

SYNTHESIS AND STRUCTURAL STUDIES OF OXOVANADIUM (IV) COMPLEXES

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Abstract; Complexes containing amide group ligands are prepared by condensing the anhydride and amines in ether solution. These were investigated by various spectral studies. The complexes of vanadium are prepared by refluxing amide ligand and vanadyl sulphate in methanolic solution. These complexes were studied by CHN, Infrared, Electronic, Electron spin Resonance and Thermogravimetric, Differential Thermal Analysis Studies to evaluate the structures.

Key words; Amide group ligands, Oxovanadium complexes, Elemental analysis, IR, Electronic, ESR spectrum, TGA, DTA studies.

Introduction:

Proteins possessing amide bonds are building blocks in biological systems. These incorporating a metal ion and an amide group, play an important role in biocatalysis and in the metabolism of all living organisms [1-3]. Several biological processes of 3d series of transition metal complexes with amide group ligands have been studied to understand the chemistry and essential biological role played by these elements [4-8]. Among them however, vanadium has received the least attention. [9-12]. This element has been known as an essential nutritional requirement in higher animals for nearly three decades. It is required for the proper growth of the bones and connective tissues [13]. It decreases the insulin

requirements of diabetic rats and supplementation of vanadium in the diet, at sub-toxic levels, leads to variety of metabolic changes including disturbances in the sulphur metabolism and cholesterol synthesis [14,16]. Accumulation of selectively higher concentrations of the element has been found in the mushroom and certain species of tunicates or seasquirt [17]. Recently, vanadium containing enzymes called nitrogenase and bromoperoxidase have been isolated from living organisms and reported to catalyze reduction of dinitrogen to ammonia and bromination of organic substances [18-20]. Biological significance of oxidation states of vanadium are +3, +4 and +5. V^{+4} is stable under acidic conditions (pH ~ 3) in absence of oxygen. It is rapidly oxidized by dissolved oxygen at physiological pH. It exists as blue vanadyl cation [21].

Materials and methods:

All the solvents, acids, organic compounds and metal salts used were of Analar grade. Methylated spirit and commercial methanal were distilled by standard procedures before use. The solvents like petroleum ether and diethyl ether were distilled and stored over sodium wire. The double distilled water was obtained by redistilling the dematerialized water.

Vanadium complex were prepared by using ($VOSO_4, 5H_2O$). 25CC of hot aqueous methanolic solution of metal salt (1m mole) was added 25 CC of hot methanolic solution of ligand (3m mole) with constant stirring. The resultant solution was refluxed on water bath for 8 hours. During this process the colour of the reaction mixture changes from blue to green then the solution volume was

reduced to half which was further refluxed for one hour. The isolated crystalline product was filtered, washed with small amount of methanol and dried in vacuum.

Results and Discussion:

All the vanadyl complexes are crystalline, nonhygroscopic, and stable at room temperature. The colour of these complexes vary from green to snuff. The complexes are soluble in DMF and DMSO but insoluble in organic solvents like methanol, ethanol and acetone.

The complexes are analyzed for carbon, hydrogen, nitrogen, sulphur. On the basis of analytical data, the stoichiometry between the metal and ligand found to be 1:1 in the complexes of NCPM, NSPS, NAPP and 1:2 in the remaining complexes. Further complexes of CMIMAH₂, CMISAH₂, CMIBAH₂, contain water molecules, and the complex of NAPP associated with SO₄⁻².

Conductivity measurements of the complexes are carried out in 10⁻³M DMSO solution. The molar conductance data shows that the values are in the range of 6.5 to 13.0 ohm⁻¹ cm² mole⁻¹ suggesting that they are non-electrolytic in nature [22].

The thermogram of [VO(CMIBAH₂). H₂O] is shown in Fig.1 and it exhibits three clear cut stages. The first step corresponding to the dehydration of lattice-held water molecule and the second to the expulsion of coordinated water and third to the expulsion of coordinated water and third to the decomposition process of the ligands. Complexes 1, 2 & 3 show initial weight loss in the

temperature range of 70 - 120⁰ C corresponding to the loss of water molecules. The loss of water molecules in this temperature range indicates that the water molecules are of lattice type [23, 24]. The expulsion of water molecule in the temperature range of 150 - 200⁰C corresponding to the expulsion of coordinated water molecule. The presence of water molecules in these complexes is further evidenced by the endothermic peaks in DTA curves.

