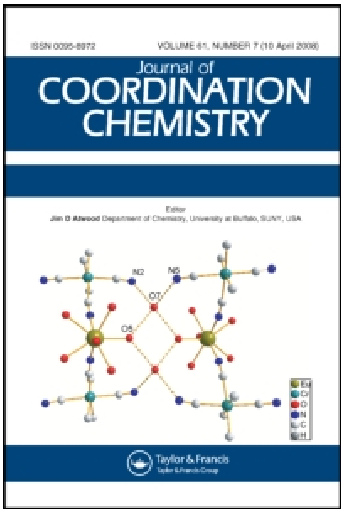

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Synthesis and characterization of oxovanadium(IV), vanadium(IV) and oxovanadium(V) complexes of tetradentate Schiff bases. Attempted preparation of vanadium-carbon bonded compounds through desilylation

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Condensation of 1,3-diaminopropane-2-ol with diacetylmonoxime, acetylacetone, salicylaldehyde and orthohydroxyacetophenone yielded the tetradentate Schiff bases *N*,*N′*-(2-hydroxy) propylenebis{(2-imino-3-oximino)butane} (H_2dampnol), *N*,*N′*-(2-hydroxy)propylenebis (acetylacetoneimine) (H_2acacpnol), *N*,*N′*-(2-hydroxy)propylenebis-(salicyalaldimine) (H_2salpnol) and *N*,*N′*-(2-hydroxy)propylenebis(7-methylsalicylaldimine) (H_2ohacpnol), respectively. The ligands form complexes with oxovanadium(IV), vanadium(IV) and oxovanadium(V) salts. Some mixed ligand complexes involving σ-bonded phenyl and benzyl radical along with tetradentate ligand, H_2L (where, H_2L stands for H_2dampnol, H_2acacpnol, H_2salpnol or H_2ohacpnol) of the types $[(L)V(C_6H_5)_2]CH_3OH$ and $[(L)V(CH_2Ph)_2]CH_3OH$ have been synthesized, characterized and also provide the syntheses of some new organovanadium(IV) complexes. Silylation coupled with desilylation have been employed as a route to new organovanadium(IV) complexes. All the complexes have been characterized with the help of elemental analyses, molar conductance values, molecular weights, magnetic moments and spectroscopic (IR, UV-Vis, ESR) data.

Keywords: Schiff base; Organovanadium; Desilylation; ESR spectra; Electronic spectra

1. Introduction

The biological importance of vanadium compounds in different oxidation states is many faceted [1–8]. Vanadium complexes are also of major concern because of their adverse effect on hydroprocessing catalysts used in the refining of crude oil [9, 10]. The revelation that coordination complexes of vanadium in different oxidation states can play a vital role in nitrogen activation and nitrogen fixation and many other

