.27(29.09)	206.5

$[SnCl_6][CdCl_4][LH]_4$ and $[SnCl_6]$ $[NiCl_4][LH]_4$.

Conductance measurements

Molar conductance values of lignocaine associated complex anions in acetonitrile solutions were found to be in the range 196.2 to 206.5Ohm^{-1} cm^2 mol^{-1}, TABLE 1, suggesting that the complexes are ionic in nature. However, the values obtained are slightly more when compared with earlier reported values for monometallic tin complexes with amide group ligands[10,41] there by suggesting that the complex ions dissociate in solution and this could account for 2:4 electrolytic nature[10,36].

Electronic absorption spectra

UV-Visible spectra of the complexes were recorded as their acetonitrile solutions are shown in figures 1a, 1b and 1c. Important spectral bands are listed in TABLE 2. The prepared complexes show characteristic absorption bands in the region 220-247nm. Since there is no ligand field stabilization effect for both Sn^{4+} and Cd^{2+} ion because of their completed d shells, their stereochemistry is determined solely by consideration of size, electrostatic forces and covalent bonding forces. Further ions having d^0 and d^{10} configuration have no characteristic absorption spectra[42]. Absorption of$[CdCl_4]^{2-}$, $[SnCl_6]^{2-}$ and lignocaine were found to be in the region 220-247nm[10] Further such a feature has been noticed in almost all the complexes; hence an envelope band in the region 200-240nm is assigned to $[CdCl_4]^{2-}$,$[SnCl_6]^{2-}$ and lignocaine. However on the basis of literature[10,43-45] tetrahedral geometry may be assigned to complex anion $[CdCl_4]^{2-}$ and[10,46-48]octahedral geometry for the complex anion $[SnCl_6]^{2-}$.

The complex $[SnCl_6][FeCl_4][LH]_3$ shows additional absorption bands at 357nm, 312nm, The bands at 242nm, 315nm and 363nm have been used for identification of complex anion[14,49]$[FeCl_4]^-$. In the complex, $[SnCl_6][FeCl_4][LH]_3$ commonly observed high intensity band in the UV region at 242nm is missing, whereas the remaining two bands at 312nm and 363nm are at the expected region. Except high intensity charge transfer band it is similar to the observations made by Gill[50] and the visible spectra are also similar to the observations of Lindenbaum[51] and Costant et al[52]., which unequivocally support tetrahedral geometry for$[FeCl_4]^-$ complex anion. Hence tetrahedral geometry is assigned to anion $[FeCl_4]^-$.

