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Synthesis and Characterization of Novel Oxovanadium Metal Complexes

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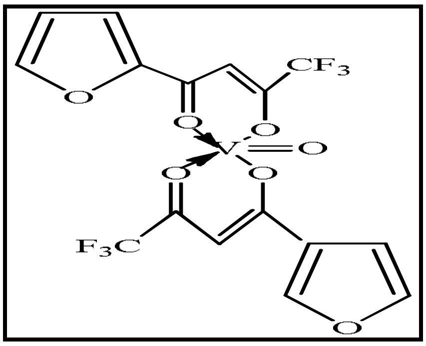
ABSTRACT

Few novel Vanadium binary metal complexes are prepared using substituted acetyl acetones viz., 4,4,4-trifloro-(2-furyl)-1,3-butadione (TFFAA), 3-methyl-2,4-pentadione (MEAA), 3-ethyl-2,4-pentadione (EAA), 3-n-butyl-2,4-pentadione (BAA). These complexes have been characterized using various analytical techniques. These binary complexes showed the square pyramidal geometry. All these metal complexes are found to be neutral. Diabetes activities of these complexes would be evaluated, Since Vanadium metal complexes are known to have anti diabetic activity in type-II diabetic mellitus patients.

Graphical Abstract



Keywords: TFFAA, MEAA, EAA, BAA, Vanadium.

INTRODUCTION

The French physicians [1], before 1922 (year of discovery of insulin) were administrating sodium vanadate ($NaVO_3$) to improve the health of patients suffering with Diabetes mellitus (DM). A series of landmark studies [2-4] in 1979 and 1980 demonstrated the activity of Na_3VO_4 (Sodium ortho vanadate), $NaVO_3$ (Sodium metavanadate) and $VOSO_4$ (Vanadyl sulphate) to have insulin like biological effects of glucose uptake and metabolism in skeletal muscle and adipose tissue in vitro. These findings led to further interest in Vanadium compounds which was dramatically accelerated where Heyligher *et al* [3] in 1985 first reported successful treatment of STZ diabetic rats with oral vanadate. Blood glucose concentrations were lowered without a change in insulin concentration substituting the activity of vanadate to mimic insulin in vivo. Since there extensive studies exploring vanadium chemistry including the synthesis of novel compounds as well as the biological effects of vanadium on cells and tissues in vitro and in vivo have been performed. Later, it was proved that vanadium metal complexes are better choice than simple salt ($VOSO_4.XH_2O$). Few vanadium metal complexes were prepared using ligands like maltol, kojic acid, dipicolinic acid [4-7] and they are found better in absorption/assimilation than simple salt. Because of importance of the vanadium complexes in treatment of Type-II DM, various vanadium metal complexes have been synthesized and characterized using various analytical techniques. In this study the substituted acetyl acetones used are14,4,4-trifloro-(2-furyl)-1,3-butadione (TFFAA), 3-methyl-2,4-pentadione (MEAA), 3-ethyl-2,4-pentadione (EAA), 3-n-butyl-2,4-pentadione (BAA).

MATERIALS AND METHODS

Reagents and solvents: Vanadium Sulphate ($VOSO_4.xH_2O$) was purchased from Sigma-Aldrich and is used as it is. The ligands are used to prepare metal complexes are acetyl acetone(pentane 2,4-dione)(AA),4,4,4-trifloro-(2-furyl)-1,3-butadione(TFFAA),3-methyl-2,4-pentadione (MEAA), 3-ethyl-2,4-pentadione (EAA),3-n-butyl-2,4-pentadione (BAA). They were purchased from Merck, Alfa Aesar and Sigma Aldrich Chemical Company. These ligands used without further purification. Sodium carbonate was purchased from SRL Pvt. Ltd. Other solvents (Petroleum-ether, Di ethyl ether, Methanol, Ethanol, Sulphuric acid, Chloroform) were of analytical reagent grade obtained from Merck and Sigma-Aldrich, Finar, Himedia and were used without further purification.

