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SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF Cr(III) COMPLEXES DERIVED FROM 2-BENZOYLPYRIDINE AND 2-BENZOYLTHIOPHENE WITH THIOSEMICARBAZONE AND SEMICARBAZONE

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Keywords:

Mass, IR, NMR, EPR, Bidentate, Cr (III), Thiosemicarbazone, Semicarbazone, Magnetic Moment

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ABSTRACT: The complexes of chromium(III) are synthesised with thiosemicarbazone (L^1&L^3) and semicarbazone (L^2) derived from 2-benzoylpyridine and 2-benzoylthiophene having general composition $[CrL_2X_2]X$ (Where $L=L^1$&L^3(L^1&L^3= thiosemicarbazone ligand and L^2= semicarbazone ligand) and X= NO_3^- and OAc^-) have been synthesised. The complexes and ligand under study are characterised by elemental analysis, IR spectroscopy, UV-Vis spectroscopy, mass spectra, conductivity measurement, magnetic susceptibility, EPR spectral studies and NMR Spectroscopy. IR spectral study indicates that ligands behaves as bidentate and coordinated to metal ion through nitrogen, sulphur / oxygen donor atoms. The molar conductance was measured by using DMSO as solvent. The higher value of molar conductance suggests that the complexes are 1:1 electrolyte in nature. The value of magnetic susceptibility indicates that complexes are of high spin. On the basis of above spectral studies an octahedral geometry may be proposed for all the complexes.

INTRODUCTION: Coordination chemistry covers a major portion of inorganic chemistry which involves properties, structure and reaction of complexes which are derived from ligands coordinated to a transition metal centre. Sulphur containing heterocycles are well known for their therapeutic application in medicinal chemistry [1]. In recent years metal based drugs has gained significant importance in medicinal field [2] for their application in treatment of diabetes, cancer, anti-inflammatory and cardiovascular diseases [3-4].

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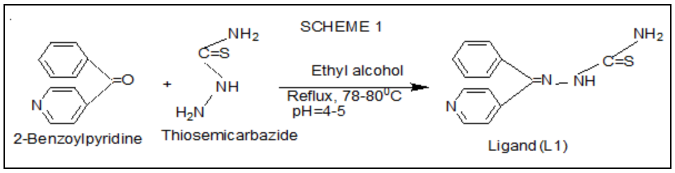
Metal complexes of thiosemicarbazone which has nitrogen and sulphur donor atoms and semicarbazone which has nitrogen and oxygen donor atoms were found to have pronounced carcinogenic properties [5] against a wide range of transplanted neoplasia [6-11]. Schiff's base nitrogen and sulphur donor ligand have dragged a special interest because of their mixed hard-soft donor character and versatile coordination behaviour [12-13].

As compared to free thiosemicarbazone and semicarbazone their metal complexes show more activity like anticancer [14], fungicide, antibacterial [15-16], antiviral [17-18], antifungal [19-20], anti-HIV [21], anti-tumour activity [22] and other biological activities. Thiosemicarbazones and their metal complexes are also important because of their pharmacological activity [23].

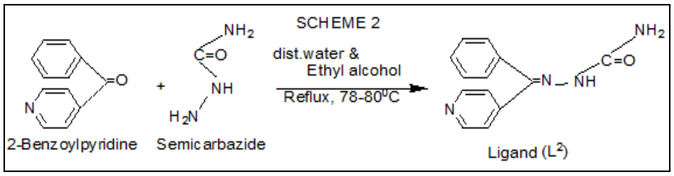
Due to these applications it is highly desirable to synthesise and characterise transition metal complexes with such ligands. In present paper we report the synthesis and characterisation of complexes with thiosemicarbazone (L^1) and semicarbazone (L^2) derived from 2-benzoylpyridine according to scheme 1 and scheme 2 and with ligand (L^3) derived from 2-benzoylthiophene and thiosemicarbazone according to **Scheme 3**.

Experimental Section: All reagents were commercially available and used without further purification purchased from sigma Aldrich and metal salts were purchased from E. Merck. Solvents were spectroscopic pure from SRL/BDH or purified by conventional methods.

