Studies on Synthetic, Analytical, Spectral and Magnetic Properties of Oxovanadium (V) Complexes of Schiff Bases

M.N.MOOKERJEE, R.V.SINGH AND J.P. TANDON*
Department of Chemistry, University of Rajasthan, Jaipur-302004, India

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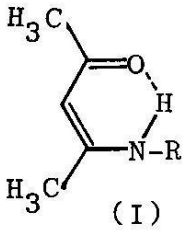
Summary: Reactions of oxovanadium triisopropoxide with nitrogen donor ligands under controlled and anhydrous conditions have yielded two interesting series of oxovanadium (V) complexes of the type: (i) $VO(OPr^i)_2(SB)$ and $VO(OPr^i)(SB)_2$ and (ii) $VO(OPr^i)(S'B')$ and $(VO)_2(S'B')_3$ (where SBH and $S'B'H_2$ represent the monofunctional bidentate and bifunctional tridentate Schiff base molecules, respectively). The alcoholysis reactions further give $VO(OBu^t)_2(SB)$, $VO(OBu^t)(SB)_2$ and $VO(OBu^t)(S'B')$ type of derivatives in presence of excess of t-butanol. All the resulting complexes are coloured solids or semisolids and behave as non-electrolytes in anhydrous DMF. The IR, UV, ^1H NMR and magnetic measurements have been discussed in support of the proposed structures.

Introduction

During the last two decades, considerable amount of work has been reported on the coordination chemistry of oxo-vanadium species [1-4]. The complexes of acetylacetone and other β-diketones have received major attention from the stand point of preparation, adduct formation, magnetic and spectral studies. Comparatively, scanty references are available on the Schiff base derivatives of vanadium. Theriot et al. [5] have reported oxovanadium (IV) complexes with tridentate Schiff bases derived from salicylaldehyde and amino acids. Ravenko et al. [6] prepared some subnormal complexes of oxovanadium (IV) with ONS donor ligands having μ eff in the range 1.27 to 1.33 B.M.

A resume of the literature survey reveals that most of the studies on Schiff base complexes of vanadium pertain to oxovanadium (IV) species. Furthermore, the work reported so far on vanadium (V) pertains to the solution studies and very few oxovanadium (V) complexes of Schiff bases have been isolated [7,8].

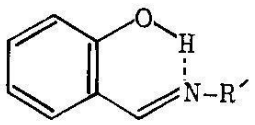
In view of the above and the success achieved in synthesizing the Schiff base complexes of niobium (V) and tantalum (V) reported earlier from these laboratories [9-11], it was considered of interest to syntesize and study a variety of Schiff base derivatives of oxovanadium (V) by the reactions of oxovanadium (V) triisopropoxide with different types of ketamines and aldimines, during the course of present investigations and suggest possible structures to the resulting new derivatives. The Schiff bases used in these investigations are of types (I) and (II).



(I)

Where (i) R=n-C_3H_7

(ii) R= -CH_2-CHOH
|
CH_3



(II)

R´=n-C_3H_7, n-C_4H_9, O-$CH_3C_6H_4$

m-$CH_3C_6H_4$ and p-$CH_3C_6H_4$

R´=CH-CH_2OH
|
CH_2-CH_3

Results and Discussion

The reactions of oxovanadium (V) triisopropoxide with the above ligands in 1:1, 1:2 and 2:3 stoichiometry in the medium of refluxing benzene can be represented by the following general equations:

$$VO(OPr^i)_3 + SBH \longrightarrow VO(OPr^i)_2(SB) + Pr^iOH$$

$$VO(OPr^i)_3 + 2SBH \longrightarrow VO(OPr^i)(SB)_2 + 2Pr^iOH$$

$$VO(OPr^i)_3 + S'B'H_2 \longrightarrow VO(OPr^i)(S'B') + 2Pr^iOH$$

$$2VO(OPr^i)_3 + 3S'B'H_2 \longrightarrow (VO)_2)\ (S'B')_3 + 6Pr^iOH$$

These reactions have been found to be quite facile and could be completed in 8-12 hours of refluxing. Their progress as well as completion could be ascertained by estimating the liberated isopropanol in the binary azeotrope with benzene oxidimetrically.

