Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry
2018, 7 (5): 1223-1230
(International Peer Reviewed Journal)

Synthesis and characterization of various Vanadium metal complexes

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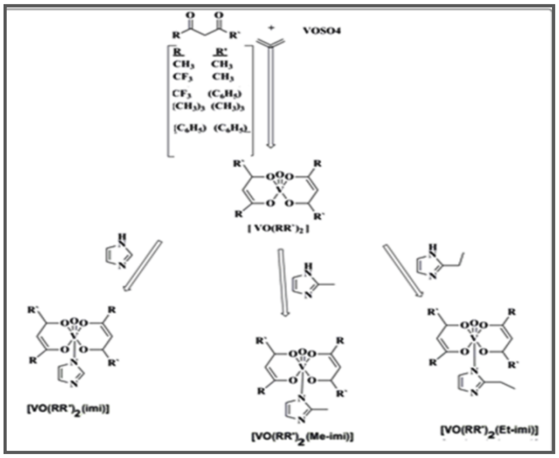
Accepted on 11th September, 2018

ABSTRACT

Various Vanadium binary and ternary complexes using substituted acetyl acetones were synthesized and characterized by analytical techniques. The substituted acetyl acetones used in this study are 1,3 -diphenyl-1,3-propanedione(DPhAA),1,1,1-trifluoro-2,4-pentanedione(TFAA),4,4,4-trifluoro-1-phenyl -1,3-butanedione(TFPhAA),2,2,6,6-tetramethyl-3,5-heptanedione (TMH)and the other auxiliary ligands used are imidazole(imi), 2-Methyl-imidazole(me-imi), 2-Ethyl-imidazole(et-imi). The binary complexes and ternary complexes showed the square pyramidal and octahedral geometries respectively. All these metal complexes are found to be neutral. Diabetes activities of these complexes would be evaluated.

Graphical Abstract



Keywords: DPhAA, TFAA, TMH, TFPhAA, imi, me imi, et imi.

INTRODUCTION

The discovery in 1899 by Lyonnet and Martin **[** 1, 2] that Diabetes Mellitus(DM) patients excreted less glucose in their urine after treatment with $VOSO_4$ giving enough evidence that transition metal compounds may have an important role to play in the treatment of DM. Later it was shown that

$VOSO_4$ does not enhance a insulin action in Type - I patients [3] but relatively improve insulin action in Type - II DM patients [4]. Later, studies have 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 [5-8] and they are found better than simple salt in absorption/ assimilation. Owing to the importance to the vanadium complexes in treatment of Type-II DM, we have synthesized various vanadium metal complexes and characterized using analytical techniques. In this project the substituted acetyl acetones used include 1,3-diphenyl-1,3-propanedione(DPhAA), 1,1,1-trifluoro-2,4-pentanedione(TFAA), 4,4,4-trifluoro-1-phenyl-1,3-butanedione(TFPhAA), 2,2,6,6-tetramethyl-3,5-heptanedione (TMH), and other ligands are Imidazole(imi), 2-Methyl-imidazole(me-imi),2-Ethyl-imidazole(et-imi). Binary and ternary metal complexes were synthesized and characterized.

MATERIALS AND METHODS

Metal Salts: The metal salt used in this work is Vanadium Sulphate ($VOSO_4.xH_2O$). The metal salt is used as it is without further purification. The metal salt is obtained from Sigma-Aldrich Chemical Company.

Ligands: The Ligands used in this study (Acetyl acetone(pentane 2,4-dione)(AA) , 1,3-diphenyl-1,3-propanedione(DPhAA),1,1,1-trifluoro-2,4-pentanedione(TFAA),4,4,4-trifluoro-1-phenyl-1,3 butane-dione (TFPhAA), 2,2,6,6-tetramethyl-3,5-heptanedione (TMH), Imidazole(imi), 2-Methyl-imidazole (me-imi), 2-Ethyl-imidazole(et-imi).) were obtained from Merck, Alfa Aesar and Sigma Aldrich Chemical Company. These ligands used without further purification. Sodium carbonate was purchased from SRL Pvt.Ltd. All the other solvents (Pet-ether, di ethyl ether, ethanol, methanol, sulphuric acid, deionized water, Chloroform) were of analytical reagent grade obtained from Finar, Himedia, Merck and Sigma-Aldrich, and used without further purification.