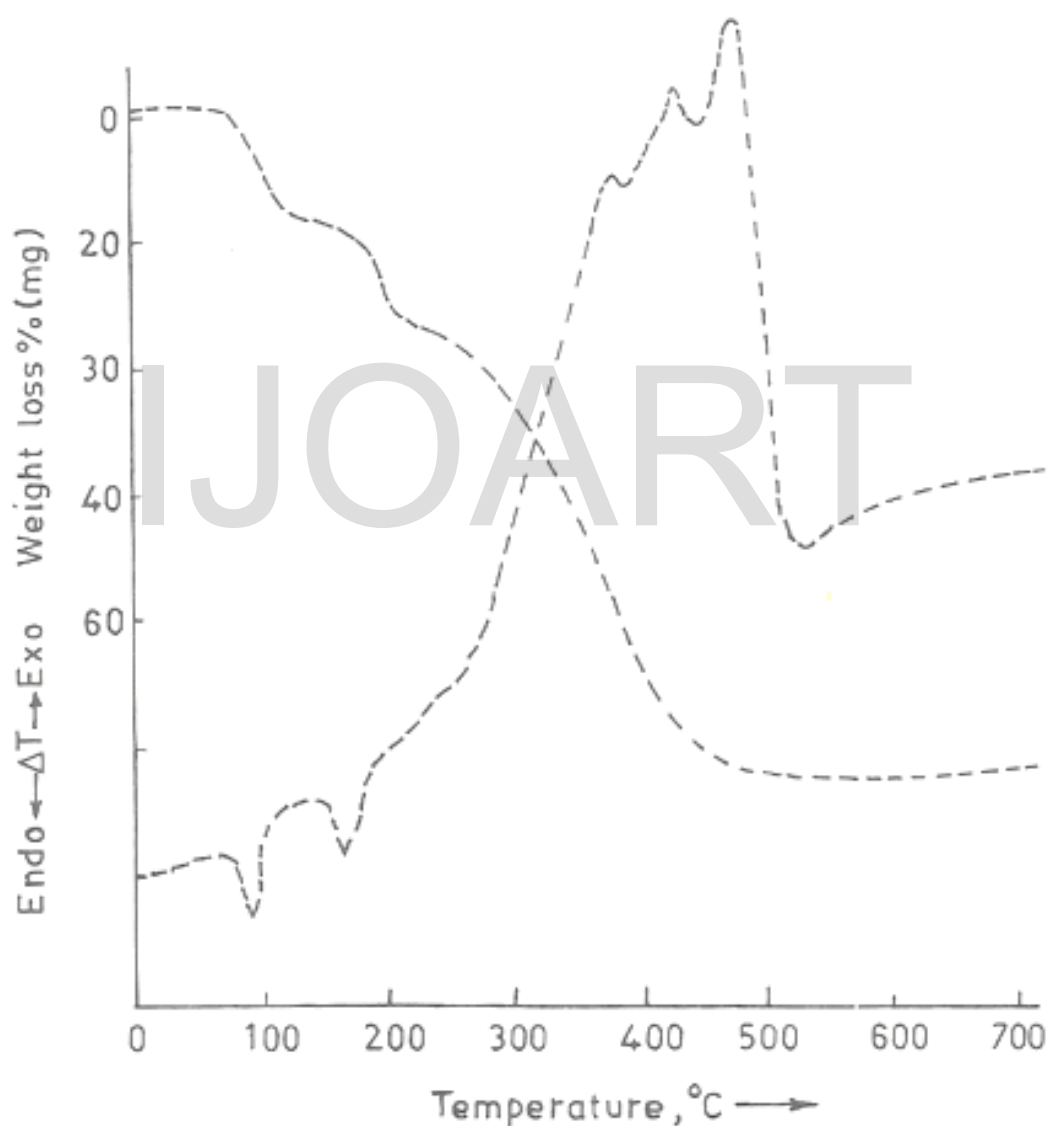


Fig.1 TGA and DTA curves of [VO(CMIBAH)₂H₂O]H₂O

The VO (II) complexes of remaining complexes show only a single stage devoid of any water molecules and all are found to be thermally stable upto 230⁰C. The absence of water molecule in these complexes is further confirmed by their DTA curves which do not give endothermic peak Fig. 2.

