

Synthesis, Characterisation and Electrochemical Studies of Co (III) Complex of (E)-4-(2-(4-Methoxyphenyl) Diazenyl) Benzene 1, 3 Diol Including Antibacterial Activity.

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Abstract: Co(III) obtained by persulphate oxidation of Co(II) forms a chelated complex with L_1 , a synthesised azo-dye. (already reported in J. Indian Chem Soc. Vol. 92 January 2015 pp. 43-50). Formation of the complex has been studied in both solid state and aqueous phase using different spectroscopic techniques. Co(III) form 1:3 metal ligand complex with L_1 at pH = 7.528. Thermal decomposition has been predicted from TGA-DSC analysis. Cyclic Voltametry of this complex has been studied to ensure the presence of Co (III) in complex $[Co(L_1)_3]$. The complex might be an innermetallic complex of 2nd order. Magnetic susceptibility of the complex $Co[L_1]_3$ has been taken at a constant magnetic field of 5 KG with powder sample in the temperature range 20-35K. The complex also shows higher antibacterial activity than L_1 . The structure of the complex has been predicted from elemental analysis, UV-Vis, IR, Mass spectrophotometry.

Keywords: Azo-dye Co(III) complex, Antibacterial activity, Cyclic Voltametry, TGA, UV-Visible.

I. Introduction

A large number azo-dye compounds have been ever synthesised and characterised which contains potential donor groups, most of which are bi-dentate or tridentate, having the ability to bind the metal ions forming differential varieties of complexes, and there is a vast literature there available on the metal azo-dye interaction [1]. Azo-dyes are of special significance as a colouring agent in textile Industry. Their brilliant colour has been known to involve in colour fastness[2], light fastness and wash fastness on relevant fabric. Moreover interaction with metal ions however increases the colour intensity [3] owing to the charge transfer. It is again very useful in textile industry in mordant technology. Many azo-dyes have their colours in aqueous medium distinctly different from that of its metal complex and such metal complex are suitably used as metal ion indicators in complexometric titrations [4], with vast application. Due to presence of azo-group which by itself is a potential co-ordinating group, the presence of other groups such as phenolic -OH or -NH₂ allow such compound to interact with cells or DNA that may be probed to study their interaction in several biological activity or in medicine[5]. However this particular area of research work has not been explored in this paper or there is not much data available showing interaction of metal azo- complexes with DNA. But antibacterial activity of these complexes have been investigated[6]. Our actual interest in sending on such type of complexes originate from the fact that when Co(II) complexes have been studied earlier but Co(III) complexes have not yet been explored. From academic point of view stereochemistry, stability and their magnetic moments are specially important.

Co(III) complexes of azo-dye have large analytical, industrial and biological application including anticancer activity[7] which are yet to be studied. In this paper, we present the results of an investigation aimed to accurately characterize the formation of a Co(III) complex with the already prepared azo-dye L_1 (MDD) [8] both aqueous solution and in crystalline state, the spectral pattern and redox behavior. TGA of this complex has also been studied to predict relative thermal stability of the complex.

1. Experimental

All chemicals and solvents are of the highest purity from commercial suppliers such as Merck, BDH etc. All chemicals are used without further purification. $CoSO_4$ (High grade purity) are lyed to prepare freshly precipitated $CoCO_3$ which is used to prepare $Co(ClO_4)_2$. It is purified by fractional crystallisation. It is the starting material for preparing $[Co(L_1)_3]$ complex. Azo-dye ligand L_1 has been recrystallised to get ligand of 99% its purity. Ammonium persulphate, sodium acetate (anhydrous), double distilled water, all are of analytical grade used for this purpose. For reference electrolyte used in CV, Tetrabutyl ammonium perchlorate of A.R. quality has been used.

Melting points of $[Co(L_1)_3]$ complex was measured on electrically operated melting point apparatus of Sunder Industrial Products, Mumbai, India without calibration. The UV-Vis absorption spectra was recorded in Perkin-Elmer Lambda 40 (UV-Vis) [2] spectrophotometer in aqueous medium. The infrared spectra were

recorded on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr discs ($4000 - 400 \text{ cm}^{-1}$). Elemental analyses (C, H, N, O) were carried out using a Perkin-Elmer 2400 II elemental analyser. Cyclic voltammetry experiments were performed using model no. DY2300 series potentiostat, Digi-IVY. Instrument was used for the analysis of TGA-DSC, SDT Q600 V8.2 Build 100.

