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Synthesis, spectral, thermal and antibacterial studies of oxovanadium(IV) complex of an azo dye derived from 4–aminoantipyrine

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Abstract

Synthesis of oxovanadium (IV) complex with anazodye 4–[(*E*)–(4–hydroxy–2,5–dimethylphenyl) diazenyl]–1,5–dimethyl–2–phenyl–1,2–dihydro–3*H*–pyrazol–3–one (HL) derived from 4–aminoantipyrine and 2,5-dimethylphenol are reported. The complex has been characterized by elemental analysis, molar conductance, magnetic susceptibility data, FT–IR, UV–Vis, NMR and ESR spectra.The physico–chemical studies and spectral data indicate that HL acts as a bidentate chelating ligand. The thermal behaviour of the complex was investigated by thermogravimetric techniques. The complex is found to be neutral and a square pyramidal geometry has been tentatively proposed. The ligand HL and complex were screened for antibacterial activity.

Keywords: Azo dye, Oxovanadium(IV) complex, Thermal studies, Antibacterial

1. INTRODUCTION

In the last few years, there was growing interest in the synthesis and physico-chemical studies of first row transition metal complexes with a number of azo dye ligands [1]. Azo dyes are used for dyeing of polyester fabrics,cotton and wool [2], certain metal complexes of azo dyes were also found to be effective for non–linear optical materials [3,4], IR cut–off filters, water ink-jet links, recordable digital video disks, etc [5]. Metal complexes of azo dye ligand have played a major role in the development of coordination chemistry.The interest of chemists in the study of oxovanadium(IV) complexes is due to their powerful influence in inhibiting the function of a large range of enzymes and promoting the function in effect of diabetic animals and these types of complexes are reported to have antiviral, antitumor and antibacterial activities [6,7].They are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis [8].In the present study the synthesis and spectral characterization of oxovanadium(IV) complex of an azo dye, HL was reported along with its thermogravimetric analysis and antibacterial activity.

2. EXPERIMENTAL

The chemicals used for the synthesis of the compounds were obtained from Merck Chemical Company, Mumbai, India and used without any further purification.The solvents used were of AR grade.

2.1. Synthesis of ligand (HL)

Synthesis of ligand, HL ($C_{19}H_{21}N_4O_2$) was carried out by diazotization of 4-aminoantipyrine followed by coupling reaction with 2,5–dimethylphenol [9]. The product (HL) obtained was filtered under suction, washed with cold water, dried and recrystallized from methanol.The purity was ascertained by TLC. The structure of HL is shown in Figure 1.

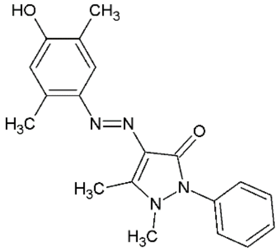

Fig. 1: Structure of dimethylphenol azoantipyrine, HL

2.2. Synthesis of oxovanadium(IV) complex

The oxovanadium complex was prepared by the method reported earlier [10]. A hot ethanolic solution (20 mL) of vanadyl sulphate hydrate (2 mmol) was added to a hot ethanolic solution (20 mL) of the ligand (2 mmol) and refluxed on a water bath for about 3–5 hours.The resulting solution was concentrated to half of its volume and allowed to cool. The solid complex formed was filtered and washed with ethanol and finally dried over calcium chloride in a desiccator.