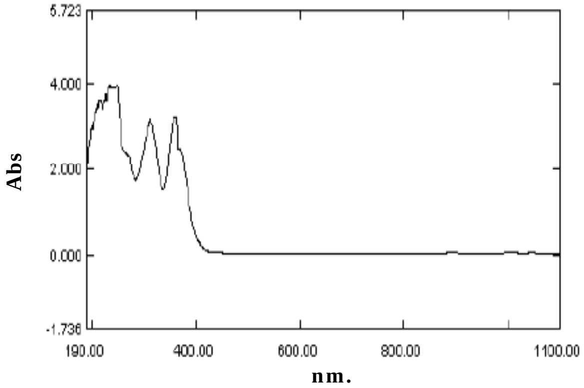

Figure 1(a) : UV-visible spectrum of $[SnCl_6][FeCl_4][LH]_3$

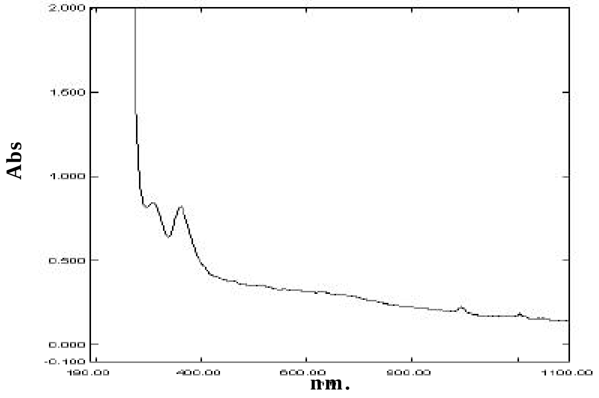

Figure 1(b) : UV-visible spectrum of $[SnCl_6][NiCl_4][LH]$

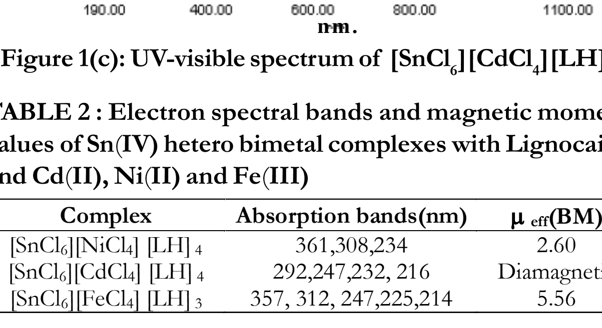

Figure 1(c): UV-visible spectrum of $[SnCl_6][CdCl_4][LH]_4$

TABLE 2 : Electron spectral bands and magnetic moment values of Sn(IV) hetero bimetal complexes with Lignocaine and Cd(II), Ni(II) and Fe(III)

Complex	Absorption bands(nm)	μ_{eff}(BM)
$[SnCl_6][NiCl_4]$ $[LH]_4$	361,308,234	2.60
$[SnCl_6][CdCl_4]$ $[LH]_4$	292,247,232, 216	Diamagnetic
$[SnCl_6][FeCl_4]$ $[LH]_3$	357, 312, 247,225,214	5.56

The characteristic bands for tetrahedral Ni(II) complex should be in the region 300-421nm[14] and the prepared complex, $[SnCl_6][NiCl_4][LH]_4$ is having the bands at 361 and 308nm suggesting the tetrahedral geometry to complex anion $[NiCl_4]^{2-}$.

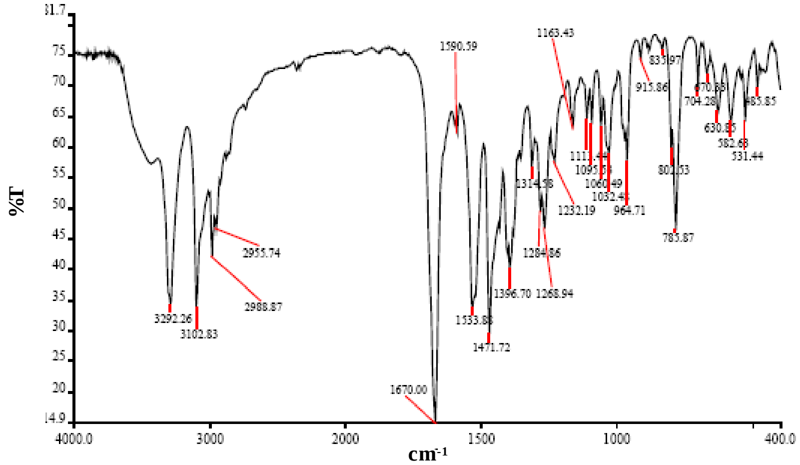

Figure 2 : IR spectrum of $[SnCl_6][FeCl_4][LH]_3$

TABLE 3 : IR spectral bands of Sn(IV) hetero bimetal complexes with lignocaine and Cd(II), Ni(II) and Fe(III)

Lignocaine hydrochloride (cm^{-1})	Complexes of tin and LH with			Assignment tentative
	$[NiCl_4]$ (cm^{-1})	$[CdCl_4]$ (cm^{-1})	$[FeCl_4]$ (cm^{-1})	
3259	3291	3293	3292	νNH or νN^+H Stretch
1660	1669	1669	1670	νC=O Amide
1498	1471	1470	1473	νC=C Aromatic
2450	2455	2448	2452	νNH
2969	2988	2988	2988	νC-H of C_2H_5
764	786	785	786	ν C-H aromatic