2. Synthesis of $\text{Co(L}_1\text{)}_3$ Complex

Cobalt Perchlorate, $\text{Co(ClO}_4\text{)}_2$ (99.9%) is collected and is dissolved in 100ml triple distilled water to get a solution of 10^{-1} (M). To this solution was added 0.5 gm. Pure Ammonium per sulphate ($\text{NH}_4\text{)}_2\text{S}_2\text{O}_8$ followed by addition of 10 ml lique ammonia and the mixture is refluxed for 1 hr. This solution after cooling is mixed with a few crystal of NH_4I till excess perdisulphate is decomposed and oxygen evolution takes place. To this mixture is then added saturated solution of L_1 in methanol such that Co(III):L_1 is 1:3[9]. The mixture is then taken in a well stopped synthesis conical flask which is then placed over a magnetic stirrer followed by heating at constant temperature of 50°C for 2 hrs. The mixture is then filtered under suction pump. The deep brown solid is repeatedly washed by methanol, water mixture till the filtrate is almost colour-less. The deep brown residue is then re-crystallised.

3. Cyclic Voltammetry

Cyclic voltammetry experiments were performed using model no. DY2300 series potentiostat, Digi-IVY. The experiments were carried out using the conventional three-electrode system at 25°C Pt wire electrode served as the working electrode Ag/AgCl , KCl (Saturated) was used as reference electrode while a platinum wire served as the counter electrode and working electrode. Electrochemical measurements were performed in a 10 ml electrochemical cell. 5×10^{-3} (M) metal complex was prepared using 0.1M Tetrabutyl Ammonium Perchlorate (TBAP) solution. Tetrabutyl Ammonium Perchlorate was used as supporting electrolyte[10].

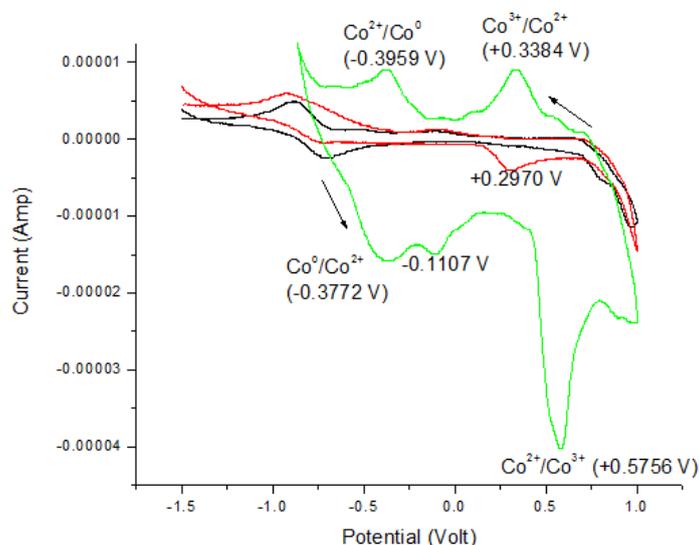


Fig. 1: Cyclic voltammogram of 5×10^{-3} (M) Co(III) L_1 complex is recorded using platinum electrode at scan rate 50 mVs^{-1}

Cyclic voltammetry of L_1 and its Co(III) complex was carried out in pure dimethyl Sulfoxide (DMSO) using tertiary butyle ammonium perchlorate as supporting electrolyte and Ag/AgCl , KCl (saturated) as reference electrode. The Co(III) complex of L_1 showed two reduction (cathodic) peak at $+0.3384\text{V}$ ($\text{Co}^{3+}/\text{Co}^{2+}$) and -0.3959V ($\text{Co}^{2+}/\text{Co}^0$) respectively in fig. 1.

The reduction peak obtained for L_1 was in excellent agreement with azo- group. For the complex the first reduction was attributed to reduction of $\text{Co(III)} \rightarrow \text{Co(II)}$ due to single electron gain $\text{Co(III)L}_1 / \text{Co(II)L}_1$ while the second-reduction was of $\text{Co(II)} \rightarrow \text{Co(O)}$ due to double electron gain $\text{Co(II)L}_1 / \text{Co(O)L}_1$.

In addition to these two reduction (cathode) peaks for the complex, there was two sharp oxidation (anodic) peak at -0.3772V which was due to generation of a $\text{Co}^0/\text{Co}^{2+}$ species Co^{2+}L_1 and at $+0.5756\text{V}$ $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ that was supported by a recent finding where an almost identical condition was used for a Co(II) complex. [8]. In addition oxidation peak could also be seen in the case of L_1 at $+0.2970\text{V}$. Whereas in Co(III)L_1 complex a small oxidation peak was appeared at -0.1107V . Plot of cathodic peak current I_{PC} with square root of scan rate ($v^{1/2}$) being linear, both the reductions for Co(III) complex fig. 2 indicate a diffusion controlled process with no adsorption on the electrode surface.