Synthesis of binary complexes: Vanadyl salt ($VOSO_4.xH_2O$) (0.163 g, 1 mmol) was dissolved in 10% H_2SO_4 to prevent hydrolysis. 0.2 mL (2 mmol) of acetyl acetone (2, 4- pentanedione) was added and the solution was stirred for 10 min. The solution was neutralized by adding a solution of 2 mmol of sodium carbonate dissolved in 10 mL of water slowly with continuous stirring to avoid excessive frothing. The precipitate was collected by filtration on a Buchner funnel. Recrystallization was done by dissolving in the minimum amount of hot chloroform (about 4 mL) in a small Erlenmeyer flask, filtering hot by gravity through fluted filter - paper, cooling to room temperature and adding 10 mL of hot chloroform to complete the precipitation. Filer and which was allowed to dry in air. Synthesis of above vanadium complex of acetylacetone is as per literature [9]. Total four binary complexes were prepared namely, $[VO(DPhAA)_2]$, $[VO(TFPhAA)_2]$, $[VO(TMH)_2]$, and $[VO(AA)_2]$, abbreviated as 7B, 2B, 4Band 8B respectively. The general scheme of formation of 1:2 metal binary complexes is given in figure 1.

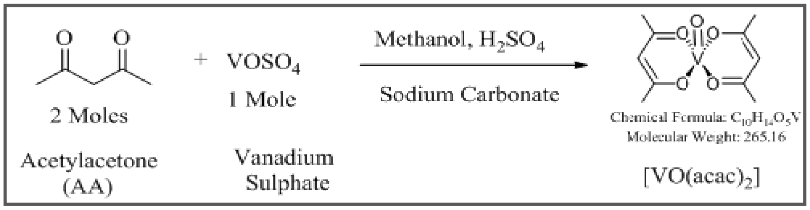


Figure 1. Scheme of formation of 1:2 binary complexes.

Synthesis of ternary complexes: Bis(acetylacetonato)oxo vanadium (IV) (0.265 g, 0.001 mol) was dissolved in methanol (about 10 mL). To the resulting solution Imidazole (0.068 g, 0.001 mol) was added. The reaction mixture was stirred for about 5-6 h and then the solution was concentrated by distillation to obtain the maximum yield. Red wine colored precipitate of the adduct was formed.

Obtained residue dissolved in ether and cooled to 10°C and the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride.

Total twelve ternary complexes were prepared viz., [VO(DPhAA)$_2$(IMI)], [VO(DPhAA)$_2$(Me-IMI)], [VO(DPhAA)$_2$(Et-IMI)], [VO(TFPhAA)$_2$(IMI)], [VO(TFPhAA)$_2$(Me-IMI)], [VO (TFPhAA)$_2$ (Et-IMI)], [VO(TMH)$_2$(IMI)], [VO(TMH)$_2$(Me-IMI)], [VO(TMH)$_2$(Et-IMI)], [VO(AA)$_2$(IMI)], [VO (AA)$_2$(Me-IMI)] and [VO(AA)$_2$(Et-IMI)] abbreviated as 7-imi,7-me imi, 7-et imi, 2-imi, 2-me imi, 2-et imi, 4-imi, 4-me imi, 4-et imi, 8-imi, 8-me imi and 8-et imi respectively. The general scheme for the formation of ternary adducts is given in figure 2.