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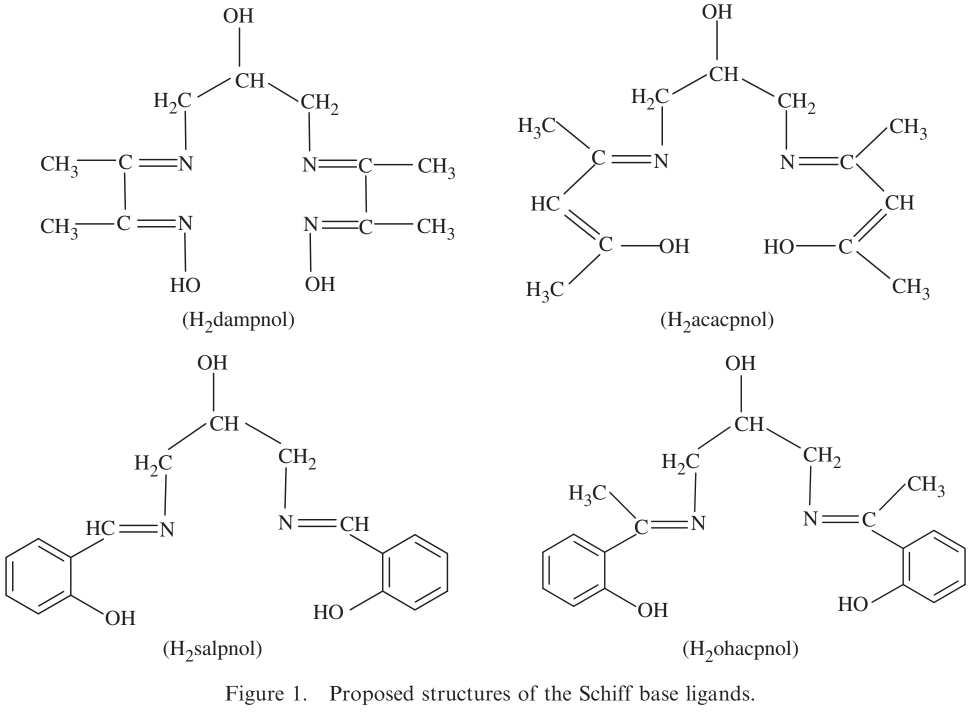
biologically important reactions [1–8, 11–14] has stimulated interest in the synthesis, characterization, stereochemistry and reactivity of its coordination compounds that contain diazo-, hydrazido- and imine- group because they can provide information on the mechanism of metalloenzymatic reduction of dinitrogen and are capable of confining metal atoms and controlling their properties and functionality [14].

Our investigation on vanadium complexes in different oxidation states mainly concerned synthesis and characterization of vanadium complexes with different types of ligands and also studies of their biological activity and their reactions with biologically active molecules. The present work is a continuation of our recent work on vanadium(III) complexes with different tetradentate Schiff bases [15, 16] using oxovanadium(IV), vanadium(IV) and vanadium(V) ions. The Schiff bases used in the present study are *N*,*N*′-(2-hydroxy)propylenebis{(2-imino-3-oximino)butane}, *N*,*N*′-(2-hydroxy) propylenebis(acetylacetoneimine), *N*,*N*′-(2-hydroxy)propylenebis-(salicyaldimine) and *N*,*N*′-(2-hydroxy)propylenebis(7-methylsalicylaldimine) synthesized by condensation of 1,3-diaminopropane-2-ol with diacetylmonoxime (H_2dampnol), acetylacetone (H_2acacpnol), salicylaldehyde (H_2salpnol) and orthohydroxyacetophenone (H_2ohacpnol); structural formulations are shown in figure 1.

This article also includes the attempted preparation of some mixed ligand complexes (involving σ-bonded phenyl and benzyl radical) along with tetradentate ligand, H_2L (where, H_2L stands for H_2dampnol, H_2acacpnol, H_2salpnol or H_2ohacpnol), $[(L)V(C_6H_5)_2]CH_3OH$ and $[(L)V(CH_2Ph)_2]CH_3OH$. Of these $[(salpnol)V(CH_2Ph)_2]CH_3OH$ and $[(ohacpnol)V(CH_2Ph)_2]CH_3OH$ are stable at room temperature. Para-dibenzyl bridged oxovanadium(V) is also reported briefly in this communication.



(H_2dampnol) (H_2acacpnol)

(H_2salpnol) (H_2ohacpnol)

Figure 1. Proposed structures of the Schiff base ligands.

Recently we studied [16] the trimethylsilylation of H_2salpnol and H_2ohacpnol affording the trimethylsilylated Schiff bases, which in turn reacted smoothly with $VOCl_2 \cdot 2H_2O$, $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(CH_3)_2SnCl_2$ yielding a series of bimetallic oxovanadium(IV), organotitanium(IV) and organotin(IV) compounds. A recent report [17] on the synthesis and catalytic reaction of an oxovanadium(IV) complex with an H_2salpnol type ligand is comparable with our results on similar systems.