Synthesis of binary complexes: A mixture of 1mmol of vanadyl salt ($VOSO_4.xH_2O$) (0.163g), 10% H_2SO_4 ,2 mmol of 2, 4-pentanedione(0.2 mL) was refluxed for 10 min and then neutralized by 2 mmol of sodium carbonate solution slowly and stirred continuously to avoid excessive frothing. The resultant super saturated solution was collected as precipitate by filtration on a Buchner funnel. Recrystallisation was done from hot chloroform and cooled to room temperature in dried air. Synthesis of above vanadium complex of acetyl acetone and its substituted acetyl acetones is as per literature [5]. Total four binary complexes were prepared namely,[VO(TFFAA)$_2$], [VO(MEAA)$_2$], [VO(EAA)$_2$], [VO(BAA)$_2$] abbreviated as [V-furyl], [V-methyl], [V-ethyl] and [V-butyl] respectively.

RESULTS AND DISCUSSION

Various physical properties like Melting temperature, Magnetic moments, Conductivity measurements, Colors of synthesized Vanadium metal complexes are given in table 1. Decomposition/ Melting temperatures are recorded in the range of 214°C (for [V-furyl]) to 270°C (for [V-butyl]). The molar conductivity (Λ_m) values of the oxovanadium complexes were measured and the obtained values indicating their non-electrolytic nature, suggesting neutrality of these complexes. Magnetic moments of oxovanadium (IV) complexes were measured at room temperature and effective magnetic moment (μ_{eff} (BM)) values of are given in table1. The magnetic moment of vanadium complexes were range from 1.73 to 1.76 BM, which corresponds to the presence of single unpaired electron [6]. Colors of these complexes are due to transition of single unpaired electrons.

Table 1. Physical properties of different vanadium metal complexes

S. No	Complex	Decomposition Temp.(°C)	Λ_m (Scm^{2}mol^{-1})	μ_{eff} (BM) 300 K	Color
1	[V- methyl]	258	0.72	1.74	Dark Green
2	[V-ethyl]	264	0.76	1.76	Dark Brown
3	[V-furyl]	214	0.42	1.74	Slight Green
4	[V-butyl]	270	1.4	1.73	Dark Green

IR Spectra: The formation of complexes has been ascertained by scanning their infrared spectra in 4000-200 cm^{-1} region. The important infrared spectral bands of the vanadium metal complexes are presented in table 2. The tentative assignments of the observed bands for the complexes were made as follows. A band was disappeared in the region of 1610 cm^{-1} indicating that C-O group of β-diketones was not free in the complexes suggesting the chelation of metal to the C-O group. Diketones shows two bands, one at 1700 cm^{-1} and other at 1725 cm^{-1}, they were not observed upon chelation. Absorption bands were observed below 700 cm^{-1} in all the complexes which are caused by metal-oxygen (V-O) vibrations. The V=O stretching mode was lowered in the binary complexes $[VO(AA)_2]$ (997 cm^{-1}) [7] when compared to free salt. This indicates the coordination of acetyl acetone(AA) to metal. The characteristic V=O stretching frequency for substituted β-diketones was much lower than $VO(AA)_2$. The further lowering of V=O stretching frequency is due to the electron withdrawing group attached to the *β*-diketones. As a representative case the IR spectra for [V-furyl] is given in figure 1.

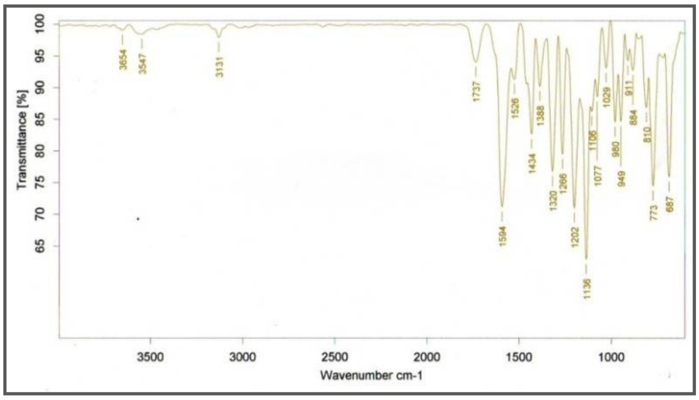


Figure 1. IR spectra for [V-furyl] complex.