IR spectra

IR spectrum of the complex $[SnCl_6][FeCl_4][LH]_3$ and spectral data of lignocaine associated bimetal complex anions and lignocaine hydrochloride regenerated from the complexes are given in TABLE 3 and in figure 2. The weak absorption bands in the region 2977-2976cm^{-1} indicate nC-H of N-C_2H_5, which is almost unaltered, compared to the nCH of N-C_2H_5 of lignocaine hydrochloride. This is in agreement with the observation made by Patel and Patel[53], indicating the absence of lone-pair of electron on nitrogen atom and hence protonated lignocaine in all the complexes. In lignocaine complexes, the íNH of amide group shifts towards higher region compared to its position in the spectrum of lignocaine thereby indicating non-participation of amide nitrogen atom in coordination bond formation. This behavior of nitrogen atom was accorded by the presence of bulky phenyl group attached to it, which hinders the coordination of nitrogen.

Magnetic susceptibility measurements

Magnetic measurements provide information on the electronic structure and oxidation state of the metal ions in the complexes. The magnetic moment values calculated for the heterobimetal complexes of Sn(IV) with Cd(II), Ni(II) and Fe(III) are given in TABLE 2. The measured magnetic moment values of complexes $[SnCl_6][FeCl_4][LH]_3$ and $[SnCl_6][NiCl_4][LH]_4$ are found to be 5.56 BM and 2.60BM respectively, which is slightly less than the expected[54-57] spin only value of d^5 and d^8 system there by indicating that there is a spin-spin interaction leading to antiferromagnetic coupling at normal temperature itself[36,14]. Therefore complex $[SnCl_6][FeCl_4][LH]_3$ is a high spin complex with five unpaired electrons. High spin octahedral and tetrahedral complexes of Fe(III) are having same ground state term $^6A_1$ and moments are expected to be close to spin only value. As a result it is difficult to assign geometry to complex based on magnetic moment value alone, however, magnetic data coupled with the data on elemental analysis and conductometric measurements support tetrahedral geometry for complex anion, $[FeCl_4]^{2-}$. The measured magnetic moment value of the complex, $[SnCl_6][NiCl_4][LH]_4$ is in agreement with tetrahedral structure[58-60] and hence tetrahedral geometry is assigned to anion$[NiCl_4]^{2-}$. The complex$[SnCl_6][CdCl_4]$ $[LH]_4$ as expected it was found to be diamagnetic one, hence tetrahedral and octahedral geometry may be assigned to complex anions $[CdCl_4]^{2-}$ and $[SnCl_6]^{2-}$ respectively.

The prepared complexes $[SnCl_6][FeCl_4][LH]_3$ and $[SnCl_6][NiCl_4][LH]_4$ contain Sn(IV), which is expected to be diamagnetic[61,10] with octahedral geometry . Therefore the experimental magnetic moment values of the complex will depend on other metal ions in that respective complex and the values obtained

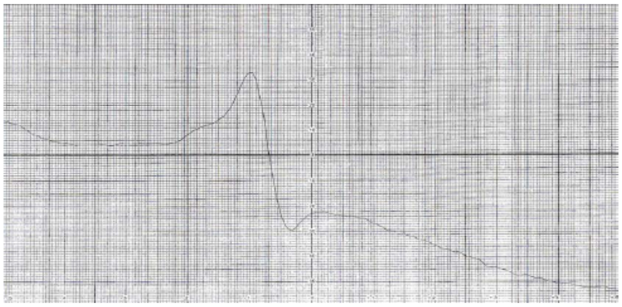

Figure 3 : ESR spectrum of $[SnCl_6][FeCl_4][LH]_3$

TABLE 4: ^1H and ^{13}C-NMR data of lignocaine hydrochloride, complex and lignocaine(Regenerated)

Chemical shift in δ(ppm) assigned to the different protons and carbon atoms				
^1H-NMR			^{13}C-NMR	
Lignocaine HCl	Complex $[SnCl_6][CdCl_4][LH]_4$	Group	Lignocaine (Regenerated)	Group
7.07	7.2-6.5	(Ar-H)	171.8	(-CO-)
3.21	3.26	$(-CO-CH_2-N)$	125-140	(Phenyl C-atom)
2.69	2.40	$(-CH_2-CH_3)$	58	$(-CO-CH_2-NH)$
2.23	1.10	$(Ar-CH_3)$	49	$(-CH_2-CH_3)$
			13	$(-CH_2-CH_3)$

