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SYNTHESIS AND CHARACTERIZATION OF 1&1,5-DI SUBSTITUTED BIS(ACETYLACETANATO)OXOVANADIUM(IV) OCTAHEDRAL METAL COMPLEXES AND THEIR 3,4&4-DISUBSTITUTED PYRIDINE ADDUCTS

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ABSTRACT

Monomeric six coordinated adducts of 1,5-disubstituted bis(acetylacetonato)oxovanadium(IV) having general formula, [$VO(RCOCH_2COR')_2(L)$], [R= phenyl, CF_3R'= Napthyl,CF_3 and L= 4-Methyl pyridine, 3-Amino-4-Hydroxy pyridine] have been synthesized and their adducts with 4-Methyl pyridine & 3-Amino-4-Hydroxy pyridine prepared. The compounds were characterized by magnetic moment and molar conduct studies, Mass Spectroscopy, Infra red spectroscopy, electronic spectroscopy, ESR Spectroscopy, Powder X-ray diffraction, magnetic and conductivity measurements having 1:1 stochiometry. The adducts were found to be paramagnetic and their magnetic moments at room temperature lie within the 1.68-1.79 B.M. range and this indicates the presence of one unpaired electron. The values are in accordance with the octahedral geometry. The magnetic moment measurements and electronic spectra illustrates a octahedral geometry around the vanadium centre.

Keywords: Synthesis , Ligands , bis(acetylacetonato)oxovanadium(IV), Mass, IR, UV, ESR, XRD.

INTRODUCTION

The coordination chemistry and reactivity of vanadium has constant to assist a significant role not only for the reason that of physiological consequence of the metal but also for its activity in diverse industrial processes. Several therapeutic effects have been described for vanadium as well as Cardiovascular, hormonal, insulin mimetic and anti carcinogenic activities.[1-5]. Recently, in a study of various coordination modes of vanadyl complexes, a vanadyl methylpicolinate complex with long-acting character and low toxicity was found to be the most effective in the treatment of insulin and non-insulin dependent diabetes mellitus (NIDDM) in rats when administered orally. Because of the various functions of this metal, its complexation behaviour with organic ligands remains of continued interest [6-10].

Oxovanadium(IV) β-diketonates be exceedingly stable complexes having a square-pyramidal structure with the vanadium atom near the center of magnitude[11]. The sixth coordination site of these complexes has

been used as reference acid in establishing a quantitative measure of donor strengths of nitrogen bases, tertiary amides, substituted pyridines Adducts.

In the present study, we have synthesized oxovanadium(IV) complexes of β-diketones [RCOCH2COR'] varying the R & R' position's in 2,4-pentanediones with substituents like methyl (CH_3), Tetramethyl $(CH_3)_2$, Hexamethyl (HM) and subsequently their 4-methyl- pyridine and 3-Amino-4-Hydroxy pyridine adducts[12-14]. Their magnetic, infrared, Mass, XRD , ESR and electronic spectral properties are discussed.

MATERIALS AND METHODS

Oxo vanadium(IV) sulphate procured from Aldrich. The β- di ketones namly Acetyl acetone(pentane2,4-dione) (AA) , Trifluorophenylacetylacetone(4,4,4-trifluoro-1-phenyl-1,3-butanedione)(TFPHAA),Napthyltrifluoroacetone(4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione)(NTFA) , 4-Methyl pyridine (4-MP) , 3-Amino-4-Hydroxy pyridine(3A4HP), Sodium carbonate , were Aldrich and merck products. All the solvents (Pet-ether, Ethanol , Methanol , Isopropyl alcohol, Sulphuric acid) are Analytical Reagent grade only.

