

Synthesis and Characterization of Oxoperoxo Complex of V(V) and Mo(VI) by using Ethyl Acetoacetate as OO Donor Ligand

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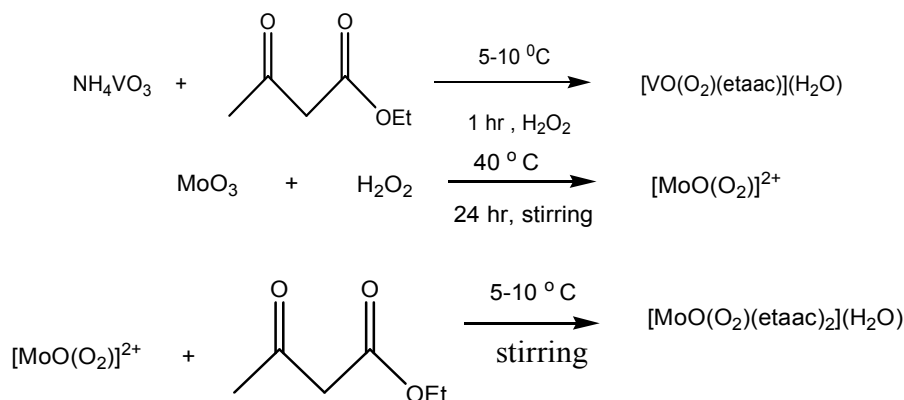
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Abstract: A pair of oxoperoxo ethyl acetoacetate complex of V(V) and Mo(VI) of formula $[\text{VO}(\text{O}_2)(\text{etaac})](\text{H}_2\text{O})$, **1** and $[\text{MoO}(\text{O}_2)(\text{etaac})_2](\text{H}_2\text{O})$, **2** have been synthesized and characterized by using ethyl acetoacetate as OO donor ligand where etaac is ethyl acetoacetate. The compounds were prepared by the interaction of $[\text{MO}(\text{O}_2)]^{m+}$ (where M= Mo, V and n is the oxidation state of the metal cations) with ethyl acetoacetate monitoring the P^{H} of the system. These complexes have been characterized by elemental analysis, electronic spectroscopy, IR spectroscopy, ^1H NMR and ^{13}C NMR spectroscopy. β -Diketones and β -diketo esters are capable of forming coordination compounds with transition metals due to their keto and enol form at different pH value. Acetyl acetone complexes of different metals have been synthesized and evolved their utility as catalyst in organic synthesis. Ethyl acetoacetate act as similar way as acetyl acetone and it is worthwhile to synthesis ethyl acetoacetate complexes of transition metals and study their electrical, catalytic property as well as structure analysis. Keywords: ethyl acetoacetate, hydrogen peroxide, β -diketo ester, acetyl acetone, oxoperoxo complexes, NMR spectroscopy.

Graphical Abstract



1. Introduction

Monoperoxo complexes of V(V) and Mo(VI) with suitable ligands have been studying for last few decades, owing to their catalytic properties as well as their biological activity¹⁻⁴. The coordination chemistry of vanadium complexes has drawn considerable attention to reveal the vanadium's redox mechanism in some biological systems⁵⁻⁷. Oxovanadium(IV), oxovanadium(V), oxomolybdenum(VI) serve as good oxidant in various organic synthesis⁸⁻¹⁰. Most importantly VO(acac)₂ (where acacH- acetyl acetone) and MoO₂(acac)₂ catalyse epoxidation of organic substrate (allylic alcohols, alcohols, alkenes) with either alkyl hydrogen peroxide or hydrogen peroxide and thus provide a useful route to epoxy compounds¹¹⁻¹⁵.

β -Diketoenolates are well established chelating molecule having two donor sites forming a very stable six membered chelate ring including central metal ion¹⁶⁻¹⁷. Literature survey on β -diketoenolate complexes of transition metals reveal that Cu (II), Ni (II) and Pd (II) complexes of etaaH have been isolated and synthesized satisfactorily before¹⁸⁻²⁰. The electronic form of etaaH is stable due to the inter electronic H-bonding (Fig. 1). At room temperature, it exists as about 92.4% of keto and 7.6% of enol form. The intermediate of the two forms involve in the migration of protons and the shifting of bonding electrons. EtaaH and AcacH show similar chemical behaviour because of their similarity in the structure. However acacH is more stable ligand than etaaH. Both of them have two oxygen donor atoms and can link to metal atom. Interestingly etaaH is an environmentally benign solvent as compared to acacH. So it is worthwhile to study the coordination chemistry of oxoperoxo complex of V(V) and Mo(VI) using etaaH as O donor ligand. In this article, we reported the synthesis and characterisation of the above mentioned complexes which are investigated with the help of physico-chemical techniques.