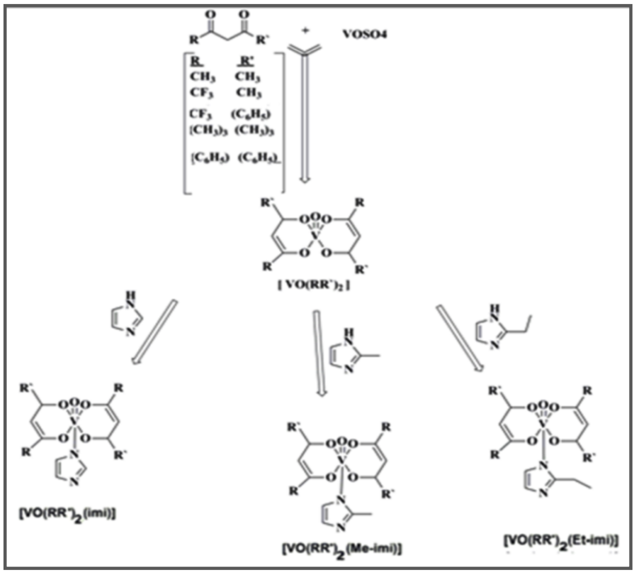


Figure 2. The general scheme for formation of various ternary adduct complexes.

RESULTS AND DISCUSSION

Physical properties of different Vanadium metal complexes are given in table 1. Magnetic moments measured at 300K are found in the range 1.56 –1.89 BM suggesting single unpaired electron in these complexes. Conducting measurements on these complexes reveals that these are non-electrolytes, suggesting neutrality in these complexes. Colors of the complexes are due to transition of single unpaired electrons.

Table 1. Physical properties of different vanadium metal complexes

S.No.	Complex	Decomposition Temp.(°C)	μ_{eff} (BM) 300 K	Λ_m (Scm^2mol^{-1})	Color
1	7-imi	171	1.802	3.33	Thick Brown
2	7-me imi	186	1.891	5.62	Thick Brown
3	7-et imi	195	1.716	5.29	Thick Brown
4	2-imi	161	1.74	4.87	Light Brown
5	2-me imi	177	1.748	3.64	Light Brown
6	2-et imi	185	1.721	5.72	Light Brown
7	4-imi	166	1.707	4.15	Light Yellow
8	4-me imi	178	1.677	3.18	Yellow
9	4-et imi	183	1.683	4.22	Dark Yellow
10	8-imi	142	1.74	5.85	Blue Green
11	8-me imi	152	1.712	3.42	Olive Green
12	8-et imi	156	1.718	4.55	Blue Green

IR spectra: The characteristic V=O stretching mode was observed at 997cm^{-1} in [VO(AA)$_2$] complex [**10**]. The V=O stretching mode was lowered in the binary complexes when compared to free salt. This is an indication of coordination of acetylacetone (AA) to metal. Similarly, in substituted acetylacetones, the characteristic V=O stretching mode was observed at 920 - 940cm^{-1}.The further lowering of stretching frequency of V=O is due to the electron withdrawing group attached to the β-diketones. The IR stretching frequency of different ternary metal complexes are given in table 2. As a representative case the IR spectra for 7-B, 7-imi, 7-me imi, 7-et imi are given in figure 3.