2.3. Characterization

The melting points of the compounds were studied by using Analab melting point apparatus. FT-IR spectra of ligand and complex were recorded using KBr pellets on a Perkin Elmer Spectrum 65 FT-IR spectrophotometer in the region 400–4000 cm^{-1}. The UV-Vis absorption spectrum was measured in the range 200–800 nm using quartz cuvette on a Perkin Elmer Lambda 25 UV-Vis Spectrophotometer in methanol solution and its ^1H NMR spectrum was recorded on a (DMSO-d6, ppm) 500 MHz Bruker/ TOPSIN NMR instrument using TMS as a reference. Elemental analysis(C, H, N) were carried out by CHNS Rapid analysis instrument.The electron spin resonance (ESR) measurements of the complex at liquid nitrogen temperature were recorded on Electron Spin Resonance Spectrometer-JEOL equipment.Vanadium and sulphate were estimated in the complex by standard methods [11,12].The molar conductance of the complex in methanol solution (10^{-3} M) at room temperature was measured using a Systronics direct reading conductivity meter. Magnetic susceptibility of the complex was measured at room temperature (28±2 °C) on a Sherwood Scientific Magnetic Susceptibility Balance.The thermo gravimetric measurements were made on Shimadzu DTG–60 differential thermogravimetry equipment at a heating rate of 10 °C/ min in nitrogen atmosphere with the temperature range 0–1000 °C.The antibacterial studies of the ligand and complex were conducted at Biogenix Research Centre, Valiyavila, Thiruvananthapuram.

3. RESULTS AND DISCUSSIONS

The ligand, HL and complex are non-hygroscopic solids. The ligand melt in the range 239–240 °C and the complex remain intact up to 300 °C. The complex is soluble in organic solvents like chloroform, DMF and DMSO. The molar conductance of 10^{-3} M solution of the complex exhibited non-electrolyte behaviour in methanol. The results of elemental analysis and magnetic susceptibility values of the complex are listed in Table 1.

Table 1: Analytical data of ligand and complex

Ligand/ complex	**Color**	**% of C**		**% of H**		**% of N**		**% of S**		**% of V**		**μ_{eff} in BM**
		Obs.	**Cal.**	**Obs.**	**Cal.**	**Obs.**	**Cal.**	**Obs.**	**Cal.**	**Obs.**	**Cal.**	
HL	Red	66.87	67.85	4.55	5.93	15.96	16.21	–	–	–	–	
[VO(HL)(SO_4)]	Dark brown	45.01	45.69	4.43	4.01	11.49	11.22	6.62	6.41	10.86	10.2	1.74

3.1. Spectral measurements

The characteristic IR spectral assignments of ligand and complex are presented in Table 2. A new band is formed at ~ 3434 cm^{-1} (instead of 3118 cm^{-1}) [13] which implies that the H-bond of ligand was broken and the OH group in the ligand does not participate in coordination with the VO(IV) ion. The stretching vibration of C=O in the pyrazolone ring [14],of the ligand is shifted to ~1596 cm^{-1} in the complex showing the participation of the C=O group in coordination. The stretching vibration N=N group exhibits a negative shift to 1444 cm^{-1} [15] in the complex which indicates the participation of N=N group of the ligand in the complex formation. A new band is formed at 974 cm^{-1} in the spectrum of the complex, which indicate a strong V=O stretching band [16,17]. Thus IR data suggest neutral bidentate ligand behaviour in the complex. Also the IR spectra of the complex shows a weak intense band which may be due to νV–N (490 cm^{-1}) [18] and νV–O respectively.The presence of an ionic sulphate group in the complex is confirmed by the appearance of three bands at 1130–1135, 955–960 and 602–608 cm^{-1} [17] respectively.

Table 2: Spectral measurements of VO(IV) complex of HL

Ligand/ complex	**IR spectra $\nu(cm^{-1})$**	**NMR (ppm)**	**UV-Vis spectra (in ethanol) $\nu(cm^{-1})$**	**ESR**
HL	3118 (OH), 1635(C=O), 1494 (N=N)	δ 9.85 (s, proton of OH group), δ2.65 (s, proton of >C–CH_3), δ3.37 (s, proton of N–CH_3), δ 7.25-7.42 (m, protons of phenyl rings)	39062 ($\pi\rightarrow\pi^*$) 26881 ($n\rightarrow\pi^*$)	-
[VO(HL)(SO_4)]	3434 (OH), 1596 (C=O), 1444 (N=N), 974 (V=O), 490 (V–N), 1130-1135(SO_4) 955-960 (SO_4)	δ 10.2 (s, proton of OH group)	38910 ($\pi\rightarrow\pi^*$) 31545 ($n\rightarrow\pi^*$) 14814 (d- d)	A_{ll} (200), $A_{\perp}$lar (80), A_{av} (120), g_{ll}(2.543), $g_{\perp lar}$(2.19), g_{av}(2.3076)

The assignments of ^1H NMR spectrum of HL is based on earlier reports [19, 20] and listed in Table 2. On analyzing the spectrum of [VO(HL)SO_4], the presence of singlet due to phenolic proton indicates the non-participation of the –OH group during coordination, which is also confirmed by the IR spectra.