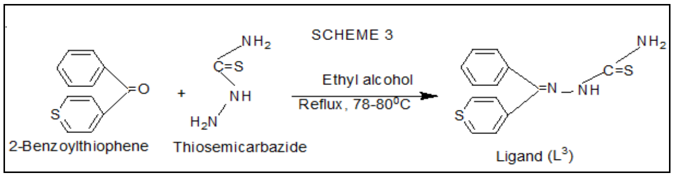
Preparation of ligand(L^1): Thiosemicarbazide (0.091g, 0.01mol) was dissolved in minimum quantity of ethanol. To this hot ethanolic solution of (0.18g, 0.01mol) 2-benzoylpyridine was added very slowly with constant stirring. The resulting solution was refluxed at 78-80°C for 8hrs.and the pH was adjusted to approximately 4-5 by using acetic acid (according to **Scheme 1**). On cooling bright yellow coloured crystals were separated out. These crystals were washed out several times with cold ethanol. The ligand is highly soluble in water.



Preparation of ligand(L^2): Semicarbazide (0.11g, .01mol) and sodium acetate (0.11g, .01mol) were dissolved in little amount of distilled water and added to alcoholic solution of (0.36g, 0.02mol) 2-benzoylpyridine with constant stirring and refluxed for 7-8 hrs. at 78-80 °C according to **(Scheme 2).** The resultant solution was cooled for 24 hrs. On cooling white shiny crystals were separated out which were washed with ethanol and ether several time to remove excessive reactant and dried over P_4O_{10}.



Preparation of ligand (L^3): Thiosemicarbazide (0.91g, 0.01mol) was dissolved in minimum quantity of ethanol. To this solution hot ethanolic solution of (0.01 mol) 2-benzoylthiophene was added very slowly with constant stirring. The resulting solution was refluxed at 78-80 °C for 6hrs.and the pH was adjusted to 4-5 by using acetic acid (according to **Scheme 3**). On cooling bright light yellow coloured crystals were separate out. These crystals were washed out several times with cold ethanol and dry ether several times to remove excessive reactant and dried over P_4O_{10}.



Preparation of transition metal complexes with ligand (L^1): Hot aqueous solution (20 ml) of corresponding metal salts (0.01mol) were mixed with hot aqueous solution of the ligand (0.02mol) with constant stirring and refluxed for 7-8 hrs. at 65-70 °C. On cooling the contents, the coloured precipitates were separated out in each case. It was filtered, washed with ethanol and ether. The resultant mixture was dried over P_4O_{10}.

Preparation of transition metal complexes with ligand(L^2 &L^3): Hot ethanolic solution (20 ml) of corresponding metal salts (0.01mol) were mixed with hot ethanolic solution of the ligand (0.02mol) with constant stirring and refluxed for 7-8 h at 78-80 °C. On cooling the contents, the coloured precipitates were separated out in each case. It was filtered, washed with ethanol and ether. The resultant mixture was dried over P_4O_{10}.

Analytical and physical measurement: Elemental (CHN) analysis was carried out on a Perkin Elmer sercise-II-2400. IR was recorded using a Thermo scientific Nicolet 6700 FT-IR on KBr disc in the wave number ranged 4000-400cm^{-1}. Mass spectrum was recorded using Bruker microtop-QII.

^{1}H NMR spectra were recorded on Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent and TMS as an internal solvent. Electronic spectral studies were conducted on a perkin elmer-lambda 25, UV spectrophotometer. The EPR spectra were recorded in solid as polycrystalline sample at room temperature on E_4-EPR spectrometer using DPPH as g marker.

RESULTS AND DISCUSSION: All the chromium(III) complexes were synthesised by condensation reaction between ligands and corresponding metal salts. All complexes were synthesised at 6-7pH range. The synthesised complexes were coloured and stable at room temperature and were found to be soluble in DMSO and DMF. The molar conductivity value lies in the range from 70-80 (ohm^{-1} cm^2 mol^{-1}) which indicates 1:1 electrolytic nature. Thus these complexes may be formulated as $[CrL_2X_2]$ X where [L= ligands(L^1, L^2& L3)] and [X= $NO_3^-$and OAc^-]. This is further supported by elemental analysis values. The physical and analytical data together of synthesised complexes is listed in **Table 1**.