3.1 The Effect of Scan Rate

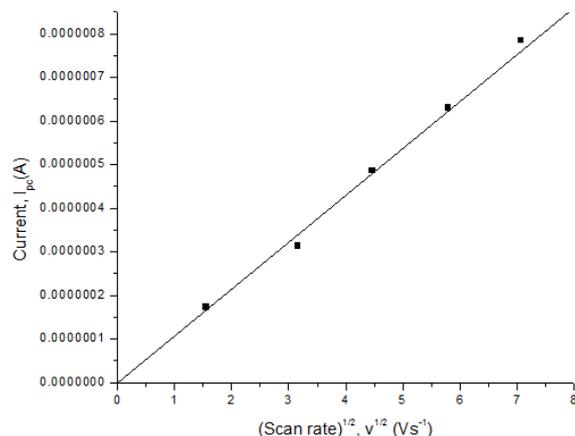


Fig. 2: Dependence of the cathodic peak current on the square root of scan rate for the reduction of Co(III) complex of L₁ in Dimethyl Sulfoxide (DMSO) as solvent.

This reduction of the complex is irreversibly in different solvents with increasing scan rates shows a negative peak potential shift as well as an increasing in current intensity.

The plot of I_p vs v^{1/2} for 5 mM complex solution at the surface of platinum electrode was shown in Fig. 2. As seen from Fig.1 suggesting that at sufficient over-potential the reaction is diffusion limited[10].

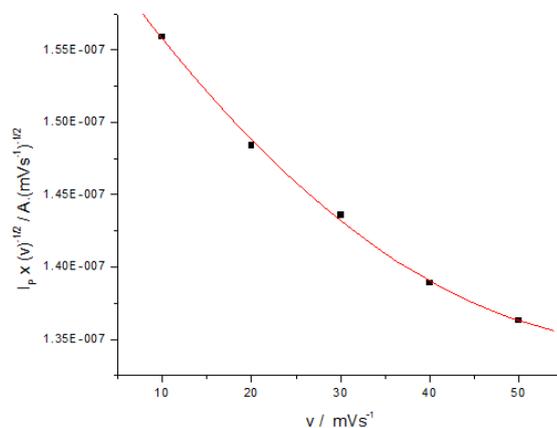


Fig. 3: Variation of the scan rate normalized current ($\frac{I_p}{v^{1/2}}$) with scan rate

Also a plot of the scan rate normalized current ($\frac{I_p}{v^{1/2}}$) Vs. scan rate (v) exhibits the indicative shape typical of an EC nature process Fig. 3.

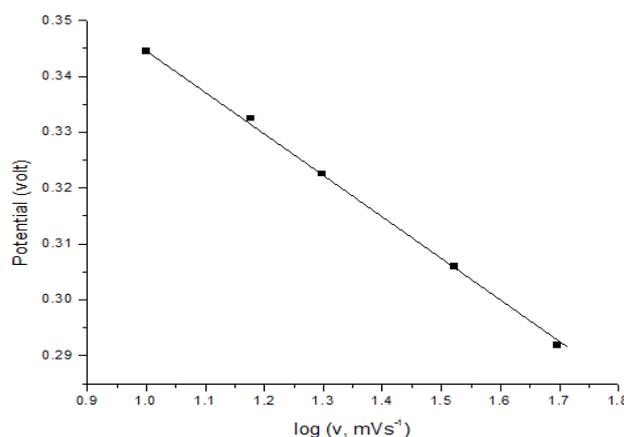


Fig. 4: Plot of E_{PC} Vs. log v

The E_{PC} of the reduction peak was also dependent on scan rate. The plot of E_{PC} Vs. $\log v$ was linear having a correlation co-efficient of 0.9951 in fig. 4 and this behavior was consistent with the EC nature of the reaction. Fig.5 shows a Tafel plot was drawn from data of the rising part of the current voltage curve recorded at scan rate of 100 mVs^{-1} .