Experimental procedures :

Preparation of Oxovanadium(IV) Complexes - A mixture of V_2O_5 (2.0g 0.010mmol) ,Ethanol (20.0ml) ,Water (5.0ml) and sulphuric acid (4.0ml) was refluxed for one hour and then added to a solution of (2.20 g 0.021mmol) in ethanol (30ml).To the resulting solution a supersaturated solution of sodium acetate was added drop wise to bring the p^H of the reacting solution to five to six .The resulting green precipitates formed $[VO(acac)_2]$ was filtered, washed with ethanol and recrystallized from chloroform in 75% (4.86 g) yield . Other oxovanadium(IV) complexes were prepared similarly.

Preparation of adducts -

[Bis(acetylacetonato[AA])(4-Methylpyridine)oxovanadium(IV)] (1) Bis (acetylacetonato) oxo vanadium(IV) (1.00 g, 0.003 mol) was dissolved in methanol (about 10 ml). To the resulting solution 4-Methyl pyridine (0.32 g, 0.003 mol) was added. The reaction mixture was stirred for about 5-6 hrs and then the solution was concentrated by distillation to obtain the maximum yield. Green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride Yied 0.785g (60%) . The composition of the adduct was established to be $VO(acac)_2$(4MP) by the Mass spectral analysis, adduct found 361 (M^{+1}) ; calculated 360.

[Bis(acetylacetonato[AA])(3-Amino-4-Hydroxy pyridine)oxovanadium(IV)] (2) Bis (acetylacetonato) oxo vanadium(IV) (1.00 g, 0.003 mol) was dissolved in methanol (about 10 ml). To the resulting solution 3-Amino-4-hydroxy pyridine (0.33 g, 0.003 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. Dark green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride Yied 0.85 g (62%) . The composition of the adduct was established to be $VO(acac)_2$ (3A4HP) by the Mass spectral analysis, adduct found 378 (M^{+1}) ; calculated 377.

[Bis (Trifluorophenylacetylacetone(4,4,4-trifluoro-1-phenyl-1,3-butanedione)(TFPHAA), [4-Methylpyridine)oxovanadium(IV)](3) Bis()(2,2,6,6-tetramethyl-3,5-heptanedione)(DPM) oxovanadium(IV) (1.00 g, 0.002 mol) was dissolved in methanol (about 10 ml). To the resulting solution 4-Methyl pyridine (0.23 g, 0.002 mol) was added. The reaction mixture was stirred for about 5-6 hrs and then the solution was concentrated by distillation to obtain the maximum yield. Thick green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride yield 0.767 g (62%). The composition of the adduct was established to be $VO(TFPHAA)_2$ (4-MP) by the Mass spectral analysis, adduct found 469 (M^{+1}) ; calculated 468.

[Bis (Trifluorophenylacetylacetone(4,4,4-trifluoro-1-phenyl-1,3-butanedione)(TFPHAA),(3-Amino-4-Hydroxy pyridine) oxovanadium(IV)] (4) Bis (acetylacetonato) oxo vanadium(IV) (1.00 g, 0.002 mol) was dissolved in methanol (about 10 ml). To the resulting solution 3-Amino-4-hydroxy pyridine (0.33 g, 0.003 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. Dark green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride Yied 0.75 g (59%) . The composition of the adduct was established to be $VO(TFPHAA)_2(3A4HP)$ by the Mass spectral analysis, adduct found 486 (M^{+1}) ; calculated 485.

[Bis(Napthyltrifluoroacetone(4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione)(NTFA)(4-Methylpyridine)oxovanadium(IV)(5)Bis(Napthyltrifluoroacetone(4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione)(NTFA))oxovanadium(IV) (1.00 g, 0.001 mol) was dissolved in methanol (about 10 ml). To the resulting solution 4-Methyl pyridine (0.093 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. Light green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride yield 0.599g (51%). The composition of the adduct was established to be $VO(NTFA)_2$ (4-MP) by the Mass spectral analysis, adduct found 577 (M^{+1}) ; calculated 576.