2. Experimental

2.1. *Materials and instruments*

All solvents were purified and dried according to standard procedures [18] before use. Manipulations were carried out under an atmosphere of nitrogen. 1,3-diaminopropane-2-ol, diacetylmonoxime, salicylaldehyde, acetylacetone and orthohydroxy acetophenone (Aldrich) were used as such. The elemental analyses of the complexes were carried out on Elementar Vario EL III, Carlo Erba 1108 elemental analyzers at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India. Vanadium and nitrogen were analyzed in our laboratory by usual methods (vanadium as V_2O_5 and nitrogen by Duma's method). Infrared spectra were recorded in KBr, Nujol or hexachlorobutadiene (more than one media were used for some compounds) on Perkin-Elmer 1330 and L120-000A spectrophotometers. The electronic spectra were recorded on a Hitachi 200–20 and Simadzu UV-2401PC spectrophotometers. Conductance measurements were made with a conductivity bridge (Elico Pvt. Ltd., Model CM 80). The magnetic susceptibility was determined by the Guoy method at room temperature. Molecular weights were determined with a Hitachi Perkin Elmer Model 115 Vapour Pressure Osmometer by using benzene or methylene chloride as solvent. The measurements were made within five minutes of preparation of the solution.

2.2. *Preparation of the ligand*

The Schiff bases were prepared by the usual methods as described by us elsewhere [15, 16]. The $pH = 8$ was maintained during reaction by adding 15% methanolic ammonium hydroxide in all the preparations with H_2dampnol.

2.3. *Preparation oxovanadium(IV) complexes*

[VO(dampnol)] (1). The following methods are used for the synthesis.

Method A. A methanol solution (50 mL) of H_2dampnol (0.256 g, 1 mmol) and VCl_3 (0.157 g, 1 mmol) in 20 mL of the same solvent was heated under gentle reflux in excess oxygen for 2 h and filtered while hot. The light-brown solution, on concentration and cooling, gave this greenish-gray compound. The compound was washed with cold methanol and dried in *vacuo*.

Method B. The ligand H_2dampnol (0.256 g, 1 mmol) was dissolved in methanol (50 mL) and then added to a solution of [VO(acac)$_2$] (0.265 g, 1 mmol) in methanol (30 mL). The mixture was refluxed for 6 h during which the colour of the solution changed from green to light-brown and a greenish-gray precipitate formed. The solution was cooled to room temperature and the solid compound filtered off, washed with methanol and then with diethyl ether and dried in *vacuo*.

Method C. The solution of [VO(CH_3COO)$_2$] [19] (0.185 g, 1 mmol) in 35 mL of methanol was added to a solution of H_2dampnol (0.256 g, 1 mmol) in the same solution (40 mL) and stirred at room temperature for 3 h and then refluxed for 8 h. The resulting greenish-gray precipitate was filtered off, washed with methanol and diethyl ether and dried in *vacuo*.

Method D. A solution of $VOSO_4 \cdot 2H_2O$ (0.995 g, 5 mmol) in 25 mL of distilled water was added to a hot methanol solution containing H_2dampnol (1.28 g, 5 mmol) and $Na(CH_3COO)_2 \cdot 3H_2O$ (1.5 g, 11 mmol). The solution turned green with some green precipitate. The mixture was refluxed for 6 h and filtered while hot. The filtrate on cooling to 0°C overnight yielded greenish-gray precipitate, which was collected by filtration, washed with distilled water and methanol and dried over silica in a desiccator in *vacuo* at room temperature.

[VO(acacpnol)] (3), [VO(salpnol)] (5) and [VO(ohacpnol)] (7) were synthesized by the methods described above.

[VO(dampnol)Py] (9), [VO(acacpnol)Py] (10), [VO(salpnol)Py] (11) and [VO(ohacpnol)Py] (12) were synthesized by the following general method: A mixture of [VO(dampnol)] (**1**) (0.321 g, 1 mmol), [VO(acacpnol)] (**3**) (0.319 g, 1 mmol), [VO(salpnol)] (**5**) (0.363 g, 1 mmol) or [VO(ohacpnol)] (**7**) (0.421 g, 1 mmol) with methanol: pyridine (60 mL, 1 : 5 v/v) was refluxed for 36 h and filtered. The brown filtrate afforded light-brown compounds on concentration, cooling and adding petroleum ether (40–60°). The compounds were filtered off, washed with diethyl ether and dried in *vacuo*.