TABLE 1: ELEMENTAL ANALYSIS, COLOUR AND FORMULA OF Cr(III) COMPLEXES

	Colour	Found	Calculated	%
		C	H	N
$[Cr(L^1)_2(NO_3)_2]NO_3$	Dark green	41.65	3.20	20.56
		(41.60)	(3.72)	(20.01)
$[Cr(L^1)_2(OAc)_2]OAc$	Dark green	50.21	4.60	15.62
		(50.91)	(4.61)	(15.14)
$[Cr(L^2)_2NO_3)_2]NO_3$	Dark green	43.46	4.60	15.62
		(43.61)	(4.05)	(15.45)
$[Cr(L^2)_{2(}OAc)_2]OAc$	Dark green	44.88	4.40	14.96
		(44.27)	(4.65)	(14.26)

^{1}H NMR of ligand(L^1,L^2 &L^3): ^{1}H NMR of ligands (L^1, L^2&L^3) was done in DMSO on 44-300 MHz NMR. In ^{1}H NMR of ligands(L^1&L^3) (**Fig.1a,1b**) the aromatic proton appears as set of singlet, doublet and multiplet in the range 7.40-8.78ppm. The singlet for NH proton appears at 9.32ppm while two NH_2 protons resonates as a multiplet at 7.34-7.38 ppm. The NH_2 and NH protons are confirmed by their D_2O spectra. All the protons are found in their expected region.

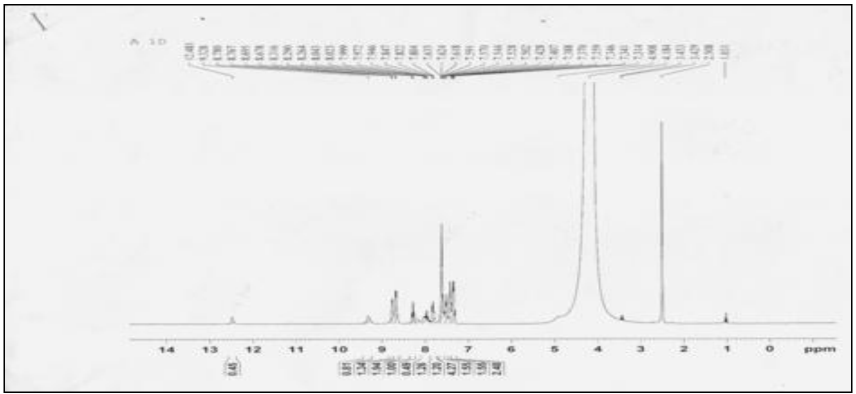


FIG. 1(a): ^{1}H NMR SPECTRUM OF LIGAND(L^1)

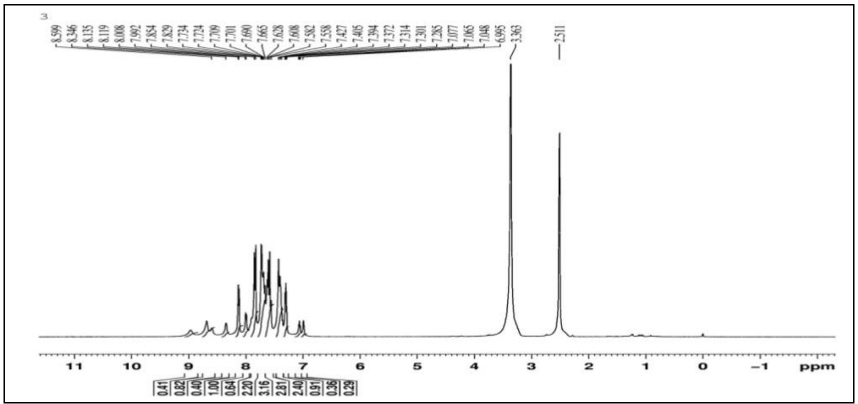


FIG. 1(b): ^{1}H NMR SPECTRUM OF LIGAND(L^3)