The resulting new derivatives have been isolated as coloured solids or semisolids after being repeatedly washed with n-hexane. These are soluble in benzene, DMF and DMSO. Attempts to distill some of these derivatives resulted in their decomposition. Their important physical characteristics are recorded in Table 1.

The monoiisopropoxy and diisopropoxy oxovanadium (V) derivatives so obtained are highly sensitive to moisture and turn into a sticky mass in the open atmosphere. However the tris Schiff base derivatives are hydrolytically stable. Being monomeric in nature, the vanadium atom in these complexes appears to be in the penta- and hexa- coordinated environment and the structures given in Figure (A) can be proposed.

ON and ONO represent the donor sets of Schiff bases, SBH and $S'B'H_2$, respectively.

The labile nature of the isopropoxy groups in $VO(OPr^i)_2(SB)_2$, $VO(OPr^i)(SB)_2$ and $VO(OPr^i)(S'B')$ type of derivatives could be demonstrated by the alcoholysis reactions, which these complexes undergo in presence of an excess of t-butanol in the medium of benzene under refluxing conditions:

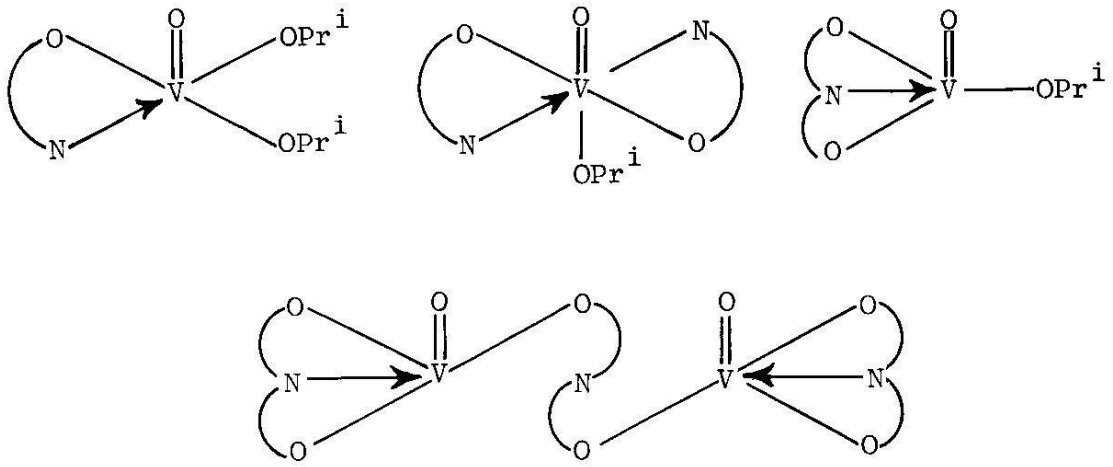


Fig.A: O⌒N and O⌒N⌒O represent the donor sets of Schiff bases, SHB and SBH_2, respectively)

$$VO(OPr^i)_2(SB) + t\text{-}C_4H_9OH \longrightarrow VO(OBu^t)_2(SB) + 2Pr^iOH$$

$$VO(OPr^i)(SB)_2 + t\text{-}C_4H_9OH \longrightarrow VO(OBu^t)(SB)_2 + Pr^iOH$$

$$VO(OPr^i)(S'B') + t\text{-}C_4H_9OH \longrightarrow VO(OBu^t)(S'B') + Pr^iOH$$

These reactions are, however, quite slow due to the bulkier nature of t-butoxy group and could be completed only on prolonged refluxing. Similar to the parent isopropoxy derivatives these are also coloured solids or semi-solids, monomeric in nature and soluble in benzene and common organic solvents. These have low values of molar conductance 10-15 $ohm^{-1}\ cm^{-1}\ mol^{-1}$ which indicate their non-electrolytic nature. Their important physical properties are summarized in table 1.