[VO(dampnol)Cl] (2), [VO(acacpnol)Cl] (4), [VO(salpnol)Cl] (6) and [VO(ohacpnol)Cl] (8) were synthesized by a common general method: A solution of H_2dampnol (0.256 g, 1 mmol), H_2acacpnol (0.254 g, 1 mmol), H_2salpnol (0.298 g, 1 mmol) or H_2ohacpnol (0.326 g, 1 mmol) in methanol (60 mL) was added to a solution of $VOCl_3$ (0.173 g, 1 mmol) in the same solvent (30 mL). The light-brown solution was heated under reflux for 3 h and filtered. The filtrate afforded brown compound which was filtered off, washed with cold methanol and diethyl ether and dried in *vacuo*.

[V(dampnol)Cl$_2$] (13), [V(acacpnol)Cl$_2$] (14), [V(salpnol)Cl$_2$] (15) and [V(ohacpnol)Cl$_2$] (16). These complexes were synthesized by a previously published method [20]. [VO(dampnol)] (**1**) (0.321 g, 1 mmol), [VO(acacpnol)] (**3**) (0.319 g, 1 mmol), [VO(salpnol)] (**5**) (0.363 g, 1 mmol) or [VO(ohacpnol)] (**7**) (0.391 g, 1 mmol) was taken in dry benzene (80 mL), to which was added $SOCl_2$ (0.772 g, 6.5 mmol). The mixture was heated under gentle reflux for 30 min and cooled. The bluish-green compound was filtered off, washed with benzene-acetone (50 : 50, v/v) mixture and dried in *vacuo*.

[(salpnol)V(C_6H_5)$_2$]CH_3OH (17), [(ohacpnol)V(C_6H_5)$_2$]CH_3OH (18) [(salpnol) V(CH_2Ph)$_2$]CH_3OH (19) and [(ohacpnol)V(CH_2Ph)$_2$]CH_3OH (20). The following method was used to synthesize the above four compounds: The complex [V(salpnol)Cl_2] (**15**) (2.09 g, 5 mmol) or [V(ohacpnol)Cl_2] (**16**) (2.23 g, 5 mmol) was taken in THF and diethyl ether (60 mL, 50 : 50, v/v) to which $Me_3SiC_6H_5$ (0.75 g, 5 mmol) or $Me_3SiCH_2C_6H_5$ (0.82 g, 5 mmol) in the same solvent (50 mL) was added at 0°C. The mixture was stirred while the temperature rose to about 30°C (room temperature). The stirring was continued for 18 h and the solution filtered. From the brown filtrate the by-product Me_3SiCl was distilled off at reduced pressure. The remaining brown solution was loaded onto a silica gel column that was packed in methanol. The first few milliliters were discarded and the subsequent eluent was evaporated almost to dryness to yield the product.

[{(salpnol)VO}$_2$(*p*-C_6H_4)] (21), [{(ohacpnol)VO}$_2$(*p*-C_6H_4)] (22), [{(salpnol)VO}$_2$ (*p*-$CH_2C_6H_4CH_2$)] (23) and [{(ohacpnol)VO}$_2$(*p*-$CH_2C_6H_4CH_2$)] (24). These four oxovanadium(V) organoderivatives bridged by –C_6H_4– or –$CH_2C_6H_4CH_2$– were synthesized by the reactions of [(L)VOCl] (where, L stands for the dianion of H_2salpnol and H_2ohacpnol) with *p*-$Me_3SiC_6H_4SiMe_3$ or *p*-$Me_3SiCH_2C_6H_4CH_2SiMe_3$ in 2 : 1 molar ratio in THF-Et_2O. Description of one such preparation is given below:

[{(salpnol)VO}$_2$(*p*-C_6H_4)] (21). The complex [VO(salpnol)Cl] (**6**) (1.99 g, 5 mmol) was taken into THF: Et_2O (70 mL, 50 : 50, v/v), and *p*-$Me_3SiC_6H_4SiMe_3$ (0.555 g, 2.5 mmol) in 30 mL of the same solvent system was added at 0°C. The mixture was stirred while the temperature was allowed to rise to room temperature (~29°C). The stirring was continued for another 20 h at about 40°C and filtered. The brown filtrate was subjected to vacuum distillation to remove Me_3SiCl formed during the reaction. Thereafter the solution was concentrated to half of its original volume and cooled to room temperature. On standing in a refrigerator brown compound **21** was obtained. It was filtered, washed with diethyl ether and dried in *vacuo*.