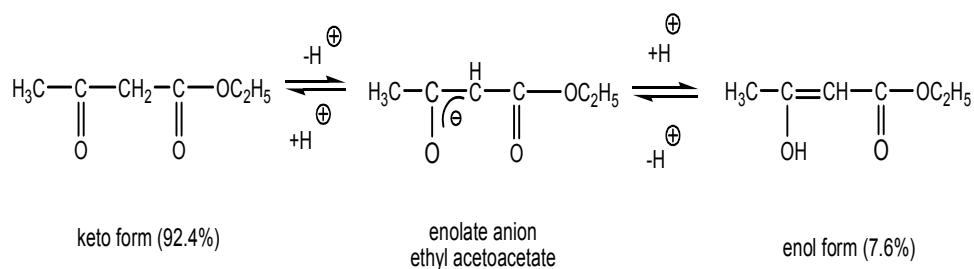


Fig. 1 Keto-enol tautomerisation of ethyl acetoacetate

2. Experimental

2.1. Materials: Solvents and reagents were obtained from commercial sources and used without further purification. Molybdenum trioxide (SRL), ammonium vanadate (CDH), hydrogen peroxide (Merck), methanol (Merck) and ethyl acetoacetate (Merck) were all of analytical grade. Solvent used was ethanol which was purified by established method²¹.

2.2. Synthesis of Complexes

2.2.1. Synthesis of complex 1: The $[\text{VO}(\text{O}_2)(\text{etaac})](\text{H}_2\text{O})$ was prepared by dissolving NH_4VO_3 (2.63 g, 20 mmol) in 10 ml of 30% H_2O_2 solution in ice cold condition. To it 5ml of ethyl acetoacetate (40 mmol) was added and stirred magnetically for 2 hr. The P^{H} of the solution is raised by adding dil NH_4OH solution drop by drop in stirring condition. The dark yellow coloured compound formed was filtered, washed with a little cold water and dried in desiccator. Yield: 1.6936 g (~64%). Analytical calculation of Complex 1: $\text{C}_6\text{H}_{11}\text{O}_7\text{V}$, Anal. Found: C, 28.14; H, 3.08; V, 19.51 Calc.: C, 29.28; H, 4.47; V, 20.73. UV-Vis (nm): 325, 277, 233. IR (cm^{-1}): $\nu_{\text{M-O}}$, 586(asym), 524(sym); $\nu_{\text{M=O}}$, 954; $\nu_{\text{C=O}}$, 1710, ν_{O_2} , 821; $\nu_{\text{O-H}}$, 3560, 3545. ^1H NMR (δ , ppm in $\text{CDCl}_3\text{-d}_6$): 4.19(q, CH_2), 5.80(s, CH), 1.71(s, CH_3), 1.30(t, CH_3). ^{13}C NMR (CDCl_3 , δ): 192.4, 166.5, 101.5, 61.40, 24.50, 14.20.

2.2.2. Synthesis of Complex 2: In the preparation of complex $[\text{MoO}(\text{O}_2)(\text{etaac})_2] \text{H}_2\text{O}$, MoO_3 (10 mmol, 1.439 g) was dissolved in 30% H_2O_2 (30 ml) and to it 5 ml of ethyl acetoacetate was added. The mixture was stirred for 2hr in ice cold condition. A pale yellow coloured compound formed was filtered and dried in desiccator. Yields: 0.9872 g (~69%). Analytical calculation of complex 2: $\text{C}_{12}\text{H}_{20}\text{O}_{10}\text{Mo}$, Anal. Found: C, 27.37; H, 4.01; Mo, 22.70. Calc.: C, 29.63; H, 4.53; Mo, 22.85. UV-Vis (nm): 271, 255, 212. IR (cm^{-1}): $\nu_{\text{M-O}}$, 615(asym), 503(sym); $\nu_{\text{M=O}}$, 954; $\nu_{\text{C=O}}$, 1708; ν_{O_2} , 898; $\nu_{\text{O-H}}$, 3562, 3545.

2.3. Physical Measurements: Microanalysis of carbon and hydrogen content of the complexes were carried out by Perkin Elmer 2400 series II CHN- Analyser. IR spectra were recorded on Perkin Elmer Serial Number 73633 type FT-IR spectrometer using KBr pellets in the range $4000\text{-}250\text{ cm}^{-1}$. Electronic spectra were recorded on Varian Carry 100 Bio UV-visible spectrophotometer from a solution in water. ^1H and ^{13}C NMR was obtained in CDCl_3 with reference to TMS on Varian MERCURY plus spectrometer

3. Results and Discussion

The oxoperoxo vanadium (V) and molybdenum (VI) complexes of ethyl acetoacetate under study were obtained by following the above mentioned procedures.