IR spectra

IR spectra of Schiff bases show broad absorption bands of strong to weak intensity in the region, 3320-2860 cm^{-1}. On account of strong hydrogen bonding, the frequency of hydrogen bonded OH is probably lowered to a considerable extent and overlaps with ν CH vibrations as reported by Freedman [12] also. These bands completely disappear in the corresponding vanadium complexes indicating the chelation of the metal atom to the oxygen and nitrogen atoms of the ligand moieties.

The characteristic band of the azomethine group (> C=N) observed at 1620 ± 10 cm^{-1} in the Schiff bases is shifted to the lower region (1605 ± 5 cm^{-1}) and is indicative of the coordination of azomethine nitrogen to the metal atom.

In the Schiff bases, a strong band is also observed at ∿ 1280 cm^{-1} and this may be attributed to the phenolic C-O stretching vibration. A considerable shifting of this band to the higher frequency (∿ 1310 cm^{-1}) in the vanadium complexes probably indicates the bonding of the metal atom to the oxygen of the C-O group. Further, the V=O streching frequency appears

Table-1: Physical Properties of Oxovanadium (V) Complexes

No.	Compound	Colour and State	M.P. (°C)	Molecular Weight Found (Calcd.)
1.	$VO(OPr^i)_2(C_8H_{14}NO)$	Yellowish brown semisolid	-	355.4 (325.3)
2.	$VO(OPr^i)(C_8H_{14}NO)_2$	Yellowish brown semisolid	-	387.2 (406.4)
3.	$VO(OPr^i)_2(C_{10}H_{12}NO)$	Dull brownish grey semisolid	-	354.4 (347.3)
4.	$VO(OPr^i)(C_{10}H_{12}NO)_2$	Brownish grey semisolid	-	461.9 (450.4)
5.	$VO(OPr^i)_2(C_{11}H_{14}NO)$	Yellowish brown semisolid	-	370.2 (361.3)
6.	$VO(OPr^i)(C_{11}H_{14}NO)_2$	Brown semisolid	-	462.8 (478.5)
7.	$VO(OPr^i)_2(C_{14}H_{12}NO)$	Light brown solid	212-14	381.5 (395.3)
8.	$VO(OPr^i)_2(C_{14}H_{12}NO)_2$	Yellowish brown solid	324(d)	590.6 (546.5)
9.	$VO(OPr^i)_2(C_{14}H_{14}NO)^*$	Yellowish brown solid	218-20	432.5 (395.3)
10.	$VO(OPr^i)(C_{14}H_{12}NO)_2^*$	Yellowish grey solid	300	558.2 (546.5)
11.	$VO(OPr^i)_2(C_{14}H_{12}NO)^{**}$	Brown semisolid	-	387.9 (395.3)
12.	$VO(OPr^i)(C_{14}H_{12}NO)_2^{**}$	Dark brown semisolid	-	551.6 (546.5)
13.	$VO(OPr^i)(C_8H_{13}NO_2)$	Grey solid	119(d)	262.4 (281.2)
14.	$(VO)_2(C_8H_{13}NO_2)_3$	Greyish black solid	228	607.8 (599.4)
15.	$VO(OPr^i)(C_{11}H_{13}NO_2)$	Brownish grey solid	290	336.3 (317.2)
16.	$(VO)_2(C_{11}H_{13}NO_2)_3$	Light greyish black solid	294	687.0 (707.5)
17.	$VO(OBu^t)_2(C_8H_{14}NO)$	Brown grey semisolid	-	365.0 (353.5)
18.	$VO(OBu^t)(C_8H_{14}NO)_2$	Yellowish grey semisolid	-	445.8 (420.4)
19.	$VO(OBu^t)_2(C_{14}H_{12}NO)$	Dull brown semisolid	-	415.2 (423.4)
20.	$VO(OBu^t)(C_{14}H_{12}NO)_2$	Dull yellow grey semisolid	-	555.9 (560.5)
21.	$VO(OBu^t)_2(C_{14}H_{12}NO)^*$	Dark brown solid	300	429.5 (423.4)
22.	$VO(OBu^t)(C_{14}H_{12}NO)^*_2$	Dark brown solid	306	585.3 (560.5)
23.	$VO(OBu^t)(C_8H_{13}NO_2)$	Greyish black solid	135(d)	281.9 (295.2)
24.	$VO(OBu^t)(C_{11}H_{13}NO_2)$	Greyish black solid	345(d)	302 (331.2)