Mass spectra of Ligand(L^1,L^2&L^3): Mass spectra of the ligands (**Fig.2a, 2b &2c**) gives the important information regarding the proposed formula of the synthesised compounds. Mass spectra of ligands L^1, L^2, L^3 shows a molecular ion peak at m/z=255, 239 and 259amu corresponding to species $[C_{13}H_{11}N_4S]^+$, $[C_{13}H_{11}N_4O]^+$ and $[C_{13}H_{12}N_3SO]^-$ respectively. The peak at m/z= 255, 239 and 259 amu indicates M+1, M+1and M-1 peaks. These values favour the proposed formulae of the ligands under study.

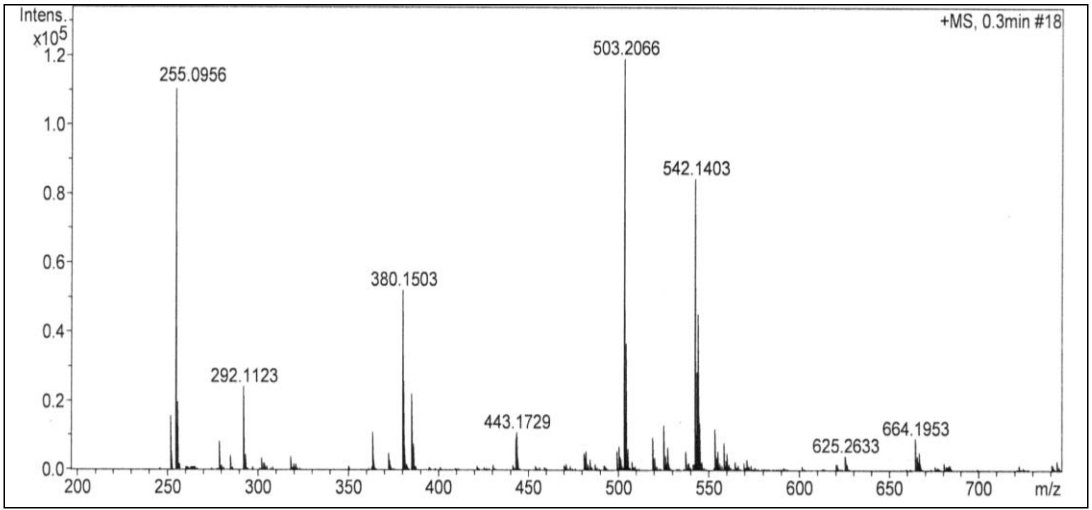


FIG. 2a: MASS SPECTRUM OF LIGAND(L^1)

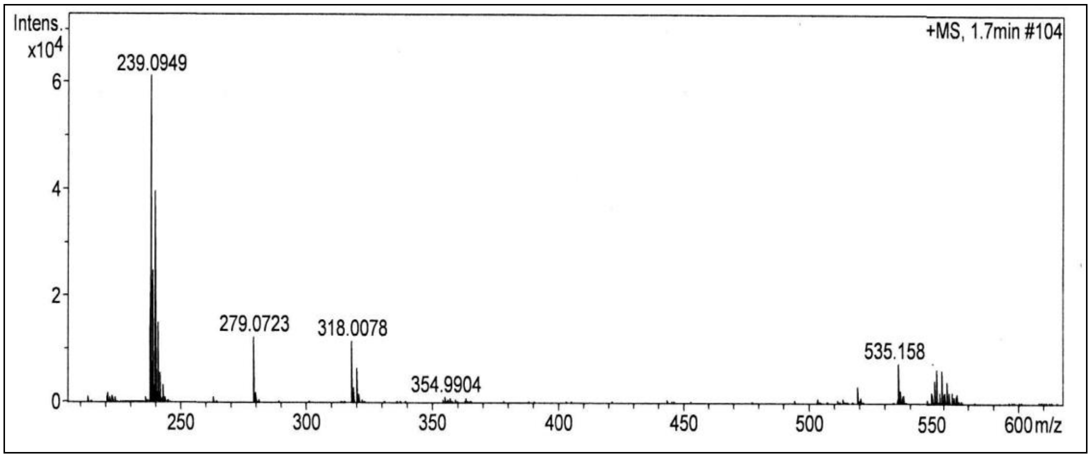


FIG. 2b: MASS SPECTRUM OF LIGAND(L^2)