[Bis(Napthyltrifluoroacetone(4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione)(NTFA)(3-Amino-4-Hydroxypyridine) oxovanadium(IV)] (6) Bis(Napthyltrifluoroacetone(4,4,4-trifluoro-1-(2-napthyl)-1,3-butanedione)(NTFA)) oxo vanadium (IV) (1.00 g, 0.001 mol) was dissolved in methanol (about 10 ml). To the resulting solution 3-Amino-4-hydroxy pyridine (0.11 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. Very light green coloured precipitates of the adduct were formed. Obtained residue dissolved in Ethanol and cooled to 10^0C the precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride Yied 0.69 g (57%) . The composition of the adduct was established to be $VO(NTFA)_2$ (3A4HP) by the Mass spectral analysis, adduct found 594 (M^{+1}) ; calculated 593.

RESULTS AND DISCUSSION

The analytical data, proportion yields , colour and room temperature magnetic moments of the complexes are existing in Table I. The complexes reveal various shades of green and were obtained in reasonable yields of 65-85% from the reaction medium. The familiar chemical equation for the configuration of the complexes are as follows.

$$VOSO_4 . x\ H_2O + 2\ RCOCH_2COR' \longrightarrow VO(RCOCH_2COR')_2 + H_2SO_4 + H20$$

where $RCOCH_2COR'$ = the various 3,4-substituted 2,4-pentanediones. The representative equation for the formation of the 4-methylpyridine and 3-Amino-4-hydroxy pyridine adducts obtained from Isopropyl alcohol solution is given below.

$$VO(RCOCH_2COR')_2 + L \longrightarrow VO(RCOCH_2COR')_2L$$

where L= 4-methylpyridine(4-MP) or & 3-Hydroxy-4-methylpyridine(3A4HP)

Magnetic moment and molar conductance studies - The adduct complexes of bis(acetylacetonato)oxovanadium(IV) are crystalline solids which are light/Dark green in colour. These are insoluble in common organic solvents such as ethanol, acetone, benzene etc. However these are soluble in THF, dimethyformamide and dimethylsulfoxide. On the basis of elemental analysis (Table 1) they have been assigned the general formula $[VO(RCOCH_2COR')_2(L)]$, [R= phenyl, CF_3R'= Napthyl,CF_3] and L= 4-Methyl pyridine, 3-Amino-4-Hydroxy pyridine]. Conductance values of these complexes in DMF fall in the range of 3.12-6.12 ohm-1 mole-1 cm. (Table 1). These values are lower than the values expected for

any uni-univalent electrolytes in this solvent suggesting that these complexes are neutral and non-ionic in character. The magnetic moments of 1:1 complexes of substituted bis(acetylacetonato)oxovanadium(IV) with heterocyclic nitrogen donor ligands fall in the range1.68-1.79 B.M (Table:1) which is in agreement with magnetic moment values observed for octahedral geometry.

Spectral studies

Mass spectra - The major Mass peaks for the $VO(RCOCH_2COR')_2L$ and the mixed ligand mass values given in table—All the complexes are displayed major molecular ion peaks. A number of fragment ion corresponding to vanadyl peaks have appeared for the mixed ligand complexes .The fragment ion M^{+1} at 252 assigned to $[V(acac)_2]^+$ is distinguishing of mixed ligand bis(acetylacetonato) 4 & 3,4-disubstituted pyridine Vanadium complexes only.The absence of the following fragments corresponding to V^{2+} or [V-L-V] are indicative of monomeric nature of complexes with molecular weight determinations and IR spectral studies.