Table 2. Important infrared spectral bands of binary metal complexes

S.No	Compound	υ (V=O)	υ (C-O)	υ (V-O)
1	[V- methyl]	970	1547	621
2	[V-ethyl]	969	1585	616
3	[V-furyl]	980	1594	687
4	[V-butyl]	988	1555	685

The mass spectrometric characterization of inorganic vanadium complexes was done by ESI technique. The peak observed at m/z ratio of 478.56(M+1), agrees with the theoretical mass of [V-furyl]. The obtained m/z ratios for various metal complexes are in good agreement with theoretical mass values, given in table 3. The mass spectrum of [V-furyl] complex is given in figure 2 as a representative case.

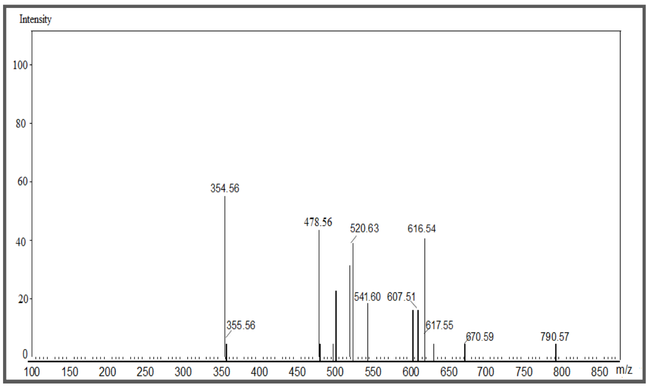


Figure 2. The mass spectrum of [V-furyl] complex.

Table 3. Mass spectral data for different vanadium metal complexes

S. No.	Complex	Theoretical mass	Observed mass
1	[V- methyl]	293	294(M+1)
2	[V-ethyl]	321	322(M+1)
3	[V-furyl]	477	478(M+1)
4	[V-butyl]	377.4	378.5(M+1)

The ESR spectra of the Vanadium complexes were recorded in DMSO solution at 300 K.ESR spectra of [V-methyl] complex is shown in figure 3. In this spectrum, EPR parameters g ∥, *g* ⊥were used to evaluate geometry of the complex. In general, value of L and e factor also called g' factor [8, 9] for a free electron is 2.00232. The value is ranging from 1.99-2.01, for organic radicals typically quite close to that of a free electron. The transition metal compounds, g values were ranging from 1.4 to 3.0. In Vanadium complexes under study, g ∥< *g* ⊥> 2.00232 which is characteristic of geometry of square pyramidal. The g ∥, g ⊥ values for other complexes are given in table 4.

Table 4. Vanadium complexes and theirg ∥, g ⊥values

S. No	Complex	g ∥	g ⊥	Structure
1	[V-methyl]	2.3014	2.4374	Square pyramidal
2	[V-furyl]	2.3014	2.4374	Square pyramidal

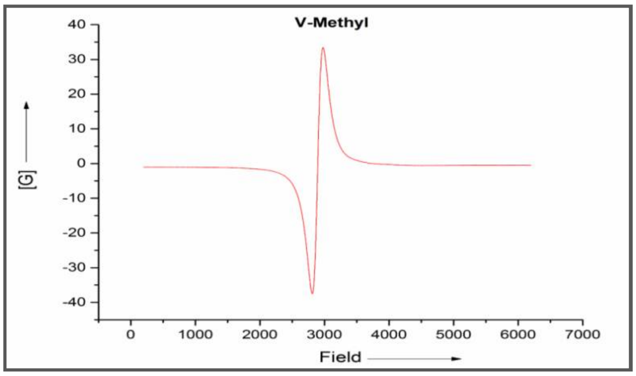


Figure 3. EPR spectra of [V-methyl] complex.