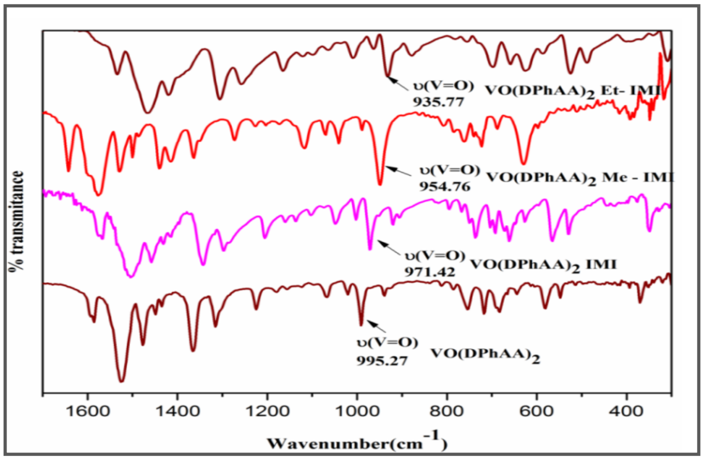


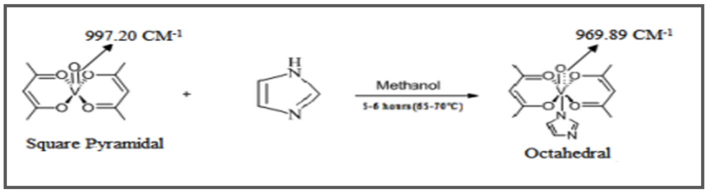
Figure 3. IR spectra of [VO(DPhAA)$_2$] and their corresponding ternary complexes.

The addition of base (viz, Imidazole or substituted Imidazole) to the different binary complexes of vanadium, changes the geometry from square pyramidal (5 coordinated) to octahedral (6 coordinated). The bases when coordinated to binary complexes of vanadium, they increase the electron density (N→V) at metal d-orbitals of vanadium and consequently the $p\pi - d\pi$ donation from oxygen to metal in V=O, is expected to be reduced, there by V=O bond lengthens, weakens and shift to lower wave number in IR spectra.

Table 2. Selected IR stretching frequencies of different ternary metal complexes

S.No.	Binary complexes	υ (V=O) cm^{-1}	Imidazole adducts	υ (V=O) cm^{-1}	Diff. in cm^{-1}
1	7 –B	995.27	[7-Imi]	971.42	23.85
2	7 – B	995.27	[7-Me-imi]	954.76	40.51
3	7 - B	995.27	[7-Et-imi]	935.77	59.5
4	2-B	951.11	[2-Imi]	935.94	15.17
5	2-B	951.11	[2-Me-imi]	928.44	22.67
6	2-B	951.11	[2-Et-imi]	922.51	28.6
7	4-B	960.17	[4-Imi]	939.84	20.33
8	4-B	960.17	[4-Me-imi]	924.41	35.76
9	4-B	960.17	[4-Et-imi]	918.54	41.63

The IR stretching frequencies of different octahedral (Imidazole adducts of vanadyl substituted acetyl acetone) complexes are given in table 2 along with the extent of lowering of stretching frequencies.



Mass Spectra: The mass spectra of (7-Imi) ternary complex as a representative case is given in figure 4. The m/z ratio obtained is 581(M+1) which agrees with the theoretical mass. The obtained m/z ratios for various metal complexes are given in table-3 which are in consistent with theoretical mass values.

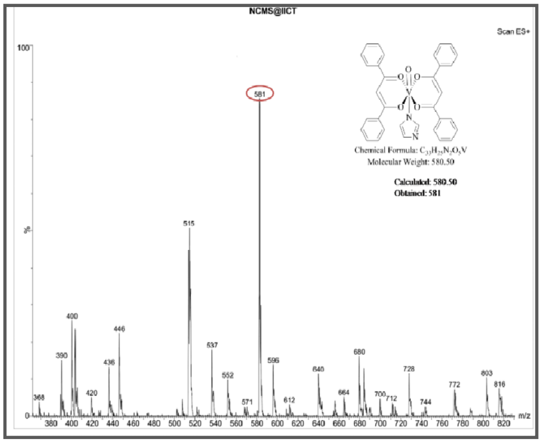


Figure 4. The mass spectrum of [7-Imi].