* and ** have been used to distinguish compounds of the same molecular formula, d = decompose.

in the region 970-980 cm^{-1} as reported earlier also [13]. Further the appearance of new bands of medium to weak intensity in the regions, 440-460 and 410-425 cm^{-1} may be attributed to ν (V-O) [14] and ν (V-N) [15], vibrations, respectively. The appearance of additional bands at $\sim$1710,1130 $\pm$ 5 and 1110 $\pm$ 7 cm^{-1} may be due to the presence of isopropoxy groups in these complexes. However, in the case of t-butoxy derivatives, such bands are observed at $\sim$1000, 920 $\pm$ 5, 790 and 770 cm^{-1}.

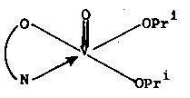
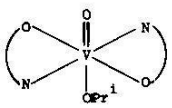
PMR spectra

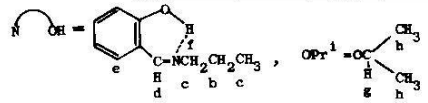
The ^1H NMR spectra of N-(n-propyl)salicylaldimine (i) and its corresponding 1:1 (ii) and 1:2 (iii) vanadium complexes have been recorded in DMSO-d_6 and the chemical shift values (δ) for the different protons are given in table 2. The following points are in support of the structure discussed above.

(I) The PMR spectrum of the ligand contains broad signal at δ 12.90 ppm, assignable to the hydrogen bonded NH or OH proton. This signal completely disappears in both the corresponding vanadium complexes (ii and iii) indicating the deprotonation of the functional groups and coordination of the vanadium atom to the oxygen as well as nitrogen atoms of the ligand moiety.
(II) The proton signal for the methine proton at δ7.60 ppm in the ligand (i) shifts downfield in the spectra of vanadium complexes on account of deshielding. This is probably due to the donation of lone pair of electrons by the nitrogen to the central metal atom and resulting in the formation of a coordinate linkage. It gets further support by the fact that the signal of methylene protons in the vanadium complexes shows a considerable downfield shift as compared to the Schiff base (i).

(III) The proton signals at 4.18 and 2.20 ppm (ii) and δ4.20 and 2.24

Table-2: ^1H NMR spectral Data (,ppm) of Schiff base and its corresponding Vanadium Complexes

No.	Compound	a	b	c	d	e	f	g	h
(i)		0.5t	1.18m	2.85t	7.60s	6.50m	12.90bs	-	-
(ii)		1.42t	2.26m	3.82t	8.62s	7.52m	-	4.18sp	2.20d
(iii)		1.20t	1.88m	3.84t	8.68s	7.40m	-	4.20sp	2.24d

*  s = singlet, bs=broad singlet, d=doublet, t = triplet, sp=septet and m=complex multiplet

* coupling constants for a and c are 7.2 and 6.6 Hz respectively.

ppm (iii) are due to the methine and methyl protons of the isopropoxy groups respectively and these are not observed in the spectrum of the Schiff base (i).