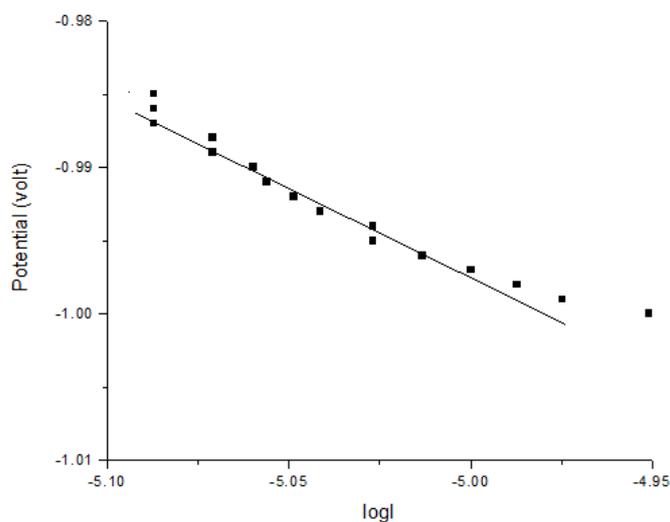


Fig. 5: Tafel plot derived from the current–potential curve recorded at scan rate 100 mVs^{-1}

3.2 Chronoamperometric Studies

Chronoamperometric measurements of Co(III)L_1 complex at platinum electrode were done by setting the working electrode potential at $+0.5\text{V}$ and used for the measurements of the diffusion co-efficient of Co(III)L_1 complex in fig. 6.

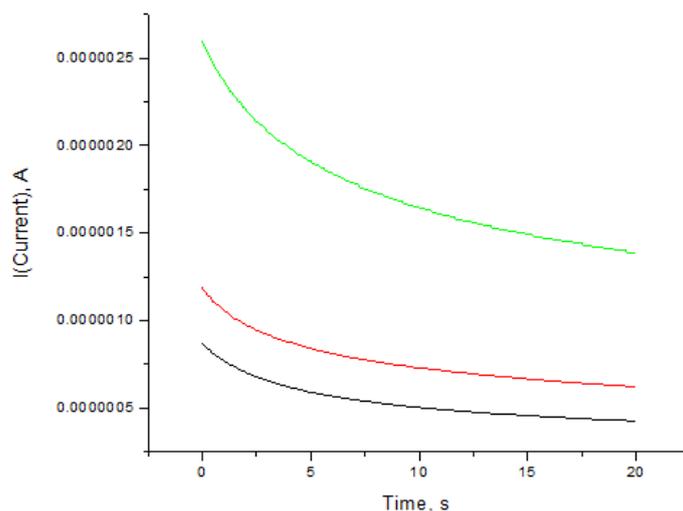


Fig. 6: Chronoamperometric response at Pt electrode for different concentration 0.5mM, 1.0mM, 2.0mM of Co(III)L_1 complex

In chronoamperometric studies the current for the electrochemical reaction of an electroactive material that diffuses to an electrode with a diffusion co-efficient (D) is described the Cottrell equation.

$$I = \frac{nFAD^{\frac{1}{2}}C}{(\pi t)^{\frac{1}{2}}}$$

Where D is the diffusion co-efficient and C is the bulk concentration in mol cm^{-1} .

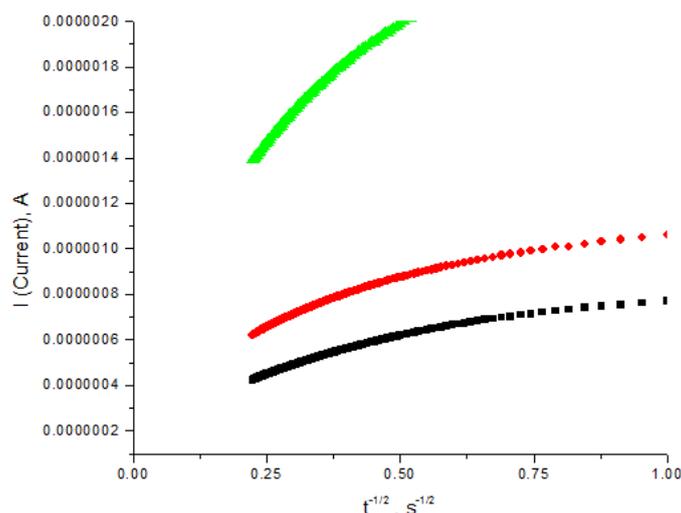


Fig. 7: plot of I Vs $t^{-1/2}$ for different concentration 0.5mM, 1.0mM, 2.0mM

Under diffusion control, a plot of I vs $t^{-1/2}$ will be linear and from the linear plot calculate the slope value and hence value of D can be obtained. Fig-7 shows a chronoamperogram of a Co(III)L₁ complex in DMSO solution, recorded for a platinum electrode.