TABLE 5: Mass spectral fragments of heterobimetal complexes of Sn(IV) with lignocaine and Fe(III)

Fragments	Molecular mass of complex $[SnCl_6][FeCl_4][LH]_3$	
(Tentative)	Observed	Cal
$\{[SnCl_6][LH]_3[FeCl_4]\}^+$	1340	1341.93
$\{[SnCl_6][Lb]_3[FeCl_4]\}^+$	1231	1232.43
$\{[SnCl_6][Lb]_3[FeCl_3]\}^+$	1196.9	1195
$\{[SnCl_6][Lb]_3[FeCl_2]\}^+$	1090.43	1093
$\{[SnCl_4][Lb]_2[FeCl_2]\}^+$	856.09	859
$\{[SnCl_3][Lb]_2[FeCl]\}^+$	785.09	780
$\{[SnCl_6][Lb][FeCl_2]\}^+$	692.75	691
$\{[SnCl_4][Lb][FeCl_2]\}^+$	625.71	626
$\{[SnCl][Lb]_2\}^+$	622.88	626
$\{[Lb]_2\}^\cdot$	469	468.68
{Lig.HCl}	269	270.84
$\{\text{Lig. Base}\}^\cdot$	235	234.34
$\{C_{12}H_{17}N_2O\}^+$	205	205
$\{C_8H_{11}N\}^\cdot$	120	121
$\{C_4H_9NO\}^+$	86	87

are corresponding to 2 or 5 unpaired electron with antiferromagnetic coupling respectively.

NMR studies

^1H-NMR spectrum of lignocaine complex shows signals at 6.5-7.2ppm for(Ar-H singlet), 3.26ppm for($-CO-CH_2-N$, singlet), 2.4ppm for($-CH_2-CH_3$, singlet) and 1.1ppm for($Ar-CH_3$, singlet). ^{13}C NMR of lignocaine hydrochloride regenerated from the complex exhibit signals at 171.8ppm for(-CO) 125-140ppm for(phenyl C-atom), 13ppm for($-CH_2-CH_3-$), 49ppm($-CH_2-CH_3-$) and 58ppm($-CO-CH_2N-$). ^1H and ^{13}C-NMR spectra of lignocaine and its complex confirm the presence of carbonyl, amide and phenyl group and also account for the non involvement of carbonyl group in coordinating with Sn(IV). The NMR data are shown in TABLE 4.

Electron spin resonance spectra

The ESR spectrum of the complex was recorded using poly crystalline 1,1-diphenyl-2-picryl hydrazyl, DPPH is used as a 'g' value standard. The magnetic field strength(H_0) at which the resonance line of the DPPH appears was measured.

The ESR spectrum of the hetero bimetal tin complex $[SnCl_6][FeCl_4]$ $[LH]_3$ is as shown in(Figure 3). Since second ion in the complex, Sn(IV) is diamagnetic, it is ESR in active. Hence, the ESR spectrum of the complex $[SnCl_6][FeCl_4][LH]_3$ is mainly due to Fe(III) ion. The values for g ll and g ⊥ have been calculated which are 1.8757 and 1.8239 respectively, which account for the anisotropic nature of the complex and it arises from the coupling of the orbital angular moment to the spin angular moment of the metal ion through spin orbit interaction. This is also in agreement with the reduced magnetic moment values obtained from the magnetic susceptibility measurements compare to spin only value for the idealized tetrahedral environment around Fe(III) ion in the complex[62].