Infrared Spectra - The significant infrared vibrational frequencies are given in Table II with their assignments. The bands appearing between 1556-1728 cm^{-1} and 1496-1647cm^{-1} have been assigned to the asymmetric stretching frequencies for ν_{as}(C=O) and ν_{as}(C=C), respectively. The symmetric stretching frequencies ν_s(C=O) and ν_s(C=C), for the compounds also appear between 1337-1492cm^{-1} and 1157-1309cm^{-1}, respectively. The ν_{as}(C=O) and ν_{as}(C=C), frequencies in the adducts appear at slightly lower frequencies measured up to the parent 1,5-substituted β-diketonates. This appears to be due to the weakening of the C=O and C=C bonds as a result of transfer of increasing amounts of charge from the 4-methylpyridine. These assignments correlate favourably with observations made by previous workers on similar systems[15-16]. The vanadyl stretching frequenciesν (V=O) for the compounds appear between 921-997cm· There is obvious reduction in the ν (V=O) frequencies (20-35$cm^{-1\ approx}$) on adduct formation compared to the parent compounds suggesting the interaction of the nitrogen of 4-methylpyridine & 3-Amino-4-Hydroxy pyridine with the sixth coordination site of the molecules except in $VO(acac)_2$4-MP where there appears to be little or no difference. Isobe et al [17] . similarly observed a shift (ca. 25cm^{-1}) in nitrogenous base adducts compared to the parent oxovanadium(IV) β -diketonates. The ν (V=O) sensitive modes also appear to follow the same pattern with reduction in the values obtained for the adducts. These facts coupled with the reduction in the ν (V=O) bands strongly suggest that the 4-methylpyridine and 3-Amino-4-Hydroxy pyridine base occupy the coordination site trans to the vanadyl oxygen. The values observed for the vanadyl stretching frequencies seem to be normal for five-coordinate, square-pyramidal and non-polymeric, six-coordinate oxovanadium(IV) complexes[18-21].

Table: 1 molar conductance, magnetic moments, melting point, adduct colour and analytical data (calculated %) of 1:1 adducts with Substituted bis (acetylacetanato)oxovanadium(IV) with heterocyclic nitrogen donor ligands.

Compound	**V_1cm^{-1}**	**V_2cm^{-1}**	**V_3cm^{-1}**	**V_{as}(C=O)**	**V_{as} (C=C)**	**V_s (C=O)**	**V_s (C=C)**	**V (V-O)**	**V(V-O)**
$VO(AA)_2$	14210	17010	23000	1656 m	1527 s	1373 s	1288 m	997 vs	609w 484s 424w 368m
$VO(AA)_2$.4MP	14800	17200	22100	1637 s	1502 s	1337 m	1249 m	985 vs	675w 586m 430w 364m
$VO(AA)_2$.3A4HP	15300	17750	22300	1614 m	1496 vs	1371 vs	1276 m	968 vs	607w 547w 453m 351w
VO(TFPHAA)$_2$	14300	17500	21700	1658vs	1535 s	1367 s	1300 vs	929 vs	601s 536w 449m 360m
VO(TFPHAA)$_2$.4MP	14900	17500	22900	1627 s	1506 m	1379 m	1309 m	996 s	669m 582m 422w 352w
VO(TFPHAA)$_2$.3A4HP	15700	17400	22500	1610 vs	1552 s	1359 s	1294 vs	960 s	594m 543m 412w 341 m
VO(NTFA) $_2$	14800	17200	22400	1728 s	1647 s	1456 s	1228	941 s	597m 514s 430w 368s
VO(NTFA)$_2$.4MP	15100	17600	22600	1637 s	1504 m	1486 w	1157 vs	921 m	605s 516m 430m 308w
VO(NTFA $_2$.3A4HP	15850	17910	22890	1663 s	1509 m	1492 vs	1157 vs	941 m	615s 516m 432w 370m

Table:2 Electronic and Infrared spectral data of 1:1 adducts of bis(acetylacetonato) oxovanadium(IV) with heterocyclic nitrogen donor ligands