3. Results and discussion

3.1. *Syntheses*

Depending on the reaction conditions the tetradentate Schiff bases H_2dampnol, H_2acacpnol, H_2salpnol and H_2ohacpnol reacted with VCl_3, $VO(acac)_2$, $VO(CH_3COO)_2$ and $VOSO_4 \cdot 2H_2O$ affording green oxovanadium(IV) complexes (**1**), (**3**), (**5**) and (**7**) of the type [VO(L)] (where, L stands for the dianion of the Schiff bases H_2dampnol, H_2acacpnol, H_2salpnol and H_2ohacpnol). Reactions of these oxovanadium(IV) complexes with pyridine under reflux yielded brown oxovanadium(IV) complexes of the type [VO(L)Py] (**9**)–(**12**). Reaction of $VOCl_3$ with the Schiff bases afforded brown oxovanadium(V) complexes of the type [VO(L)Cl] (**2**), (**4**), (**6**) and (**8**) in good yield. Reaction of $SOCl_2$ with oxovanadium(IV) complexes of the type [VO(L)] (**1**), (**3**), (**5**) and (**7**) under mild conditions in benzene produced bluish green hexacoordinate vanadium(IV) complexes of the type [V(L)Cl_2] (**13**)–(**16**). Mechanisms of such reactions have been discussed elsewhere [20]. The reactions of [V(salpnol)Cl_2] (**15**) and [V(ohacpnol)Cl_2] (**16**) with $Me_3SiC_6H_5$ and $Me_3SiCH_2C_6H_5$ resulted in the replacement of Me_3SiCl with the concomitant bond formation between vanadium(IV) and phenyl and benzyl groups, thus leading to the syntheses of new organovanadium(IV) complexes:

$$[\mathrm{V(L)Cl_2}] + 2\mathrm{Me_3SiR} \xrightarrow[-2\mathrm{Me_3SiCl}]{\mathrm{THF}} [\mathrm{V(L)R_2}]$$

(where, $H_2L = H_2$ salpnol or H_2 ohacpnol and $R = –C_6H_5$ or $–CH_2C_6H_5$)

Such desilylation has not previously been used to synthesize organovanadium(IV) compounds. Similar reactions of [VO(salpnol)Cl] (**6**) or [VO(ohacpnol)Cl] (**7**) with *p*-$Me_3SiC_6H_4SiMe_3$ or *p*-$Me_3SiCH_2C_6H_4CH_2SiMe_3$ yielded organo derivatives of oxovanadium(V) bridged by $–C_6H_4–$ or $–CH_2C_6H_4CH_2–$ (Scheme 1).

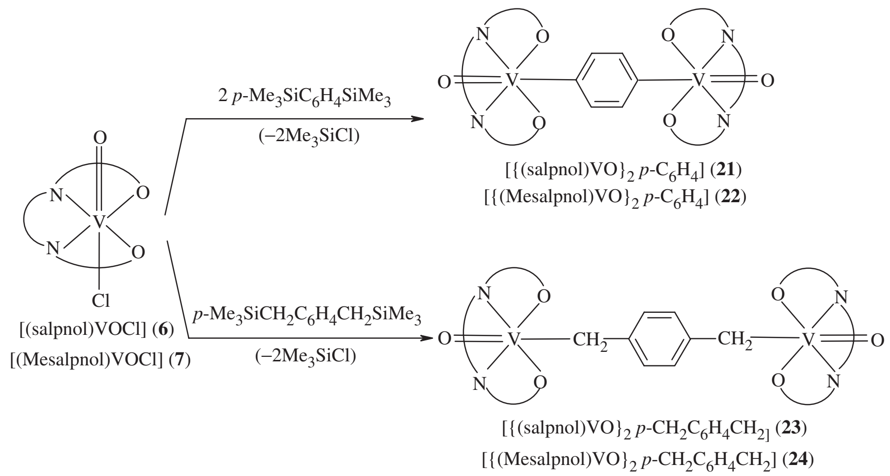
Such reactions, involving the replacement of chloride ligand by various nucleophiles are known [23], but desilylation reactions have not been used. Stability of V–C σ-bond has been discussed [21]. All complexes are fairly stable in laboratory conditions and their characterization data (table 1) support their formulations. Elemental analyses and molecular weights support the formulations of the isolated complexes. Despite our best efforts we could not grow suitable crystals for structural analyses.