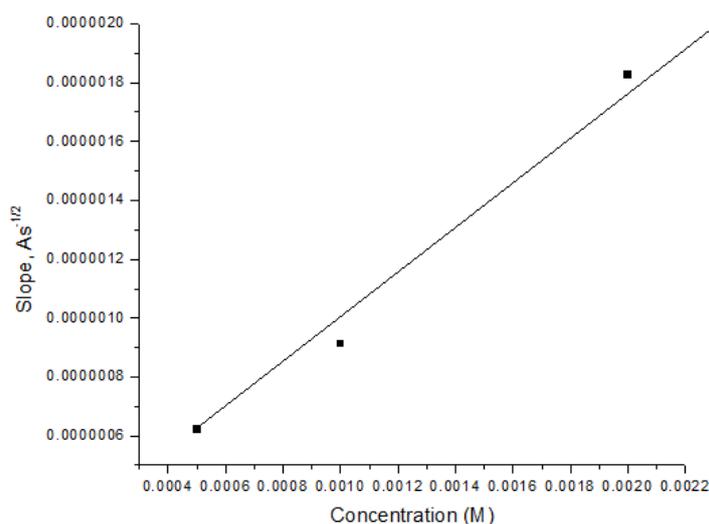


Fig. 8: Plot of the slope of straight lines against the complex concentration(0.5M,1M,2M)

The fig. 7 shows experimental plot of I Vs. $t^{-1/2}$ for a Co(III)L₁ complex in DMF solution, recorded for a platinum electrode. From the slope of this plot we calculated a diffusion coefficient of $6.95 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ for a Co(III)L₁ complex in DMF solution at platinum electrode. Draw another plot, slope of straight lines Vs. concentration of the complex Fig.8 .

II. Result and Discussion

Physical properties and elemental analysis (C,H,N,O) of Co(III)L₁ complex[11] are recorded in Table 1. It is suggested that a single spot is located in TLC, which corresponds to high purity of the complex and is supported by a low percent error (within 5%) in elemental analysis [5] and decomposition temperature has been recorded.

Table 1: Some physical properties of synthesized complex Co(L₁)₃

Name of complex	Empirical formula	Molecular Weight Found (Calc.)	R _f value	pH	Colour	M.P (°C)
Co(L ₁) ₃	Co(C ₁₃ H ₁₁ N ₂ O ₃) ₃	779.43 (787.93)	0.68	6.31	Deep brown	302

Table 2: Elemental Analysis of Synthesized Complex Co(L₁)₃

Name of complex	yield %	Carbon % Found(Calc.)	Hydrogen % Found(Calc.)	Nitrogen % Found(Calc.)	Oxygen % Found(Calc.)	Cobalt % Found(Calc.)
Co(L ₁) ₃	75	56.43(59.40)	3.97(4.18)	10.16(10.68)	17.37(18.27)	7.10(7.47)

4. FT-IR Studies

The molecular structure of the ligand L₁ has been predicted by no. of instrumental analysis as reported in the reference no. 2. Regarding the IR spectrum of Co(L₁)₃, by comparison with the same of L₁ already reported it is suggested that free OH band (at 3753.64 cm⁻¹ as a weak start stretching band) [12]. and one hydrogen bonded OH band (3456.82 cm⁻¹ as a broad band) are almost missing or appear as very weak band with high % T as specific in the figure 1. Again the figure 1 shows a strong band of 1246.75, 1177.33, 1107, 1025.94 cm⁻¹ which are in conformity with the characteristic band for C-O stretching as mixed band of alkyl C-O and aryl C-O stretching.

It is probable that the ligand L₁ being an unsymmetrical either, the two C-O bonds coupled to give antisymmetrical and symmetric C-O stretching absorption for which three different IR bands have appeared.

The band appearing at 1462.74 and 1393.32 cm⁻¹, the value distinctly less than that obtained in the free ligand L₁ in bending frequency. This lowering of $\nu_{N=N}$ in Co(L₁)₃ compared to that in L₁ (free) might correspond to partial drifting of π electron cloud towards metal.

Bond order in N-N bond slightly decreases.

This fairly indicate M – N(=N) σ bonding, ultimately leading to chelation. However linear stretching of N=N is absent as it is IR inactive.