The electronic spectral bands of VO (IV) complexes of HL recorded in methanol are given in Table 2. The $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions observed in the electronic spectra of the ligand appear in the spectra of the complex. One more band is observed in complex in the region 14814 cm^{-1} which may be due to d-d transition [21, 22].

3.2. ESR spectrum

The X-band ESR spectrum (Figure 2) of an oxovanadium(IV) complex was recorded in DMSO at room temperature and at nitrogen temperature (77K) and analyzed by the method of Mishra et al [23,24].The room temperature ESR spectra show eight lines,which are due to hyperfine splitting arising from the interaction of the unpaired electron with a ^{51}V nucleus having the nuclear spin which confirms the presence of a single oxovanadium(IV) cation as the metallic centre in the complex.The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and only g-average values are obtained. However the anisotropy is clearly visible at liquid nitrogen temperature and eight bands are observed separately which are in good agreement for a square pyramidal vanadyl complexes [25–27].The values are measured from the spectra are A_{ll}, $A_{\perp lar}$,A_{av},g_{ll}, $g_{\perp lar}$, g_{av}(Table 2) which are in good agreement for a square-pyramidal structure.

Fig. 2: ESR spectrum of [VO(HL)SO_4]

3.3. Magnetic susceptibility

The oxovanadium(IV) complex was found to be air stable and exhibit a magnetic moment at room temperature in the solid state. Oxovanadium(IV) has an electronic configuration of [Ar] $3d^1$ and hence has a single unpaired electron.The magnetic moment values of the vanadyl complexes ranges from 1.71–1.76 BM which corresponds to a single electron of the $3d^1$ system of square pyramidal [28] oxovanadium(IV) molecule.The magnetic moment value of synthesized [VO(HL)SO_4] is 1.74 BM and is shown in Table 1.

3.4. Thermo gravimetric analysis

Thermal studies were carried at the heating rate 10 °C/ min in nitrogen gas is given in Figure 3. The complex shows a plateau up to 210°C which indicates that the complex is stable up to 210 °C and no coordinated water molecule is present in the complex. The TG curve shows two stage decomposition, the first stage corresponds to a mass loss of 16.61% (210–290 °C) which can be assigned to the anionic part,the second stage corresponds to a mass loss of 80.76% (410–550 °C),to the complete decomposition of the complex to give VO_2. The16.61 and 80.76% percentage mass loss during the first and second stage decomposition is in good agreement with the theoretical value.