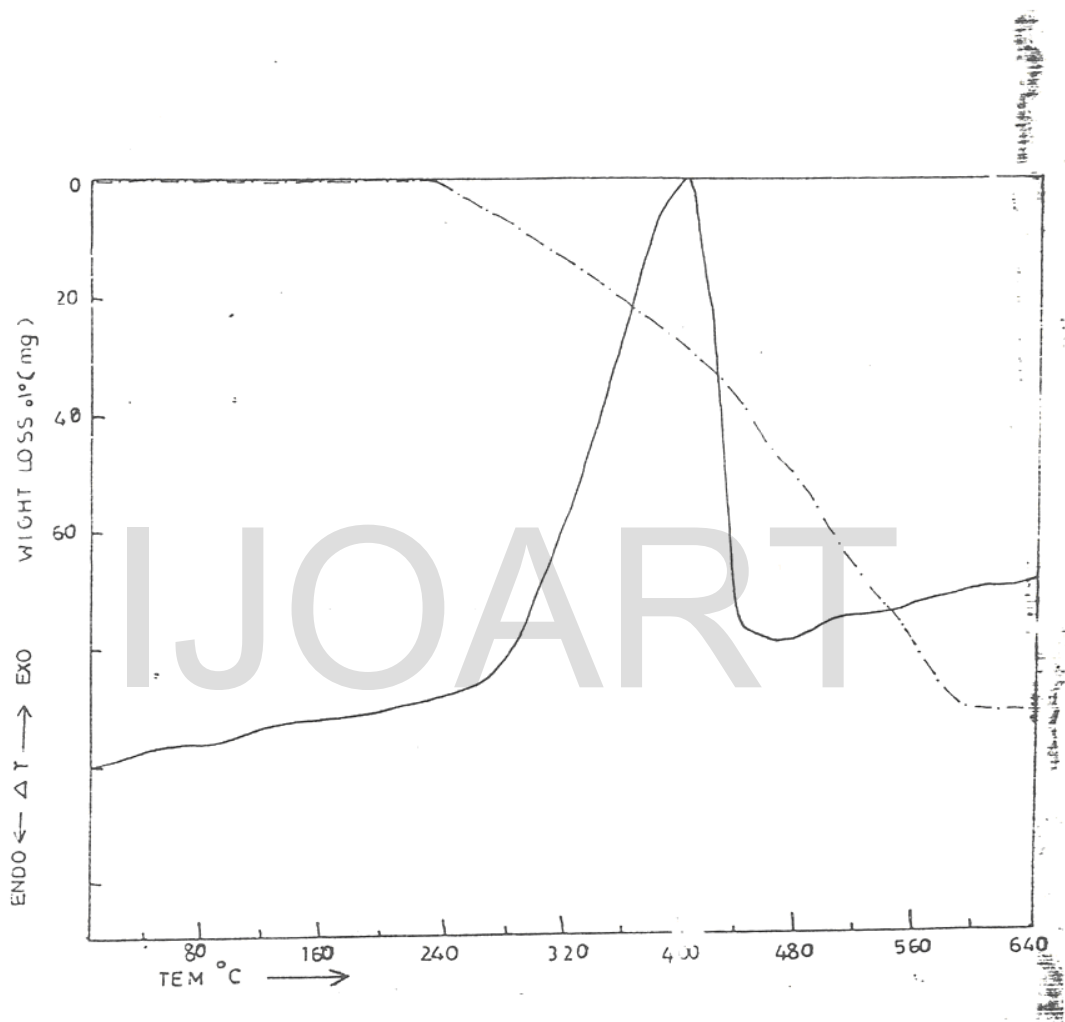


Fig.2 TGA and DTA curves of [VO(NCPM)]

The sharp decomposition associated with the loss of ligand starts above 220⁰C in the complexes. In all the cases the final products of decomposition above 450⁰C correspond to metallic oxide (VO₂).

Despite the good amount of work on thermogravimetry considerable difficulty still exists in assigning definite reasons for the increase or decrease in thermal stability of complexes with different ligands. As such there are various reasons given in literature to explain the relative order or thermal stability of complexes formed with different ligands. One among them is that the thermal stability of complexes increase with increase in π – electron delocalization and size of molecule and also nature of the rings formed [25-27]. The relative order of stability observed for the present complexes may be more or less explained in terms of these reasons.