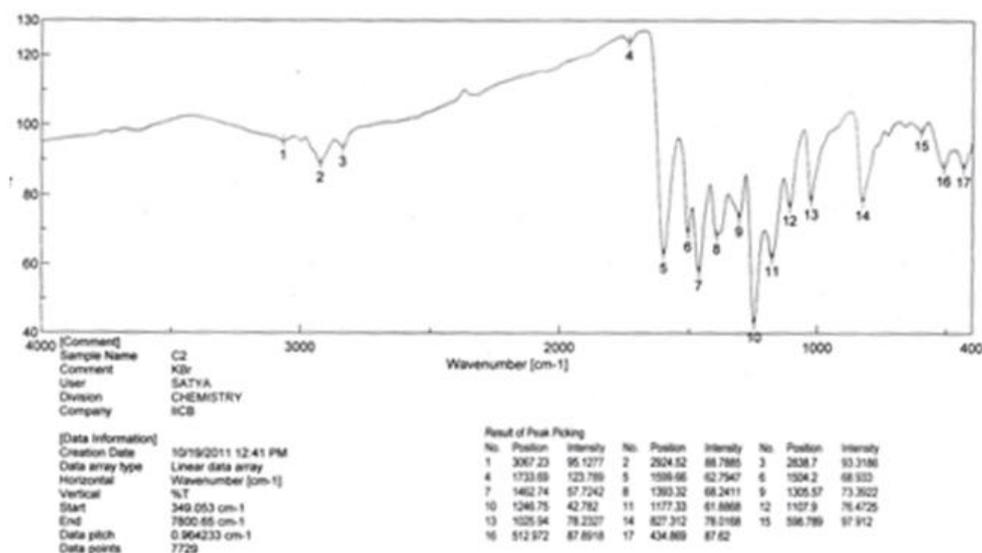


Fig. 9: IR of Cobalt Complex

From literature, it is also known aromatic C=C should appear between 1500 – 1600 cm⁻¹, recognized as 1504 (%T = 68.93%) and 1599.66 (% T = 62.79%) cm⁻¹. If the presence a very weak band nearing to 400 cm⁻¹ might correspond to M-O stretching. However M-N bonding is predicted from lowering of azo $\nu_{N=N}$ (bending) relative to that in free L₁. So on an average the IR stretching and bending as located in the spectrum roughly support the presence of functional groups and N-nitrogen, M-Oxygen binding in the synthesized complex.

A band appearing at 2924.52 cm⁻¹ is very close to the Arc-H band of theoretically known to be 3030 cm⁻¹.

5. Electronic Spectrum: (UV-VIS)

Direct experimental data of electronic spectra of Co (III) complex of L_1 has been taken from the $10^{-4}M$ aqueous solution of anticipated tris chelate complex, $Co(L_1)_3$ in Perkin Elmer Lambda 40 (UV-Vis) spectrophotometer (fig.10). The result gives two distinct ligand field bands at 465 nm ($\nu_1 = 21505 \text{ cm}^{-1}$) and 339 nm ($\nu_2 = 29498 \text{ cm}^{-1}$). The data available is well comparable to that obtained from a well known spin-paired octahedral Co(III) complex of 'en' (ethylene diammine) which is known to be fairly strong field ligand. The complex is known to be $[Co(en)_3]^{+3}$ and it shows absorption band 465 nm ($\nu_1 = 21500 \text{ cm}^{-1}$) and 338 nm ($\nu_2 = 29600 \text{ cm}^{-1}$) [20]. Thus the bands actually observed from $Co(L_1)_3$ (fig 10) are spin allowed and may be assigned to the transitions (a) ${}^1A_{1g} \rightarrow {}^1T_{1g} (\nu_1)$ (b) ${}^1A_{1g} \rightarrow {}^1T_{2g} (\nu_2)$ from the splitting of one excited RS terms 1I in high octahedral ligand field. The bands can be predicted from Tanabe-Sugano diagram (Fig. 11) using the informations on the R.H.S of cross over regions in T.S diagram[21].