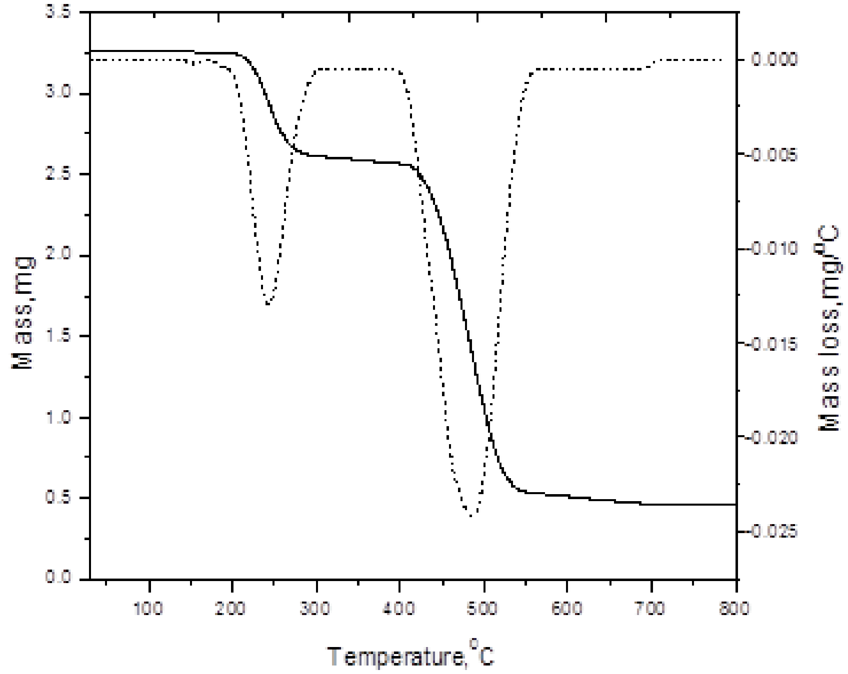

Fig. 3: TG and DTG curves of $[VO(HL)SO_4]$

The computational details and the kinetic parameters of the two stages of thermal decomposition of the complex $[VO(HL)SO_4]$ are given in the Table 3. The Coats-Redfern plots of the two stages of decomposition are given in Figures 4(a) and (b).

The energy of activation for the first stage decomposition is found to be 216.27 kJ/mol and that of second stage is 236.63 kJ/mol. The values of the correlation coefficient (r) are closer to unity indicating that the calculated kinetic parameters (Table 4) fit perfectly with the experiment.

Table 3: Computational details of the I and II stages of decomposition of $[VO(HL)SO_4]$

Temp (°C)		mg		TK		RT		W		A		gα		CR	
I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
210	410	3.24	2.56	483	683	2.07039	1.46413	0	0	0	0	0	0	-	-
220	420	3.20	2.53	493	693	2.02840	1.44300	0.04	0.03	0.0645	0.0148	0.0689	0.0149	-15.0751	-17.283
230	430	3.12	2.45	503	703	1.98807	1.42248	0.12	0.11	0.1935	0.0543	0.2400	0.0566	-13.8683	-15.981
240	440	2.99	2.34	513	713	1.94932	1.40252	0.25	0.22	0.4032	0.1086	0.6756	0.1183	-2.87259	-15.272
250	450	2.85	2.19	523	723	1.91205	1.38313	0.39	0.37	0.6290	0.1827	1.6956	0.2123	-11.9911	-14.716
260	460	2.74	2.00	533	733	1.87617	1.36426	0.5	0.56	0.8064	0.2765	4.1666	0.3513	-1.12993	-14.240
270	470	2.67	1.76	543	743	1.84162	1.3459	0.57	0.8	0.9193	0.3950	11.400	0.5714	-0.16061	-13.781
280	480	2.64	1.54	553	753	1.80832	1.32802	0.6	1.02	0.9677	0.5037	30.000	0.8389	-9.22952	-13.423
290	490	2.62	1.28	563	763	1.77620	1.31062	1.0	1.28	-	0.6321	-	1.2973	-	-13.014
-	500	-	1.05		773	-	1.29366	-	1.51	-	0.7456	-	1.9658	-	-12.624
-	510	-	0.84		783	-	1.27714	-	1.72	-	0.8494	-	3.1533	-	-12.177
-	520	-	0.69		793	-	1.26103	-	1.87	-	0.9234	-	5.2289	-	-11.697
-	530	-	0.6		803	-	1.24533	-	1.96	-	0.9679	-	9.1631	-	-11.161