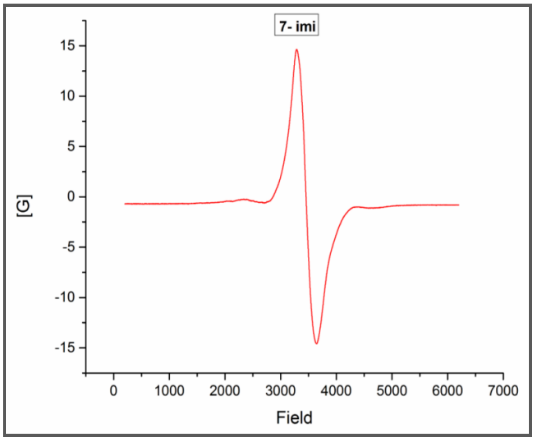


Figure 5. EPR spectra of 7-imi complex

Table 3. Mass spectral data for different vanadium metal complexes

S.No.	Complex	Theoretical mass	Observed mass
1	[7-Imi]	580.50	581(M+1)
2	[7-Me-imi]	594.53	595(M+1)
3	[7-Et-imi]	608.56	609(M+1)
4	[2-Me-imi]	578.33	579(M+1)
5	[4-Me-imi]	514.57	515(M+1)
6	[4-Et-imi]	528.60	529(M+1)
7	[8-Imi]	332.23	333(M+1)
8	[8-Me-imi]	346.25	347(M+1)
9	[8-Et-imi]	360.28	361(M+1)

EPR Spectra: In EPR spectra, for a free electron, the Lande factor (proportionality g factor^{-1}) [**11, 12**] is 2.00232. For organic radicals, the value is typically quite close to that of a free electron with values ranging from 1.99-2.01. For transition metal compounds, large variations can occur due to spin-orbit coupling and zero-field splitting and results in values ranging from 1.4 to 3.0. ESR spectra of 7-imi complex are shown in figure 5 and obtained g values are $g_{\parallel} > g_{\perp} < 2.00232$, for octahedral complex and$g_{\parallel} < g_{\perp} > 2.00232$, for square pyramidal complex. The $g_{\parallel}$, $g_{\perp}$ values for other complexes are given in table 4.

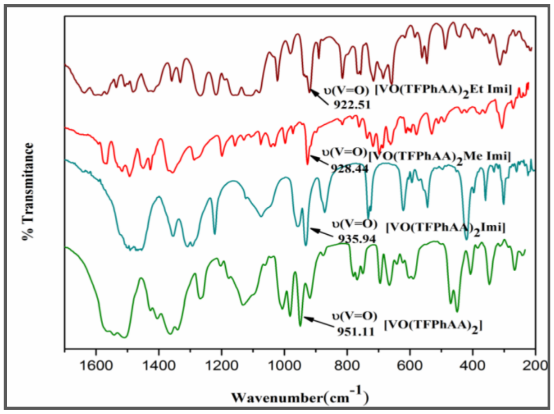
Table 4. Vanadium complexes and their g ∥, g ⊥values.

S.No	Complex	g ∥	g ⊥	Structure
1	[2-Me-imi]	2.032	1.953	Octahedral
2	[4-Me-imi]	2.0229	1.949	Octahedral
3	[7-et imi]	2.088	1.9075	Octahedral
4	[7- imi]	2.031	1.953	Octahedral

The physical data and various spectra suggest that the synthesized complexes have square pyramidal (binary complexes) and octahedral (ternary complexes) geometries and are non- electrolytes.

Supplementary information (SI): Spectral data for various complexes are available supplementary information these are IR, Mass and EPR spectra's shown in figure 6-15.

IR Graphs



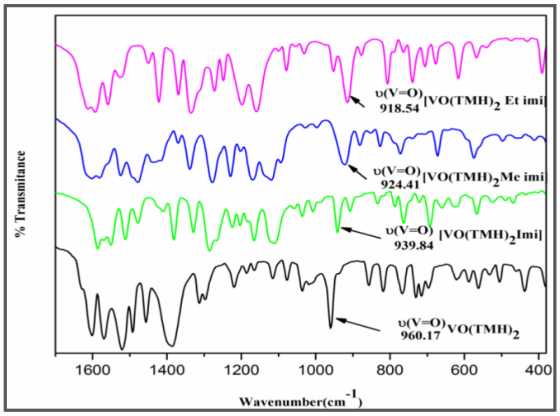


Figure 6 IR spectra of [VO(TMH)$_2$] and their corresponding ternary complexes.

Figure 7. IR spectra of [VO(TFPhAA)$_2$] and their corresponding ternary complexes.