Electronic spectral data of complexes in water are summarized in experimental section. The complex 1 display a band at 325 nm originating from LMCT arising from the enolate oxygen to an empty d orbital of V(V) centre²²⁻²⁴. The other bands observed in the spectra of the complex, 1 are because of the intra ligand transitions which are due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ transition. No d-d transition can be observed due to the absence of the d-electrons of the metal in the complex 1. In case of complex 2, the bands appear at 212 nm and 271 nm are due to intra ligand transitions²⁵⁻²⁶. There are some peaks due to LMCT at 348-343 nm²⁷⁻²⁹.

The important IR spectral bands of the complexes and their tentative assignments are given in the experimental section. The characteristic IR bands of the complexes show significant changes when compared with that of the parent ligand and shift of some of characteristic vibrational frequency of the ligand upon complexation provides evidence for the mode of binding of the ligand to the metal ion.

The ligand exhibits two bands at 1745 cm^{-1} and 1725 cm^{-1} due to the presence of two CO groups. One of the C = O band was disappeared in the spectra of both the complexes as one of the carbonyl oxygen atom of the ligand is linked to metal ion. At the same time a new band was appeared at 586, 524 and 543, 503 cm^{-1} in the spectra of complex 1 and 2 respectively for M-O stretching³⁰⁻³³. In general, the O-O vibration of superoxide ion (O^{2-}) and peroxide ion (O_2^{2-}) appears at 1140 and 800 cm^{-1} respectively³³. The bands at 898 and 821 cm^{-1} are assigned to be for O-O bond stretching. Peak for C-H stretching appear near 3070 cm^{-1} for the free ligand. In the spectra of the complexes 1 and 2, it appears at 3124 and 3157 cm^{-1} respectively. Two broad bands are visible near 3500 cm^{-1} in both the spectra of the complexes which are absent in the spectra of ligands. These peaks suggest that water molecule is attached to the metal via hydrogen bonding. There is no evidence of M-OH bonding because the stretching frequencies are relatively lower (3545 and 3562 cm^{-1}) than that of water molecules at 3652 cm^{-1} ³⁴. Fig. 2 shows the IR peaks of complexes evaluated at room temperature.