The analysis of the thermograms by way of identifying the final products offers further support to the composition of the complexes proposed on the basis of elemental analysis.

IR spectra of ligand CMIBAH₂ and its complex is given in Fig. 3. The presence of coordinated water in the complexes of CMIMAH₂, CMIBAH₂, CMISAH₂ are indicated by a broad bands at 3500 – 3000 cm⁻¹ and characteristic absorption at 860 – 880 cm⁻¹ [28,29]. The absence of broad band around 3500 – 3000 cm⁻¹ and 860 – 880 cm⁻¹ in remaining complexes indicates that neither coordinated nor lattice water is present in these complexes.

The strong bands around 1700 and 1340 cm⁻¹ corresponding to the stretching frequencies of carbonyl of –COOH and C-OH of carboxylic group are observed in the IR spectra of CMIMAH₂, CMIBAH₂, CMISAH₂, which are

replaced by new bands around 1550 and 1330 cm^{-1} in the complexes corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$. This indicates the coordination of carboxylate oxygen. Further, lower shifting of 20 to 40 cm^{-1} in the band of C = O (amide I) around 1650 cm^{-1} , indicates the coordination of the amide oxygen in these ligands [30,32].

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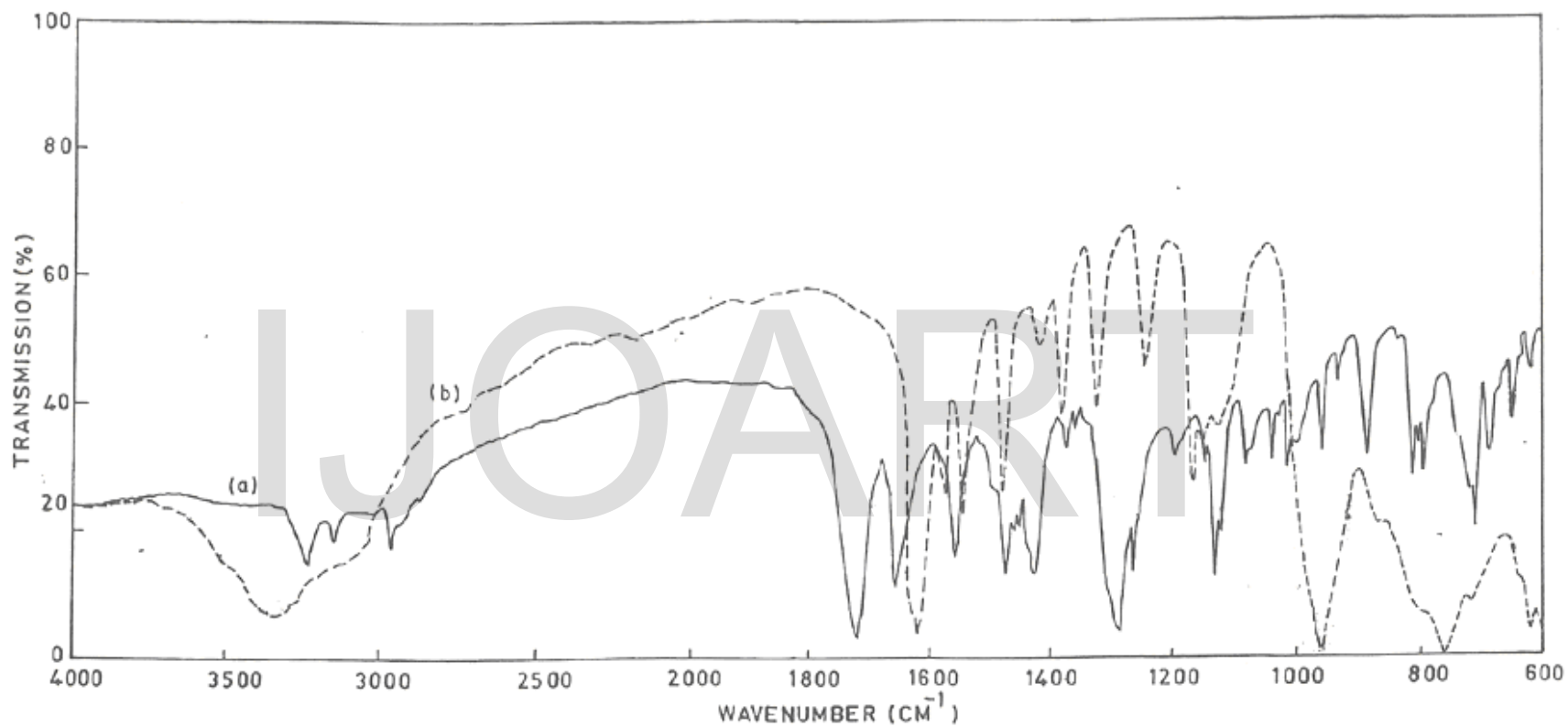