Mass Spectra

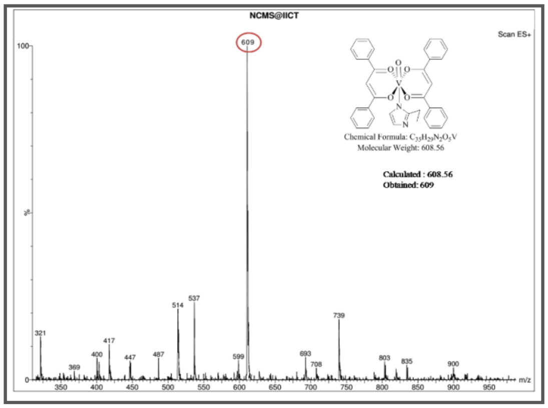


Figure 8. The mass spectrum of [7- Et Imi]

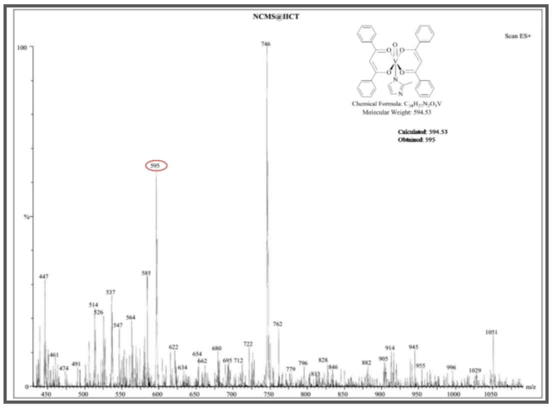


Figure 9. The mass spectrum of [7- Me Imi]

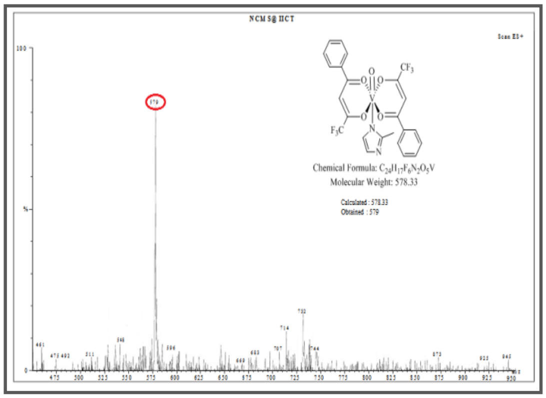


Figure 10. The mass spectrum of [2- Me Imi]

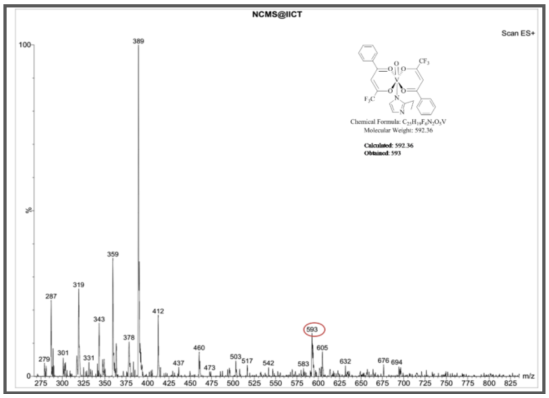
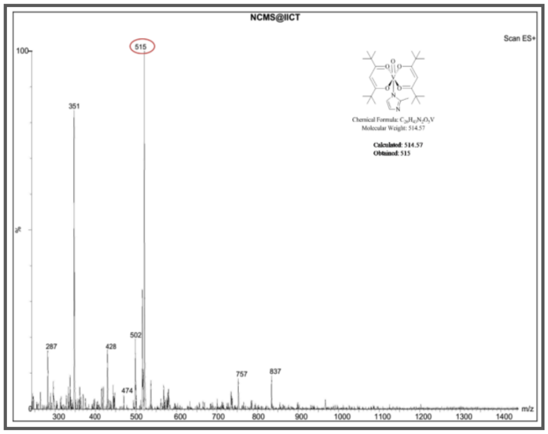