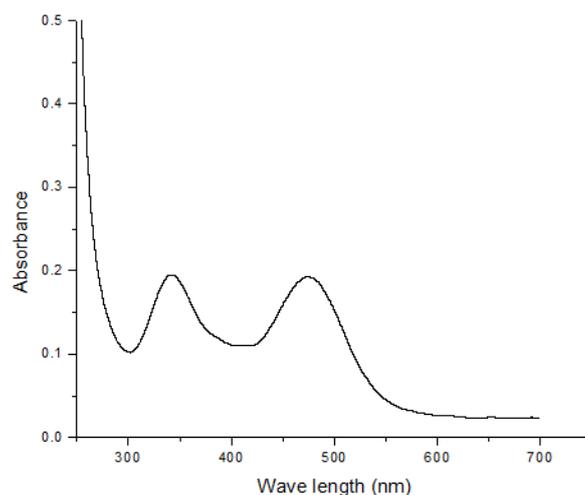


Fig. 10: UV-Vis of the Cobalt Complex

Fig.11: Spin-allowed transitions

Other transitions are spin-forbidden and lying in far UV region and hence such bands are very weak and not found in visible region. It is to be mentioned that this complex $Co(L_1)_3$ will have a redned value of B ($= 550 \text{ cm}^{-1}$) from $\nu_1/B = 39$ in T.S diagram, and $15B^7 = (\nu_3 + \nu_2 - 3 \nu_1)$, [ν_3 has not been shown graphically]. The free ion B value of Co^{+3} is 1100 cm^{-1} indicating distinct Nephelauxetic effect $\beta = B'/B = 550/1100 = 0.5$. So Co^{+3} due to its some ability to covalent interaction with π clouds of the ligand L_1 might contribute something to selected CT bands of $L_1 \rightarrow M$ where L_1 is partly reducing and M is oxidizing in character. Identification of CT bands can be roughly obtained from a proper M.O treatment of $Co(L_1)_3$ complex. The information collected so far above strongly indicate that the Co(III) complex that have here been synthesized and purified, of course, should be a low-spin octahedral in nature and the colour (reddish-brown in aqueous solution) of the complex is correctly interpreted from the absorption spectra (fig 10) where the complex solution absorbs blue (early part) and UV region of the spectral shape.

6. Mass Spectral Studies

Mass Spectral analysis of Co (III) complex is in keeping with the stoichiometry $CoC_{39}H_{33}N_6O_9$ which is roughly in agreement with a tris chelate complex of Co(III) formulated as $Co(C_{13}H_{11}N_2O_3)_3$. Highest

molecular ion peak was found at $m/z = 779.43$ (calc. 787.933). As known from the structure of the ligand L_1 (reported in J. Indian Chem. Soc. Vol. 92, Jan-2015 pp 43-50) the ligand is a N,O donor a bidentate one and also from literature suggests that most of trischelate Co(III) complex with such a fairly strong ligands (L_1) are spin paired O_h complex. Spin-pairing of the Co(III) complex is supported from its diamagnetic properties obtained from spin only magnetic moment (μ_s) at 0-20K recorded by negative χ_M at low temperature $7-9^\circ\text{C}$ [$\mu_{\text{eff}} = 2.83 (\chi_M T)^{1/2}$ B.M], χ_M was taken at constant magnetic field of 5 with powdered samples of the Co(III) complex in the temperature range 10-300K. At 300K the χ_M value become positive and μ_{eff} is higher than 2.83 B.M[13]. This indicate the excitation of one electron from t_{2g} to e_g level.

The trischelated octahedral structure of the complex is also supported from its electronic spectra.

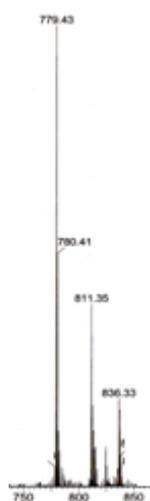


Fig. 12: Mass spectra of Cobalt Complex

The second peak obtained at $m/z = 780.41$ (calc. 790.933) is probably due to isotopic exchange between protic ${}^1\text{H}^1$ and ${}^2\text{D}^2$. Thus $m/z = 780.41$ may correspond to $\text{Co}(\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_3)_3$ where non coordinated phenolic OH is leveled as OD. The peak at $m/z = 811.35$ (calc. 810) may correspond to some sodium salt, one phenolic H may be replaced by Na. There are also other molecular ion peaks like at $m/z = 545.18$ (~50%) (calc. 544.98) which might appear due to splitting of $\text{Co}(\text{L}_1)_3$ to $[\text{Co}(\text{L}_1)_3]^+$, a change from trischelate to bischelate. The peak at $m/z = 568.26$ (~25%) may occur due to partial attachment of Na^+ to $[\text{Co}(\text{L}_1)_2]^+$ in place of phenolic H.

Fig. 13: Probable structure of Cobalt Complex $\text{Co}(\text{L}_1)_3$

7. TGA-DSC Studies

The thermo gravimetric analysis (Fig.14) gives information about the thermal stability of the complex and suggests a general scheme for thermal decomposition of this chelates. In the present [14] investigation, heating rates were suitably controlled at $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere . The thermo gram of the Co(III) complex shows two decomposition steps (Table-3) within the temperature range 25-293^o C. The first step involves loss of water molecules around 170-223^o C with an estimated mass loss 10.01% (calculated mass loss 9.13%), the second step involves loss of one molecule of ligand around 223 - 293^o C with an estimated mass loss 33.10% (calculated mass loss 33.63%). This thermo gram is (Fig.15) accompanied by two exothermic peak at 207 and 278^o C on the DSC curve[9].