Fig.3 Infrared spectra of (a) CMIBAH₂ (b) [VO(CMIBAH)₂(H₂O)]H₂O

Moreover no shift is observed in the ν C = N of ring nitrogen (1610 cm^{-1}) indicates the non-involvement of C = N ring in the coordination.

The IR spectra of complexes of CPyBAH₂, CPyMAH₂, CPYSAH₂, CMPyMAH₂, CMPySAH₂ and CMPyBAH₂ show bands for the participation of carboxylate oxygen, amide oxygen, and unaltered bands corresponding to ν C = N of ring N indicating non-violent of ring nitrogen in the coordination [33,].

The amide (N-H) frequency in NAPP has undergone a lower shift in the complex showing that nitrogen of this group is coordinating [34].

The IR spectra of all these complexes show a strong band around $980 - 1000\text{ cm}^{-1}$ which is attributed to $\nu = 0$ group [35]. The new bands present at 1220, 1460 and 1050 cm^{-1} in the complexes of NAPP confirms coordinated sulphate ion.

Further the far infrared spectra of the respective complexes show non-ligand bands corresponding to ν (M-O) vibration [36].

Electronic Spectrum shows three low intensity absorption bands are found around 11000-16000, 14500-19000, and 21000-30000 cm^{-1} in the electronic spectra of VO (II) complexes [22]. In most of the cases the 3rd band is not observed, being often buried beneath a high intensity charge transfer band.

The electronic spectrum of VO (II) complex of CMIBAH₂ is given in Fig. 4. In this spectra, VO (II) complexes of CMIBAH₂, CMISAH₂ and CMIMAH₂ show three bands in the range 11300-12500, 15500-17500 and 22000-28000 cm^{-1}

assignable respectively to the transitions ${}^2B_2 \longrightarrow {}^2E(\nu_1)$, ${}^2B_2 \longrightarrow {}^2B_1(\nu_2)$ and ${}^2B_2 \longrightarrow {}^2A_1(\nu_3)$ which are characteristic to distorted octahedral geometry.