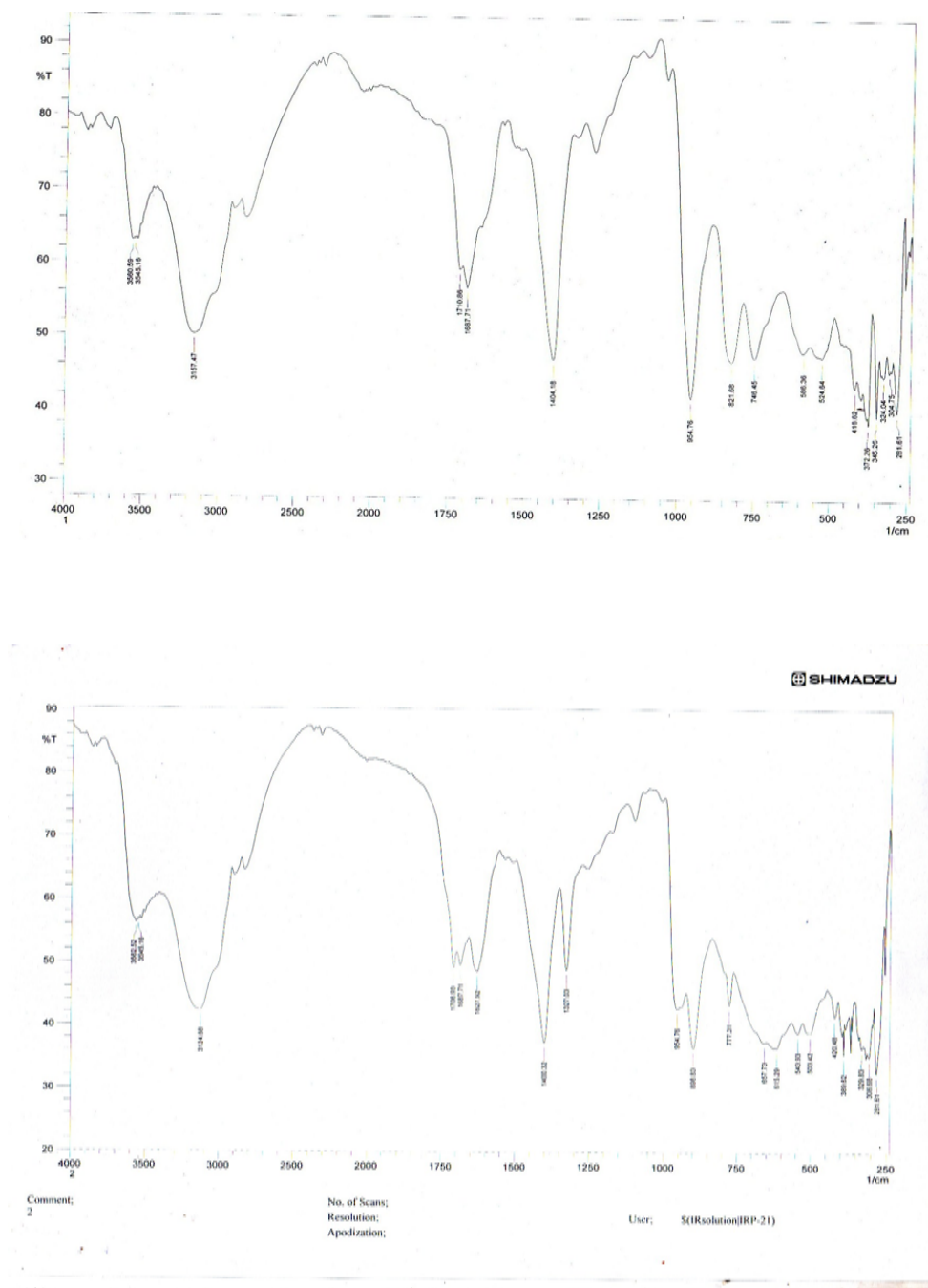


Fig. 2 IR spectral data of complex 1 and 2

The mode of coordination of the ligands in the complex was confirmed by comparing ^1H NMR spectral pattern of the ligand with the corresponding

complexes. The relevant spectral data of complex 1 are given in the experimental section. The ^1H NMR spectra of one complex namely $[\text{VO}(\text{O}_2)(\text{etaac})](\text{H}_2\text{O})$, **1** was recorded in CDCl_3 using TMS as a reference. The complex 1 display signal at $\delta = 1.30, 4.19,$ and 1.71 ppm due to $\text{CH}_3(\text{C-6}), \text{CH}_2(\text{C-3}), \text{CH}_3(\text{C-5})$ protons respectively present in the complex. There is a slight downfield shift of the C-4 proton as compared to that of free ligand ($\delta = 5.5$). This may be due to the mode coordination of the enolic form of ligand with metal via two ketonic oxygens. The absence of enolic/hydroxyl proton signal at $\delta = 15.5$ ppm in the complex indicates the coordination of enolic oxygen to the metal ion after deprotonation³⁵. On the basis of above data, it is evident that the ligand coordinates through the oxygen atom to the central metal atom in the complex. The ligand is in its enolic form. The tentative structure of both the complexes can be represented as in Fig. 3.

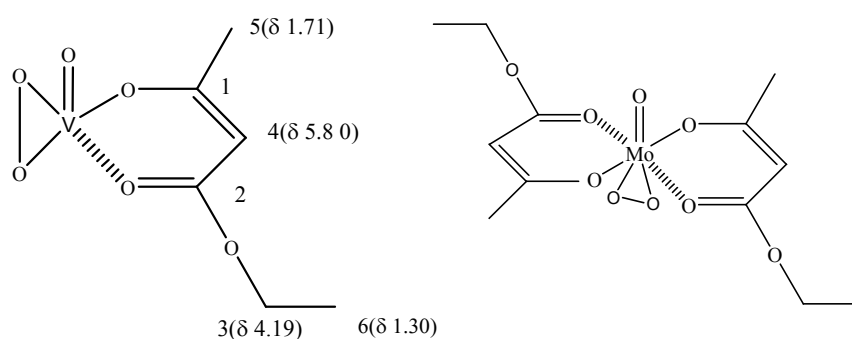


Fig. 3 A proposed structure of complex 1 and 2

Efforts were made to obtain crystals of these complexes to study the X-Ray crystallography, but owing to their poor solubility in most of the organic solvents the desired results could not be obtained. However the work is still going in the same direction to get positive result.

4. Conclusion

The satisfactory analytical data and all the studies given above suggest that the present complexes – Ethylacetoacetylmonoperoxovanadium (V), **1** and Bis (ethylacetoacetyl) monoperoxomolybdenum (VI), **2** may be formulated as $[\text{VO}(\text{O}_2)(\text{etaac})](\text{H}_2\text{O})$, **1** and $[\text{MoO}(\text{O}_2)(\text{etaac})_2](\text{H}_2\text{O})$, **2** respectively. These complexes have been isolated and characterised by several methods. The structures of the complexes yet to be established and it can be ascertained only after X-ray crystallographic analysis. As ethyl acetoacetate is an environmentally benign ligand, so formation of complexes with this ligand may lead to the formation of green complexes. These

complexes may have catalytic activity as like acetyl acetone complexes of molybdenum and vanadium. New studies must be done to know the catalytic properties of the vanadium and molybdenum complexes of ethyl acetoacetate.

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