Figure 11. The mass spectrum of [2- Et Imi]



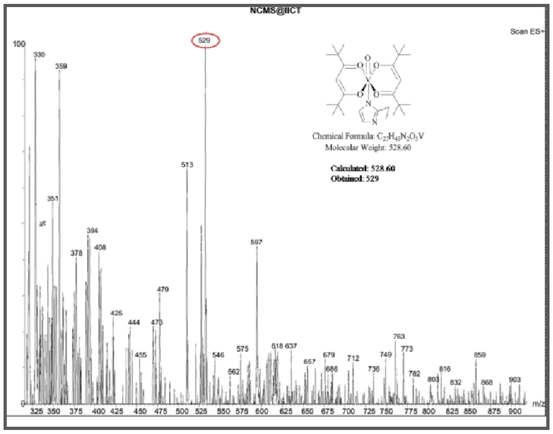
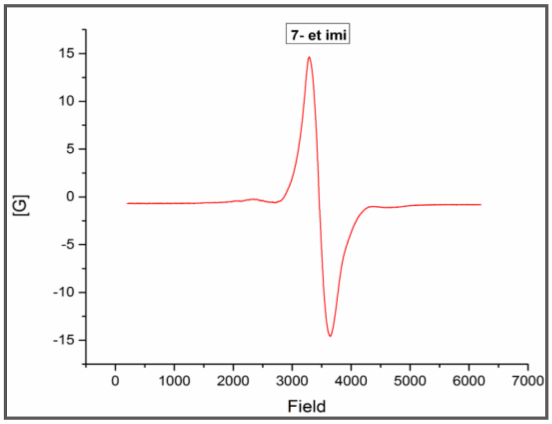


Figure 12. The mass spectrum of [4- Me Imi]

Figure 13. The mass spectrum of [4- Et Imi]

ESR Spectra



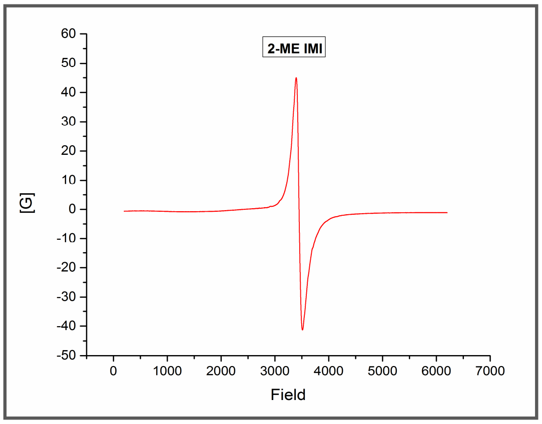


Figure 14. EPR spectra of 7-Et imi complex

Figure 15. EPR spectra of 2-me imi complex

APPLICATION

The vanadium metal complex with organic ligands instead of pure different vanadyl salts offers a far more versatile means of delivering the metal. In other words, vanadium in the form of organic metal complexes appears in many ways to be superior to the inorganic vanadate or vanadyl in terms of the absorption, distribution, tissue uptake, retention and insulin mimetic activity. Thus, the properties of the metal complex may be improved by the correct choice of *ligand* and useful therapeutic effect may be achieved. This substituted acetylacetones along with different imidazoles form a neutral ternary complexes. This neutrality of complexes will help in absorption and distribution of vanadium metal when compared to negative vanadyl ion on its substituents.

CONCLUSION

Vanadyl complexes have been synthesized, characterized. All the spectral studies revealed the coordination of vanadyl ion to the ligand (Substituted β-diketone). Based on above characterization techniques, we concluded the binary complexes attained square pyramidal geometry and ternary complexes showed octahedral geometry.

ACKNOWLEDGMENTS

The authors thank the Head, Department of Chemistry, Osmania University, India for providing necessary facilities to carry out the present investigation and DST, India for financial support. This investigation is part of outcome of the research project of DST (DST-SERB-SB/EMEQ-296/2014(SERB) dt.16-3-2016).

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