Physical properties and different spectral analysis reveal that the synthesized vanadium metal complexes attained square pyramidal geometries and are non- electrolytic in nature.

Supplementary information: Spectral data for other complexes are available are given in figures 4-7.

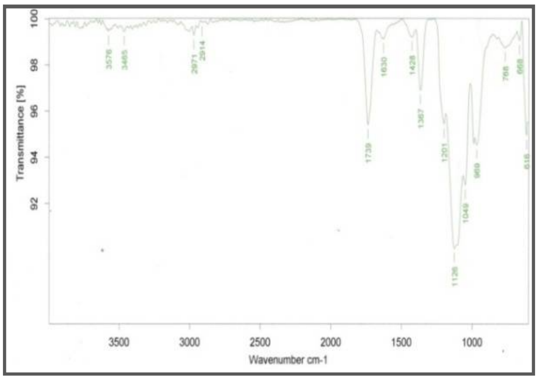


Figure 4. IR spectra for [V-ethyl] complex.

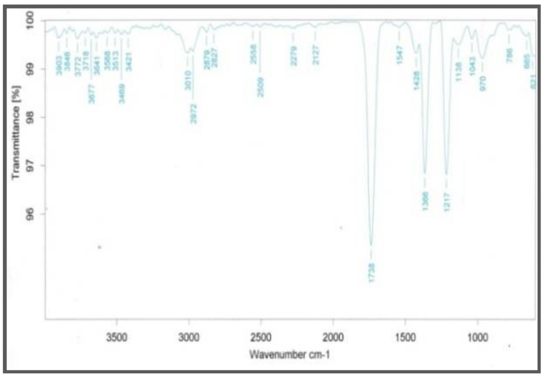


Figure 5. IR spectra for [V-methyl] complex.

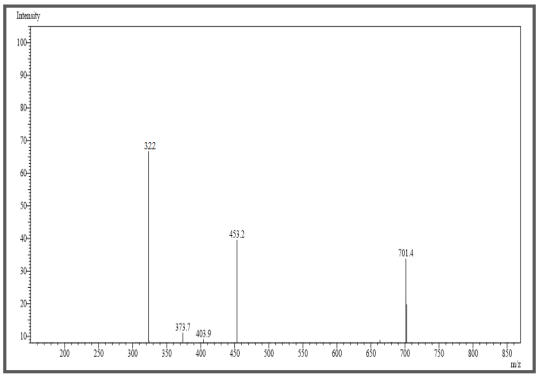


Figure 6. The mass spectrum of [V-ethyl] complex.

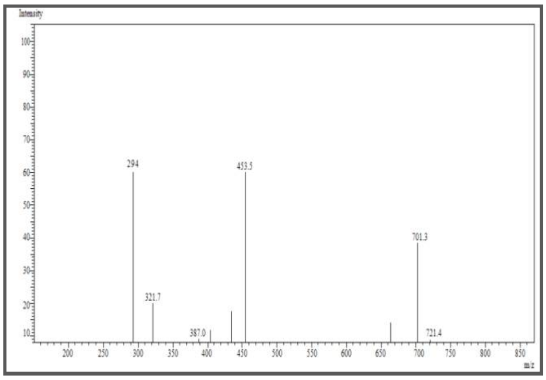


Figure 7. The mass spectrum of [V-methyl] complex.

APPLICATION

Vanadium shows insulin mimetic property better in organic form than in inorganic form of vanadate or vanadyl salt. Thus, the metal complex efficacy could be improved by choosing a correct ligand, so that useful therapeutic activity may be achieved. Since, these oxovanadium complexes are electrically neutral in nature, are good in absorption and distribution of vanadium metal in vivo when compared to vanadium ion.

CONCLUSION

Various Vanadyl metal complexes were synthesized and characterized by using different spectral techniques. All the spectral data reveals the coordination of vanadyl ion to the ligand (i.e., Substituted β-diketone) and these binary metal complexes are formed with square pyramidal geometry.

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