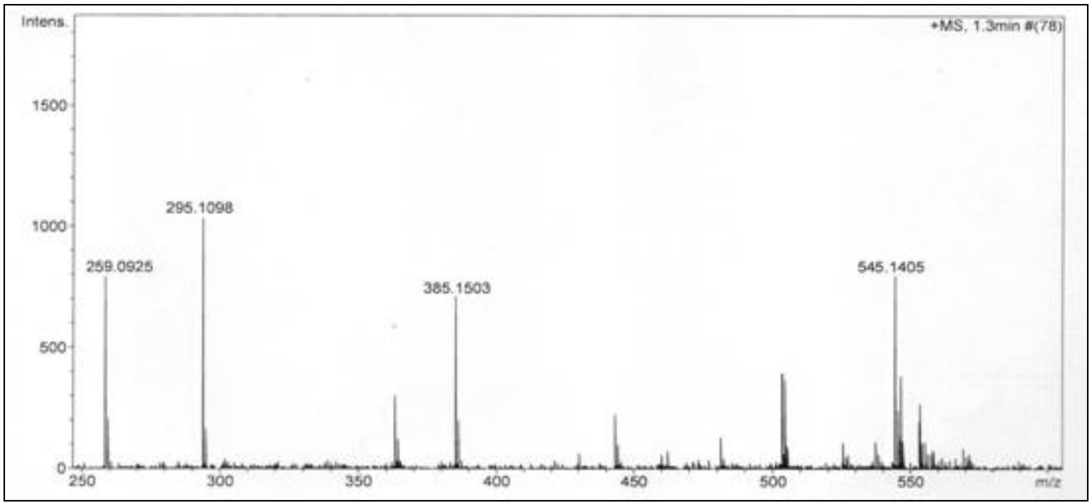


FIG. 2c: MASS SPECTRUM OF LIGAND (L^3)

IR Spectra: The IR bands of ligands and complexes (**Fig. 3a & 3b**) were recorded between 4000- 400cm^{-1} listed in **Table 2**. A band at 1618 cm^{-1} in case of ligand 1 (L^1) and 1577 cm^{-1} in case of ligand 2(L^2) and another band at 1598cm^{-1} in case of ligand 3(L^3) corresponds to v(C=N) azomethine group [24]. The band at 781 cm^{-1} and 837 cm^{-1} may be assigned to v(C=S) [25] group and the band at 1660 cm^{-1} corresponds to v(C=O) carbonyl group. In IR of complexes these value are shifted towards lower side from 10-45 cm^{-1}. This indicates that both v(C=N) and v(C=S) in ligand 1,3 and v(C=O) group and v(C=N) of ligand 2 are coordinated to central metal ion in complex formation (**Fig.3a** and **3b**). The coordination of v(C=N) group is further supported by appearance of new v(M-N) band which appeared in the region from 409-553 cm^{-1} [26] and v(M-O) band which appeared in the region from504-553cm^{-1}[27]. Thus all the ligand are bidentate and ligand 1,3 coordinated through nitrogen and sulphur with central metal ion whereas ligand 2(L^2) coordinated through nitrogen and oxygen.

IR Bands due to anion: In the IR spectra of nitrato complexes chromium (III) of ligand 1,2(L^1 and L^2) shows three bands at 1412-1425(v_5), 1313-1315, 1203-1215(v_1). The difference in $v_5$and v_1 is 209 and 210cm^{-1} suggests monodentate behaviour of nitrate group in both the complexes of ligand (L^1&L^2).

The IR spectra of acetato complexes of Cr(III) of both the ligands show appearance of bands at 1420-1448, as vC=O and 1200-1202cm^{-1} as vC-O. The difference of v_5 and v_1 is 248 and 220cm^{-1} corresponds to monodentate behaviour of acetate group [28].