Magnetic Susceptibility Measurements

The magnetic susceptibilities of some of these oxovanadium (V) Schiff base complexes as determined at room temperature (30 ± 1°C) are in the range of -0.5264 to -0.7058 ($\chi_m \times 10^{-6}$ c.g.s. units). These values support the diamagnetic nature as expected for d^0, configuration of the metal atom in these complexes.

Electronic Spectral Studies

The electronic spectra of the ligands show bands at 250 and 298 nm attributable to $\pi \rightarrow \pi^*$ electronic tranistions within the benzenoid and azomethine groupings respectively, and which appear at almost the same position in the corresponding vanadium complexes. The band at 400 nm observed in the ligand may be assigned to πn-transition of the azomethine group and it shifts to the lower wave length side ($\sim$ 20 nm) in the corresponding metal complexes due to the coordination of azomethine nitrogen to the central metal atom.

In the visible region, the metal complexes show a strong absorption maximum at $\sim$ 550 nm and which may be accounted for d-d transition presumably arising out of the ligand metal charge transfer (L→M) in the vanadium (V) species. Similar observations in the case of oxovanadium (V) complexes have been reported earlier also [15].

Table-3: Properties and Analysis of Schiff bases

No.	Schiff base	Colour and state	B.P. (°C/mm)	M.P. (°C)	Analysis (%) C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)
1.	4-(n-Propyl)amino-3-pentene-2-one ($C_8H_{15}NO$)	Yellow liquid	86/3.0	-	68.12 (68.05)	10.64 (10.70)	9.82 9.91
2.	N-(n-Propyl)salicylaldimine ($C_{10}H_{13}NO$)	Yellow liquid	91/1.0	-	73.47 (73/58)	8.14 (8.03)	8.52 (8.59)
3.	N-(n-Butyl)salicylaldimine ($C_{11}H_{15}NO$)	Yellow liquid	83/0.1	-	74.32 (74.54)	8.59 (8.53)	7.82 (7.90)
4.	N-(o-Tolyl)salicylaldimine ($C_{14}H_{13}NO$)	Yellow solid	136-39/0.1	44	79.64 (79.58)	6.28 (6.20)	6.54 (6.64)
6.	N-(p-Tolyl)salicylaldimine ($C_{14}H_{13}NO$)**	Yellowish red solid	-	94	79.40 (79.58)	6.02 (6.20)	6.59 (6.64)
7.	4-(2-Hydroxy-1-propyl)amino-3-pentene-2-one ($C_8H_{15}NO_2$)	Pale yellow needles	-	82-83	61.25 (61.12)	9.86 (9.61)	8.81 8.90)
8.	N-(1-Hydroxy-2-butyl)salicylaldimine ($C_{11}H_{15}NO_2$)	Yellow liquid	84/0.1	-	68.30 (68.37)	7.89 (7.82)	7.20 (7.24)

* and ** have been used to distinguish compounds of the same molecular formula.

Table-4: Reactions of $VO(OPr^i)_3$ with monobasic bidentate and bibasic tridentate Schiff bases