S.No	Name of The Adducts	M.P	B.M (293k)	Colour	Conductivity (μs/Cm) *10^{-6}	Elemental Analysis(%) (Calculated)					
						C	H	N	O	V	F
1	$VO(AA)_2.4MP$	158	1.68	green	5.89	55.67	7.01	3.61	20.60	13.12	--
2	$VO(AA)_2.3A4HP$	150	1.79	Dark green	3.42	50.37	6.47	6.91	23.68	12.57	--
3	$VO(TFPHAA)_2.4MP$	175	1.76	Thick green	4.74	43.56	4.26	2.82	16.12	10.26	22.97
4	$VO(TTFPHAA)_2.3A4HP$	180	1.75	Dark green	4.84	39.79	3.93	5.46	18.70	9.92	22.21
5	$VO(NTFA)_2.4MP$	198	1.69	Light green	5.12	35.78	2.50	2.32	13.24	8.43	37.73
6	$VO(NTFA)_2.3A4HP$	210	1.72	Light green	7.50	32.87	2.27	4.51	15.45	8.20	36.70

Electronic Spectra - The elucidation of the electronic spectra of oxovanadium(IV) complexes has been a subject of exhaustive and continued discussion. However, more evidences seems to favor the ordering proposed by Ballhausen and Gray [22] with some modifications by Selbin[23]. d Yang. The soothe electronic reflectance spectra and solution spectral data recorded figure:1 in methanol are presented in Table:2 Most of the complexes as solid and in solvents exhibit three-spin allowed transitions in the 14010-15,850; 17,000-18,000, and 21,700-25,000cm^{1} regions and have been assigned to $b_2 \rightarrow e^* \prod$, b2→b1 and b2→ a1 transitions, respectively[24-25]. On adduct formation the band positions experienced a slight shifts to lower energy. Equally of note is the similarity in band features in the solid state and solution suggesting no fundamental structural changes in both phases. The spectral characteristics above are consistent with lower-symmetry C2V complexes. There is a noticeable increase in the energy of the b2→ $e^* \prod$ p transition in the substituted β-diketonates and adducts.

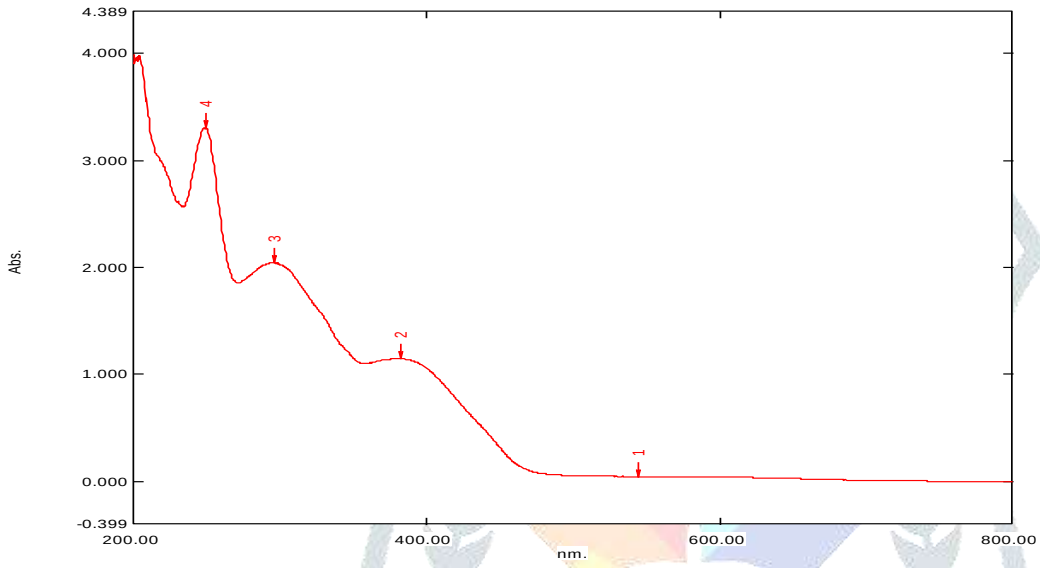


Figure:1 Electronic spectra of [Bis(1,1,1-5,5,5-hexafluoro-pentanedione[HFAA])(3-Amino-4-Hydroxy pyridine)oxovanadium(IV)]