TABLE 2: IR SPECTRAL DATA OF Cr(III) COMPLEXES OF LIGA 1, 2, 3

Compound	v(C=N)	v(C=S)	v(C=O)	v(M-N)	v(M-O)
Ligand 1 (L^1)	1618	781	-		
[Cr(L$^1_2$)(NO$_3$)$_2$]NO$_3$	1595	745	-	491	
[Cr(L$^1_2$)(OAc)$_2$] OAc	1591	751		544	
Ligand 2 (L^2)	1577		1660		
[Cr(L$^2_2$)(NO$_3$)$_2$] NO$_3$	1550		1622	402	543
[Cr(L$^2_2$)(OAc)$_2$]OAc	1557		1632	440	504

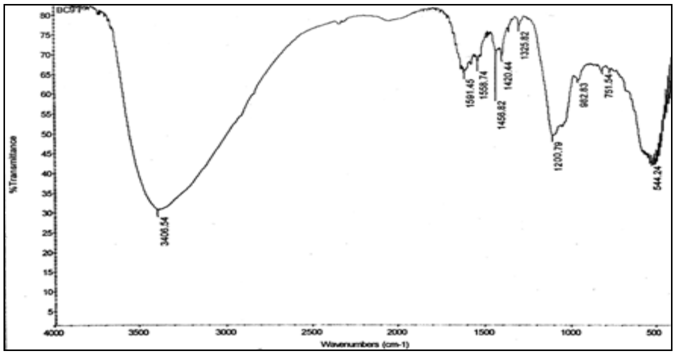


FIG. 3a: (IR SPECTRA OF [Cr(L1)2(OAc)2]OAc

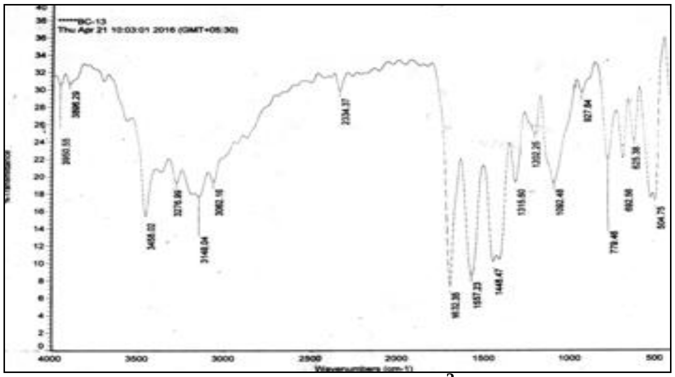


FIG. 3B (IR SPECTRA OF [Cr(L^2)$_2$(OAc)$_2$]OAc

Electronic Spectra: The magnetic moment of the chromium complexes was recorded at room temperature is 3.78-3.87 B.M. close to the spin only value also it indicates octahedral geometry around chromium ion. Three spin allowed transition were displayed by high spin chromium (III) complexes recorded in DMSO are [$^4A_{2g} \longrightarrow {}^4T_{1g}$ (P)], v_3;[$^4A_{2g} \longrightarrow {}^4T_{1g}$ (F)],v_2; [$^4A_{2g} \longrightarrow {}^4T_{2g}$(F)] ,$v_1$[29, 30].Various ligand field parameters *i.e.* Dq, B, β were calculated are listed in **Table 3**.

The β values of complexes under study indicates appreciable covalent character of the complexes under study.