No.	$VO(OPr^i)_3$ (g)	Schiff base (g)	Molar ratio	Compound and yield (g)	Pr^iOH in the azeotrope (g) Found (Calcd.)	V Found (Calcd.)	N Found (Calcd.)
1.	0.62	$C_8H_{15}NO$ (0.36)	1:1	$VO(OPr^i)_2(C_8H_{14}NO)$ (0.66)	0.150 (0.152)	[illegible] (15.45)	4.20 (4.30)
2.	0.51	$C_8H_{15}NO$ (0.59)	1:2	$VO(OPr^i)(C_8H_{14}NO)_2$ (0.69)	0.248 (0.250)	12.45 (12.53)	7.02 (6.89)
3.	0.58	$C_{10}H_{13}NO$ (0.39)	1:1	$VO(OPr^i)_2(C_{10}H_{12}NO)$ (0.65)	0.142 (0.142)	14.60 (14.66)	3.98 (4.03)
4.	0.71	$C_{10}H_{13}NO$ (0.95)	1:2	$VO(OPr^i)(C_{10}H_{12}NO)_2$ (0.98)	0.345 (0.349)	11.02 (11.31)	6.32 (6.21)
5.	0.64	$C_{11}H_{15}NO$ (0.46)	1:1	$VO(OPr^i)_2(C_{11}H_{14}NO)$ (0.71)	0.152 (0.157)	14.23 14.09)	3.80 (3.87)
6.	0.76	$C_{11}H_{15}NO$ (1.10)	1:2	$VO(OPr^i)(C_{11}H_{14}NO)_2$ (1.19)	0.369 (0.373)	10.72 (10.64)	5.87 (5.85)
7.	1.28	$C_{14}H_{13}NO$ (1.10)	1:1	$VO(OPr^i)_2(C_{14}H_{12}NO)$ (1.54)	0.312 (.314)	12.92 (12.88)	3.42 (3.54)
8.	0.69	$C_{14}H_{13}NO$ (1.19)	1:2	$VO(OPr^i)(C_{14}H_{12}NO)_2$ (1.23)	0.330 (0.339)	12.92 (9.32)	4.98 (5.12)
9.	1.04	$C_{14}H_{13}NO^*$ (0.90)	1:1	$VO(OPr^i)_2(C_{14}H_{12}NO)^*$ (1.28)	0.250 (0.254)	12.78 (12.88)	3.40 (3.54)

10. 0.73	$C_{14}H_{13}NO^{*}$	1:2	$VO(OPr^{i})(C_{14}H_{12}NO)^{*}_{2}$	0.348	9.48	5.01
	(1.26)		(1.37)	(0.359)	(9.32)	(5.12)
11. 1.08	$C_{14}H_{13}NO^{**}$	1:1	$VO(OPr^{i})_{2}(C_{14}H_{12}NO)^{**}$	0.260	12.71	3.62
	(0.94)		(1.46)	(0.264)	(12.88)	(3.54)
12. 0.49	$C_{14}H_{13}NO^{**}$	1:2	$VO(OPr^{i})(C_{14}H_{13}NO)^{**}$	0.238	9.27	5.26
	(0.85)		(0.83)	(0.241)	(9.32)	(5.12)
13. 1.22	$C_{8}H_{15}NO_{2}$	1:1	$VO(OPr^{i})(C_{8}H_{13}NO_{2})$	0.609	18.02	4.82
	(0.84)		(1.08)	(0.610)	(18.11)	(4.98)
14. 1.12	$C_{8}H_{15}NO_{2}$	2:3	$(VO)_{2}(C_{8}H_{13}NO_{2})_{3}$	0.818	17.01	6.89
	(1.08)		(1.96)	(0.826)	(16.99)	(7.00)
15. 0.72	$C_{11}H_{15}NO_{2}$	1:1	$VO(OPr^{i})(C_{11}H_{13}NO_{2})$	0.350	16.01	4.49
	(0.57)		(0.71)	(0.354)	(16 .01)	(4.41)
16. 0.84	$C_{11}H_{15}NO_{2}$	2:3	$(VO)_{2}(C_{11}H_{13}NO_{2})_{3}$	0.618	14.32	6.02
	(0.99)		(1.72)	(0.620)	(14.40)	(5.93)

*Satisfactory carbon and hydrogen analyses were obtained.

Experimental

All the chemicals of analytical grade were used and oxovanadium (V) triisopropoxide was prepared as reported elsewhere [17]. The reactions have been carried out under rigorously anhydrous conditions on a fractionating column packed with Raschig rings and fitted with a ratio head and condenser protected with fused calcium chloride

Preparation of the Schiff bases

All the Schiff bases were synthesized by heating equimolar amounts of aldehyde or ketone with appropriate amine for a few hours in benzene or absolute alcohol and purified either by distillation under reduced pressure or recrystallization from the same solvent. Their important physical properties are presented in table 3.