Mass spectra

The mass spectrum of lignocaine complex $[SnCl_6][FeCl_4][LH]_3$ is shown in(Figure 4). It is difficult to assign completely, fragmentation of the molecule, which is having high molecular weight[63]. However some fragmentation of the molecule is made and is given in the TABLE 5. Mass spectrum of the complex shows the m/z value 1340 corresponds to the molecular weight of complex having formula $[SnCl_6][FeCl_4][LH]_3$. Spectrum shows the base peak at m/z value 235 corresponds to molecular mass of the lignocaine base. The peak at m/z value 469 corresponds to molecular mass of $[Lb]_2$ radical, where Lb is lignocaine base. The peak at m/z value 86 corresponds to molecular mass of $\{C_4H_9NO\}^+$ion.

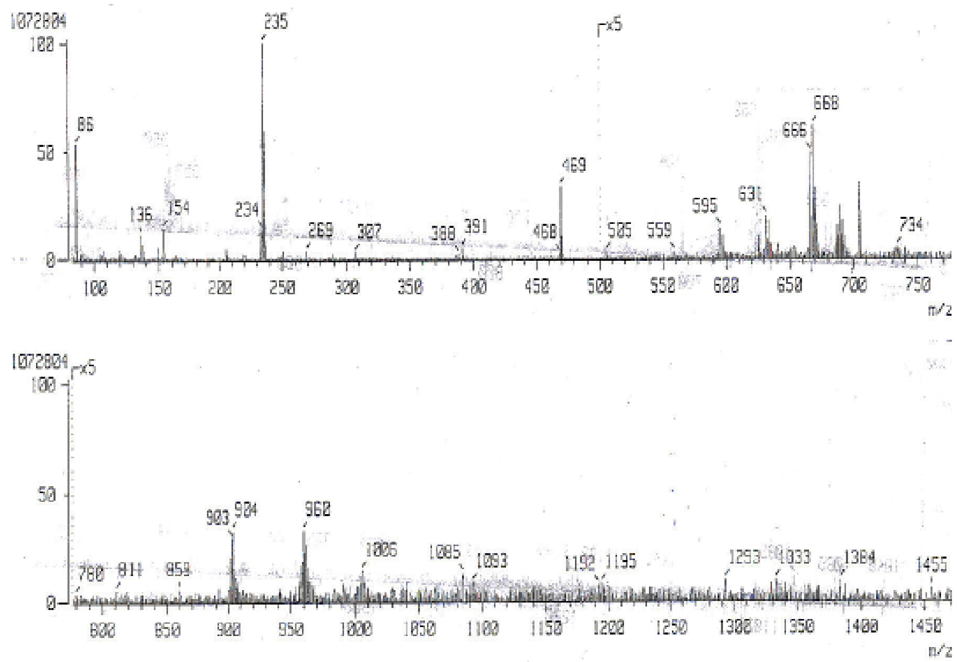

Figure 4 : Mass spectrum of $[SnCl_6][FeCl_4][LH]_3$

CONCLUSION

The data based on elemental analyses and conductance measurements of the complexes indicate that the tin: lignocainium: M, where M=Cd(II) and Ni(II) is found to be in the ratio 1:4:1 whereas for the other metal ion Fe(III) the ratio is found to be 1:3:1. From the elemental analyses data obtained for the complexes$[SnCl_6][MCl_4]$ $[LH]_4$ and $[SnCl_6]$ $[FeCl_4][LH]_3$, indicate the presence of heterometal ions in each one of the complexes and also account for the general formulae indicated as above. The conductivity measurements made for the complexes in their acetonitrile solutions account for the ionic nature of the complexes and suggest that the complexes are 2:4 electrolytes. The mass spectral analyses of the complex $[SnCl_6][FeCl_4]$ $[LH]_3$ is also accounting for the general formula molar mass of the complex. Absorption and ESR spectral studies of the complexes coupled with their magnetic susceptibility measurements would also account for octahedral geometry for the anion $[SnCl_6]^{2-}$ whereas tetrahedral geometries for $[FeCl_4]^{2-}$, $[CdCl_4]^{2-}$ and $[NiCl_4]^{2-}$ anions and hence the general formulae of the complexes suggested. The NMR and IR studies show that lignocaine is present in the complex as lignocainium ions, which are interacting with the two complex anions per complex through coulombic force of attraction.

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