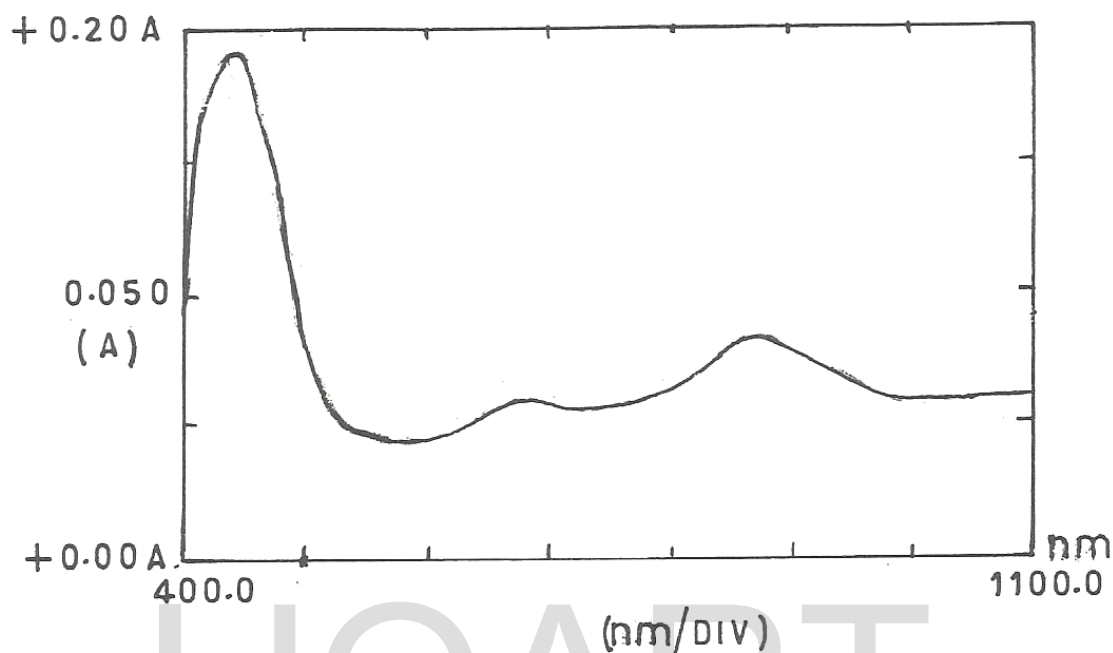


Fig. 4 Electronic spectrum of [VO (CMIBAH)₂ H₂O] H₂O

However the electronic spectra of CPyMAH₂, CPyBAH₂, CPySAH₂, CMPyMAH₂, CMPyBAH₂, CMPySAH₂ show three bands around 13000, 17000, 21000 cm⁻¹ which are corresponding to $2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions respectively and are assignable to square pyramidal geometry [37].

The magnetic data of VO (II) complexes is not sufficient in determining the geometries. The VO (II) complexes with all the ligands the μ_{eff} value are in the range 1.72 to 1.75 [37] corresponds to one unpaired electron.

The fundamental ESR parameters viz. lands effective g factor and electron nuclear spin coupling constant A, can be derived from ESR spectra, from the

position and spacing of the resonance lines respectively. Generally the 'g' value is lower than free electron value of 2.002. This lowering can be related with spin orbit interaction of the ground state, 'd_{xy}' with the low lying excited state [38].

All the ESR spectra of VO⁺² complexes are recorded at LNT. In the present studies vanadyl complex of CMIBAH₂ shown two bunches of eight line pattern. ESR spectrum of the complex of CMIMAH₂ Fig.5 gives only single line isotropic spectrum. The g₁₁, g₁, g₀, A₁₁, A₁ and A₀ values are calculated [39].

The resolution of the ESR lines into parallel and perpendicular parts and also the hyperfine structure due to electron nuclear coupling, in solid polycrystalline state is surprising. Normally a single line ESR, spectrum is expected in polycrystalline state due to intermolecular dipolar broadening.

However ESR spectrum resolutions into parallel perpendicular and hyperfine splittings are not rare and such resolution is attributed to minimization of dipolar interactions due either to large metal- metal separation or to considerable inter- molecular distance. In the present [VO(CMIBAH₂) H₂O]H₂O complex the excellent resolutions into eight line sets of parallel and perpendicular regions may also be ascribed. On similar considerations, to the absence of metal to metal interaction pathway on one hand to a possibly large intermolecular separation on the other.