Table-5: Exchange reactions of isopropoxy oxovanadium (V) Schiff base complexes with t-butanol

No.	Compound (g)	Excess of Bu^tOH (g)	Product formed and (yield(g)	Pr^iOH in the azeotrope(g) Found (Calcd.)	Analysis (%) V Found (Calcd.)	N Found (Calcd.)
1.	$VO(OPr^i)_2(C_8H_{14}NO)$ (0.48)	1.47	$VO(OBu^t)_2(C_8H_{14}NO)$ (0.44)	0.170 (0.177)	14.40 (14.41)	4.02 (3.96)
2.	$VO(OPr^i)(C_8H_{14}NO)_2$ (0.41)	1.98	$VO(OBu^t)(C_8H_{14}NO)_2$ (0.36)	0.059 (0.060)	12.02 (12.11)	6.54 (6.66)
3.	$VO(OPr^i)_2(C_{14}H_{12}NO)$ (0.39)	1.64	$VO(OBu^t)_2(C_{14}H_{12}NO)$ (0.35)	0.112 (0.118)	12.14 (12.03)	3.35 (3.30)
4.	$VO(OPr^i)(C_{14}H_{12}NO)_2$ (0.47)	1.74	$VO(OBu^t)(C_{14}H_{12}NO)_2$ (0.38)	0.050 (0.051)	9.18 (9.08)	5.09 (4.99)
5.	$VO(OPr^i)_2(C_{14}H_{14}NO)^*$ (0.38)	1.69	$VO(OBu^t)_2(C_{14}H_{12}NO)^*$ (0.33)	0.109 (0.115)	11.94 (12.03)	3.21 (3.30)
6.	$VO(OPr^i)(C_{14}H_{12}NO)^*_2$ (0.42)	1.53	$VO(OBu^t)(C_{14}H_{12}NO)^*_2$ (0.36)	0.042 (0.046)	8.92 (9.08)	4.84 (4.99)
7.	$VO(OPr^i)(C_8H_{13}NO_2)$ (0.40)	1.87	$VO(OBu^t)(C_8H_{13}NO)_2$ (0.36)	0.081 (0.085)	17.10 (17.95)	4.70 (4.74)
8.	$VO(OPr^i)(C_{11}H_{13}NO_2)$ (0.52)	1.94	$VO(OBu^t)(C_{11}H_{13}NO_2)$ (0.45)	0.093 (0.098)	15.24 (15.37)	4.04 (4.22)

Synthesis of Schiff base Complexes of Oxovanadium (V)

Oxovanadium (V) triisopropoxide was dissolved in dry benzene (35-40 ml) in a 100 ml R.B. flask and calculated amount of the Schiff base according to 1:1, 1:2 and 2:3 molar ratio reactions was added. The contents were refluxed over a fractionating column for 8-12 hours keeping the bath temperature at 120°C. The progress of the reaction was ascertained by the estimation of isopropanol in the binary azeotrope with benzene. The mono-t-butoxy and di-t-butoxy Schiff base complexes of vanadium were prepared by adding an excess of t-butanol to the solution of mono- and di-isopropoxy Schiff base derivatives of oxovanadium in dry benzene (40-50 ml) followed by refluxing till the distillate attained a constant temperature of 80°C. The products were rendered free from solvent under reduced pressure and then washed with dry n-hexane. The final resulting products were dried under vacuum at 50-60°C/ O.5mm for 2-3 hours. The details of their synthesis and analysis are recorded in Table 4 and 5.

Analytical Methods and Physical Measurements

All the analytical procedures and physical techniques of molecular weight determination, conductance measurements, infrared, proton magnetic resonance, electronic spectral and magnetic measurements are the same as reported in the previous communications [9-10].

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