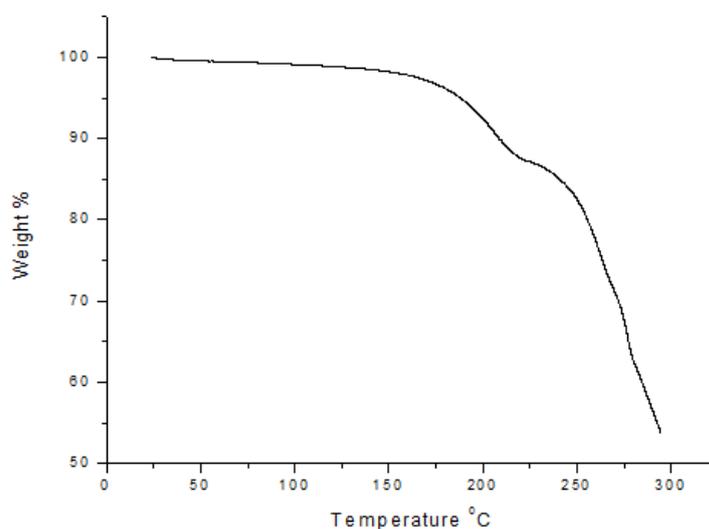


Fig. 14: TGA curve of Cobalt Complex

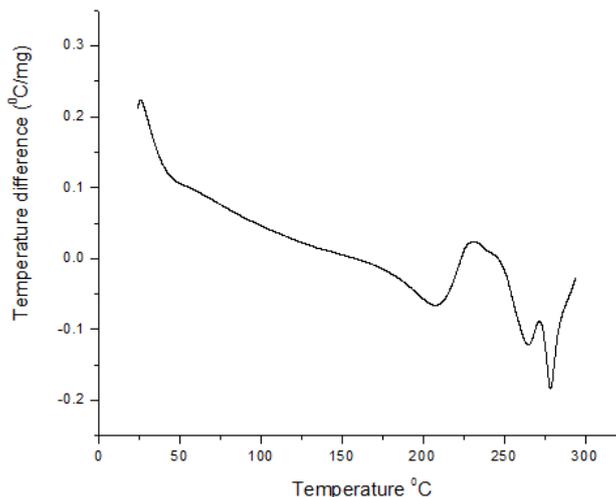


Fig. 15: DSC curve of Cobalt Complex

Table 3: Thermal analytical results (TGA,DSC) and micro analytical data of complex

Metal Complex	TGA Range(°C)	Mass loss % Estim.(Calc.)	Assignment	DSC Peak (°C)	Conductivity (S.cm ² .mole ⁻¹)	μ _{eff} B.M
Co(L ₁) ₃	170-223	10.01 (9.13)	Water loss	207	796.87	>2.83
	223-293	33.1 (33.63)	Loss of one ligand	278		

8.Antibacterial Activity

The Co(III) complex was tested against the bacteria Escherichia coli, Bacillus subtilis, Staphylococcus aureus, Swmonellatyphi. Diameter of incubation zone : 15 mm, concentration of bacterial growth 200 μg/mL, in DMSO solution(-) : Inactive. The data in the Table 4, it is observed that the Co(III) complex is more active against all the test organisms , Bacillus subtilis and Staphylococcus aureus and as well as more active compared

to the L_1 . Such increased activity of the Co(III) complex can be explained with respect to Overtone's concept and Tweedy's chelation theory[7]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only the lipid-soluble materials whose liposolubility is an important factor, which controls the antibacterial activity. On chelation, the polarity of the Co(III) ion is reduced[15]. to a great extent due to the overlap of the ligand, L_1 orbital and partial sharing of the positive charge of the Co(III) ion with donor groups. On the other hand it increases the delocalization of π electrons over the whole chelate ring and enhances the lipophilicity of the Co(III) complex. This increased lipophilicity enhances the penetration of the Co(III) complex into lipid membranes and blocking of the cobalt metal binding sites in the enzymes of micro organisms. This Co(III) complex also disturb the respiration process of the cell[16]. and thus block the synthesis of proteins, which restricts further growth of the organisms.

Table 4: Antibacterial activity of Co(III) complex

Metal Complex	Rate of oxidation (Antibacterial activity)				
	Control	Swmonellatyphi	Staphylococcus aureus	Escherichia coli	Bacillus Subtilis
Co(L ₁) ₃	7	11	12	14	16

III. Conclusion

The tris chelate complex of Co(III) azo-dye has been synthesized and structure of the complex has been established by elemental analysis, IR, electronic, mass spectroscopy, molar conductance. It has also potential application for high density optical recording media due to absorption spectra and high thermal stability. The complex act as potent bactericidal agent. Further work with analogs is needed.

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