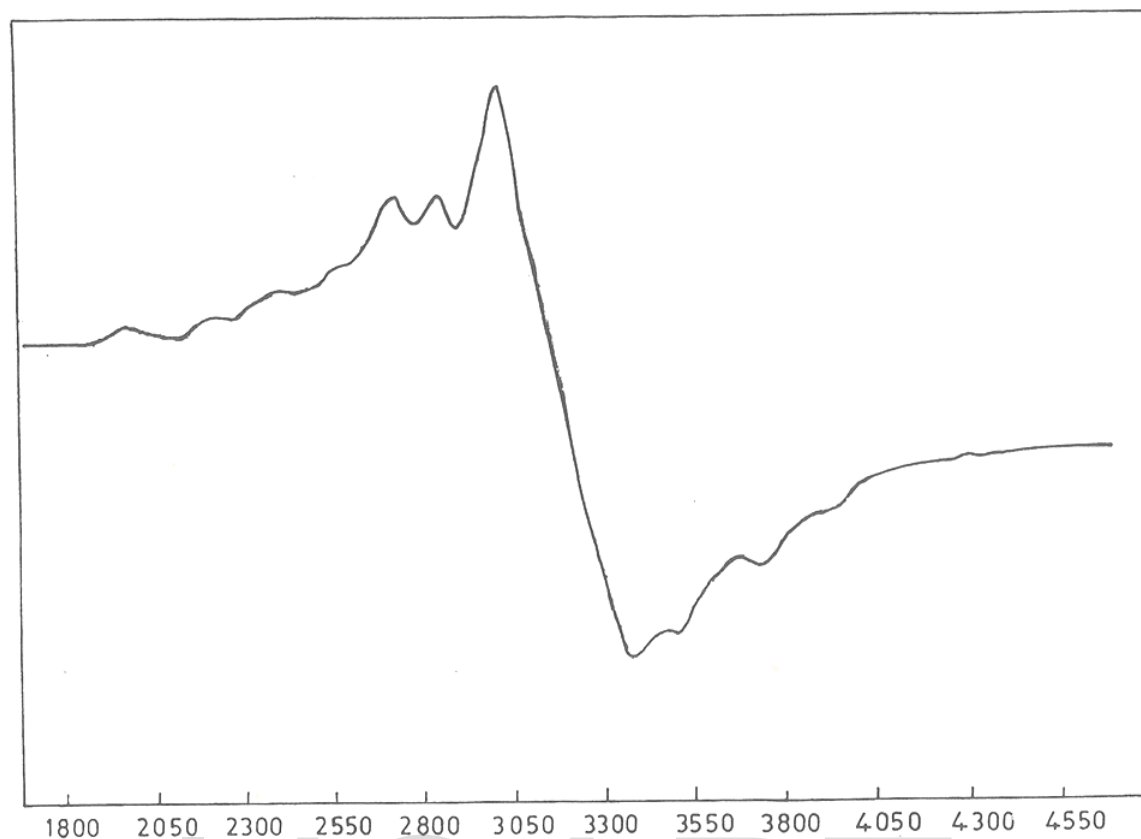


Fig. 5 ESR spectrum of [CO (CMISAH)₂ H₂O]H₂O

The proximity observed between g_{11} , g_1 values can be traced to a slight elevation of the V=O moiety from the plane defined by the two N, O atoms of NAPP and the two O, O atoms of SO_4^{-2} ion [40, 41].

Based on the above data the tentative structures of VO^{2+} complexes have been shown in Fig. 6.

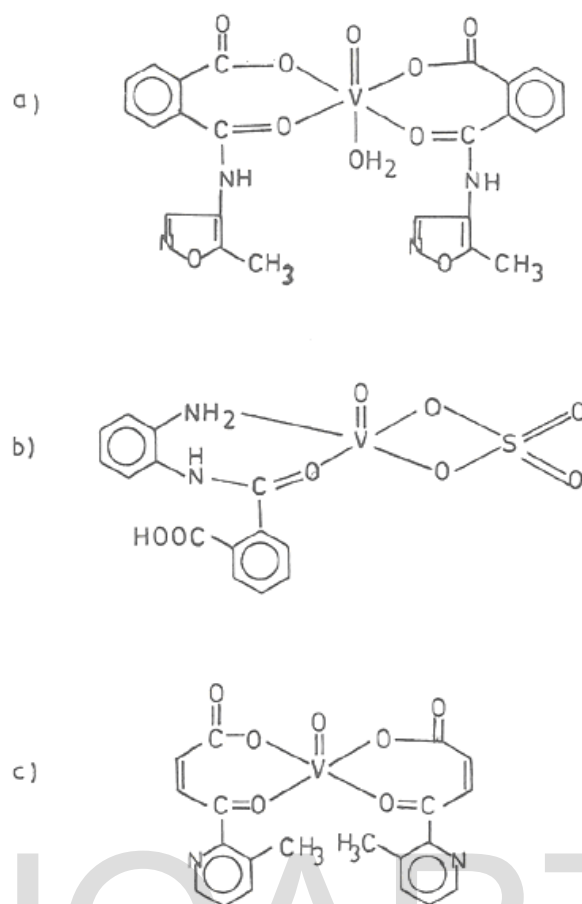


Fig. 6 Structures of VO (II) complexes

(a) [VO (CMIBAH)₂ H₂O] H₂O

(b) [VO (NAPP) SO₄]

(c) [VO (CMPyMAH)₂]

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