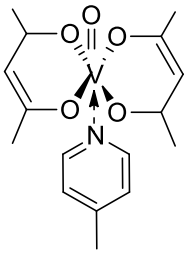
EPR Spectra - The ESR spectrum of Vanadium complexes were recorded on X-band at frequency 9.1 GHz at low temperature. The spectral data of all complexes are consistent with the typical monomeric vanadium adducts [26-27]. All Complexes exhibit more or less four gll components and a broad $g_{\perp}$ component, such broadening of the $g_{\perp}$ component is an indication of symmetry lowering, possibly due to the strain created by the substituted pyridiine ligands. According to the data, g_{ll} and $g_{\perp}$ values for all VO(IV) complexes are found to be in the range of 2.1497-2.1594, 2.0391-2.1302 respectively . The ESR spectra of [$VO(RCOCH_2COR')_2(L)$], [R= phenyl, CF_3R'= Napthyl,CF_3] and L= 4-Methyl pyridine, 3-Amino-4-Hydroxy pyridine].The ESR data of some ternary VO(IV) metal complexes [28-29] are presented in **Table-3.** From the data, it is clear that $g_{ll} > g_{\perp} > 2.0023$ (g_e) which suggest the unpaired electron present in d_{x2-y2} orbital giving $^2B_{1g}$ as the ground state and all the complexes are in Octahedral geometry. The g values are related to axial symmetry parameter G by the Hathway expression i.e. G= (g_{ll} -2.0023) / ($g_{\perp}$-2.0023). According to the data, the G values for all VO(IV) complexes are found to be more than 4 indicating the ligands are strong field and the metal ligand bonding in these complexes is covalent[30-31]. From the data it is also observed that the g_{ll} values are less than 2.3 suggesting covalent bond between metal and ligand in these complexes. The tentative structure of metal complexes shown in **Figure-2.**

Table-3. ESR data of Ternary VO (IV) complexes

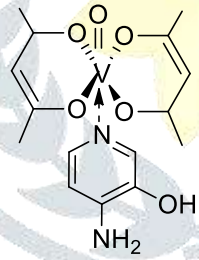
Complex	$g_{\parallel}$	$g_{\perp}$	G
VO(AA)2.4MP	2.1594	2.1302	4.67
VO(AA)2.3A4HP	2.1539	2.0402	4.28
VO(TFPHAA)2.4MP	2.1498	2.0423	5.05
VO(TFPHAA)2.3A4HP	2.1510	2.0391	4.96
VO(NTFA)2.4MP	2.1497	2.0411	5.12
VO(NTFA)2.3A4HP	2.1526	2.0426	4.76

Estimated structures for the following adducts

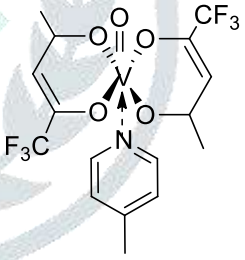
Fig : 2



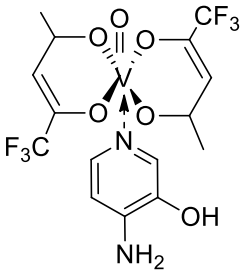
[Bis(acetylacetonato[AA])(4-Methylpyridine)oxovanadium(IV)]



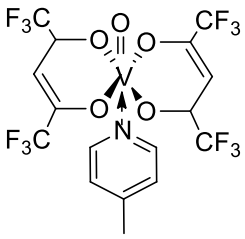
Bis(acetylacetonato[AA])(3-Amino-4-Hydroxy pyridine)oxovanadium(IV)]



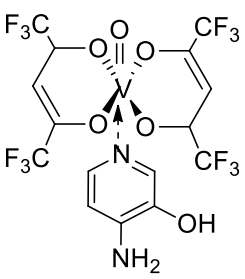
[Bis(1,1,1-trifluoro-2,4-pentanedione[TFAA])(4-Methylpyridine)oxovanadium(IV)]



[Bis(1,1,1-trifluoro-2,4-pentanedione[TFAA])(3-Amino-4-Hydroxy pyridine)oxovanadium(IV)]