TABLE 3: MAGNETIC MOMENT AND ELECTRONIC SPECTRAL BANDS OF Cr(III) COMPLEXES OF LIGAND 1, 2

Complexes	λ_{max}	μ_{eff}
[Cr(L$^1_2$)(NO$_3$)$_2$]NO$_3$	16675, 22941, 30,488, 38827	3.80
[Cr(L$^1_2$)(OAc)$_2$] OAc	17181, 22,948, 26,949, 32,206	3.78
[Cr(L$^2_2$)(NO$_3$)$_2$]NO$_3$	12,777, 17,130, 27021, 32,202	3.83
[Cr(L$^2_2$)(OAc)$_2$]OAc	17,299 ,22,222,25,235, 33,659	3.86

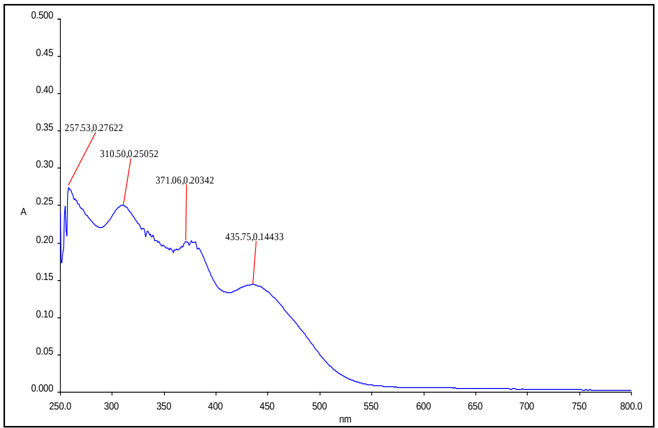


FIG. 4a: UV SPECTRA OF $[Cr(L^1)_2Ac_2]Ac$

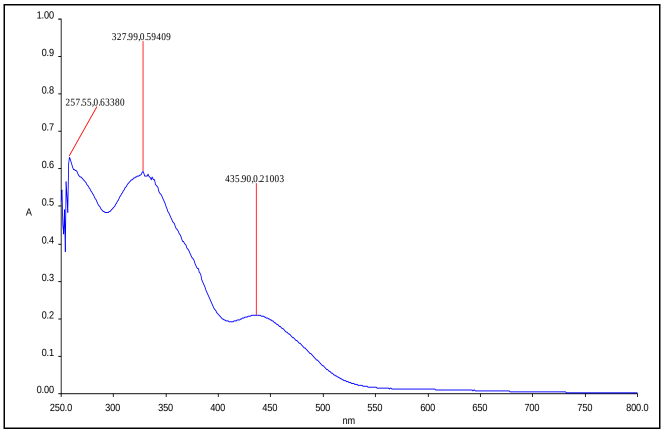
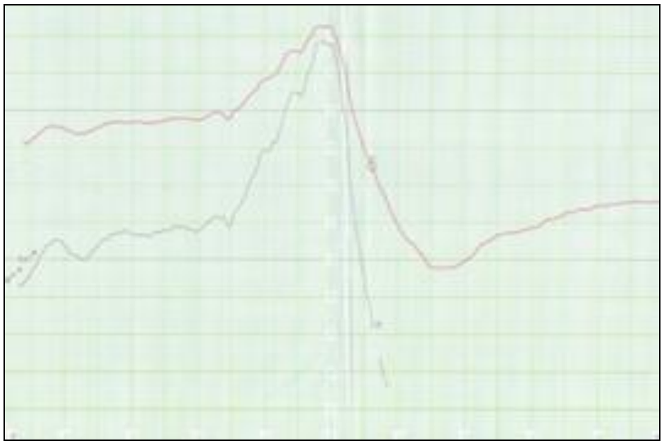


FIG. 4b: UV SPECTRA OF $[Cr(L^1)_2(NO_3)_2]NO_3$

EPR Spectra: The X-band EPR spectra of the complexes (**Fig. 5a & 5b**) under study recorded as polycrystalline sample at room temperature. The g_{iso} values obtained from the EPR spectra are recorded in **Table 4**. In The X- band spectra of all Chromium(III) complexes in solid state a broad signal in vicinity of $g_{iso} \approx 2.0$ is observed. No hyperfine line is observed so D and E parameters can not be calculated. The proposed geometry of all the Cr(III) complexes is octahedral.