$CR=\ln\frac{g(\alpha)}{T^2}$, n=2, r=0.99945

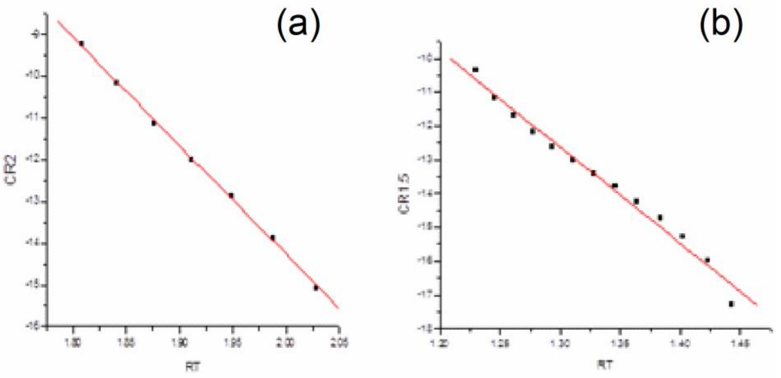

Fig. 4: (a) Coats–Redfern plot of stage I decomposition (b) Stage II decomposition

Table 4. Kinetic parameters for the thermal decomposition of $[VO(HL)SO_4]$

Stage	Peak (°C)	Activation Energy (E) (kJ/mol)	Pre-exponential Term (A) (S^{-1})	Entropy of activation(ΔS) ($JKmol^{-1}$)
I	243	216.27	1.0898×10^{14}	–214.842
II	486	236.63	1.8274×10^{14}	–243.967

On the basis of all the above spectral data and physico-chemical studies, a square pyramidal geometry (Figure 5) has been tentatively proposed for the complex.

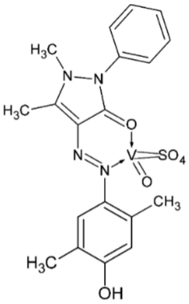

Fig. 5: Suggested structure of [VO(HL) SO4]

3.5. Antibacterial activity

The ligand HL and the complex $[VO(HL)(SO_4)]$ have been screened for their possible antibacterial activity by Agar–Well Diffusion method against Staphylococcus aureus and E coli bacteria at different concentrations (25, 50, and100 µl).The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well. Gentamycin was used as a positive control. From the result, it is clear that both the ligand and the complex show the antibacterial activity (Staphylococcus aureus and E–coli) at different concentrations.

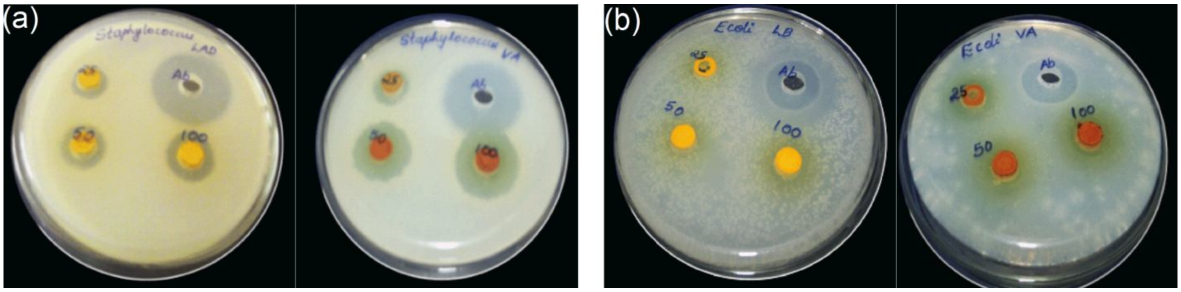

Fig. 6: Antibacterial activity of the ligand HL and its complex $[VO(HL)SO_4]$ towards (a) Staphylococcus (b) E-coli

4. CONCLUSIONS

The dimethylphenol azo antipyrine (HL) was synthesized by diazotization and coupling reaction. The synthesized oxovanadium complex was characterized by elemental analysis, molar conductance, magnetic susceptibility data, FT-IR, UV–Vis, NMR and ESR spectral studies. The molar conductance of 10^{-3} M solution of the complex exhibited non–electrolyte behaviour in methanol. The physico-chemical studies and spectral data indicate that the complex has square-pyramidal structure and the ligand HL coordinate to metal ion through the carbonyl oxygen and nitrogen of azo moiety. The thermal behaviour of the complex was investigated by thermogravimetric techniques and verifies the Coats-Redfern equation.The ligand HL and complex were screened for antibacterial activity towards staphylococcus aureus and E-coli.

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