[Bis(1,1,1-5,5,5-hexafluoro-pentanedione[HFAA])(4-Methylpyridine)oxovanadium (IV)



[Bis(1,1,1-5,5,5-hexafluoro-pentanedione[HFAA])(3-Amino-4-Hydroxy pyridine)oxovanadium(IV)]

Xrd - Powder X-ray diffraction (PXRD) pattern of the as-prepared adducts is shown in figure-3. Bragg diffraction peaks at 2θ =25.55^0 , 33.14^0, 36.37^0, 44.61^0,and 54.07^0 are the main peaks observed in the diffraction analysis.The peaks at 25.55^0 and 44.610 correspond to hexagonal vanadium complexes.The peak at 2 θ =25.55^0 with a broad diffraction signal from about 14^0 to 30^0 and an intensity of about 8800(au) units indicates the presence of large amounts of amorphous oxovanadium adducts in the as - prepared .The low intensity of the peak at 2 theta =44.61^0,is an indication of the quality of oxovanadium adducts present in the as-prepared product. The peaks at 2 θ =33.14^0,36.37 and 54.070 correspond to crystal planes of (111), (200) ,and (220) of vanadium in the substituted bis(acetylacetonato)oxovanadium (IV) used in the synthesis.

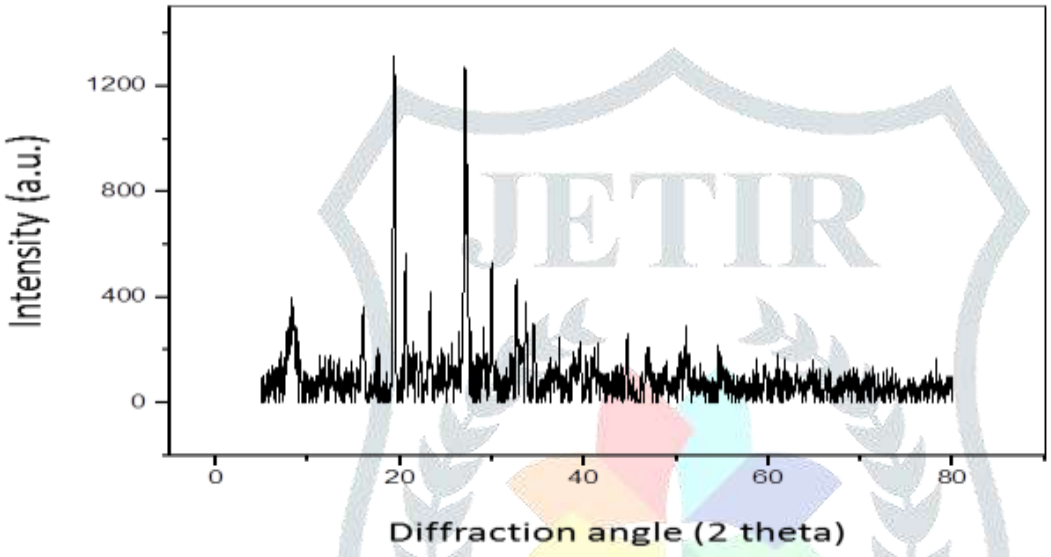


Fig:3 X-ray diffraction analysis of $VO(HFAA)_2.4MP$

CONCLUSION

The analytical data of the compounds show reaction of the VO2+ ion to ligand in the ratio 1:2 while the adduct formation with the parent complexes are in the ratio 1:1. The infrared ,Mass, and electronic spectra observed for the compounds suggest a five-coordinate square-pyramidal geometry for the parent oxovanadium(IV) 1,5-substituted β-diketonates (Fig. 1) while in the adducts an octahedral six-coordinate geometry is possible with the 4-methylpyridine base attached to the axial position of the vanadyl oxygen(fig:2). The observed magnetic moment is typical of magnetically dilute oxovanadium(IV) compounds and it also suggests that the compounds are not polymeric.

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