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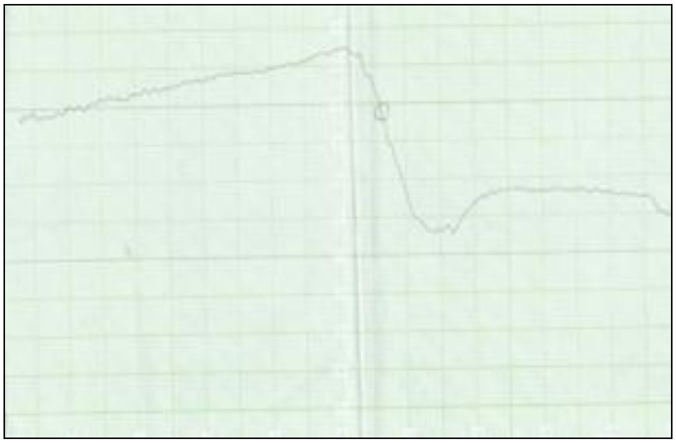

b

FIG. 5a & 5b: EPR SPECTRA OF $[Cr(L^1)_2(NO_3)_2]NO_3$ AND $[Cr(L^1)_2(OAc)_2]OAc$ COMPLEXES

TABLE 4: EPR SPECTRAL DATA OF Cr(III) COMPLEXES OF LIGAND 1, 2

Complexes	g_{iso}	Dq	B	β	LFSE
$[Cr(L^1_2)(NO_3)_2]NO_3$	1.946	1675	614	0.67	240
$[Cr(L^1_2)(OAc)_2]OAc$	1.988	1718	550	0.59	246
$[Cr(L^2_2)(NO_3)_2]NO_3$	1.978	1277	416	0.45	183
$[Cr(L^2_2)(OAc)_2]OAc$	1.958	1729	178	0.19	248

On the basis of above spectral study the following structures may be proposed for $[CrL_2X_2]X$ complexes of ligand L^1&L^2.

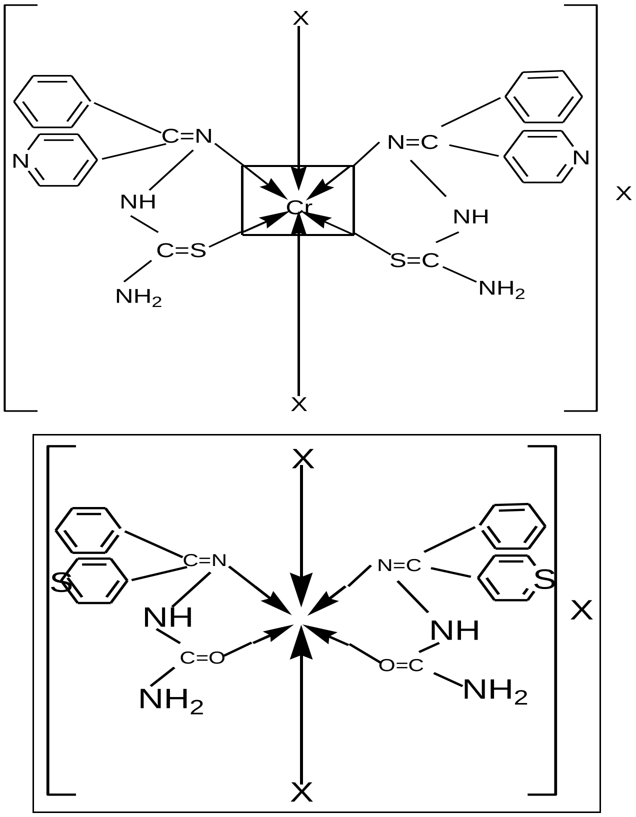

FIG. 7a, 7b: STRUCTURE OF Cr(III) COMPLEXES OF LIGAND 1, 2)(where $X=NO_3^-$,OAc^-)

CONCLUSION: The synthesised ligands and complexes were characterised by elemental analysis, IR spectroscopy, mass spectroscopy, UV-Vis, ^{1}H NMR spectroscopy and EPR spectral studies. The proposed study of complexes indicates octahedral geometry for all the chromium(III) complexes. Ligands were found to be bidentate which coordinates to metal through azomethine group as ν(C=N) and through sulphur/oxygen as ν(C=S)/ ν(C=O) group respectively.

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