3.2. *Magnetic moments*

Magnetic susceptibility measurements were made for the solid complexes. Effective magnetic moments are listed in table 1. After the appropriate diamagnetic correction the values lie in the range 1.73–1.79 B.M. for **1**, **3**, **5**, **7** and **9**–**20**, which is close to the spin-only value for d^1. These approximately normal magnetic moment values indicate that there is no significant interaction between neighbouring vanadium(IV) ions [24, 25]. On the other hand, complexes **2**, **4**, **6**, **8**, **22** and **24** are diamagnetic at room temperature, indicating that these complexes contain oxovanadium(V).

3.3. *Molar conductance values*

The molar conductance values of **1**–**12** in DMSO are found in the range $\Lambda_M = 9.8$ to $\Lambda_M = 15.06\,\Omega^{-1}\,cm^2\,mol^{-1}$ indicating non-conducting nature of the complexes. The Λ_M



Scheme 1. Proposed scheme for the formation of carbon–bonded di-oxovanadrum (V) complexes through desilylation.

Table 1. Some characterization data of the complexes.

Compound	Colour	Mol. wt found (Calcd)	Analyses found (Calcd) %					ν(V=O) (cm^{-1})	μ_{eff}[a] (B.M.)	Λ_M[b] (Ω^{-1} cm^2 mol^{-1})
			C	H	N	Cl	V			
[VO(dampnol)] (**1**)	Greenish-gray	342	41.00	5.92	17.28	–	15.72	890	1.76	9.80
$C_{11}H_{18}N_4O_4V$		(321.23)	(41.13)	(5.65)	(17.44)		(15.86)			
[VO(dampnol)Cl] (**2**)	Greenish-brown	362	37.52	5.28	15.92	9.72	14.59	940	Dia[c]	10.10
$C_{11}H_{18}ClN_4O_4V$		(356.68)	(37.04)	(5.09)	(15.71)	(9.94)	(14.28)			
[VO(acacpnol)] (**3**)	Greenish-yellow	330	48.80	6.33	8.98	–	15.70	888	1.79	11.20
$C_{13}H_{20}N_2O_4V$		(319.25)	(48.91)	(6.31)	(8.77)		(15.96)			
[VO(acacpnol)Cl] (**4**)	Brown	348	44.28	5.77	7.38	10.01	14.55	945	Dia	9.80
$C_{13}H_{20}ClN_2O_4V$		(354.71)	(44.02)	(5.68)	(7.90)	(9.99)	(14.36)			
[VO(salpnol)] (**5**)	Yellowish-green	350	56.39	4.68	7.99	–	14.29	880	1.76	12.00
$C_{17}H_{16}N_2O_4V$		(363.27)	(56.21)	(4.44)	(7.71)		(14.02)			
[VO(salpnol)Cl] (**6**)	Greenish-brown	428	51.00	4.28	7.50	8.99	12.98	945	Dia	13.02
$C_{17}H_{16}ClN_2O_4V$		(398.72)	(51.21)	(4.01)	(7.02)	(8.89)	(12.78)			
[VO(ohacpnol)] (**7**)	Gray	380	58.51	5.52	7.78	–	13.34	890	1.79	12.80
$C_{19}H_{20}N_2O_4V$		(391.32)	(58.32)	(5.15)	(7.16)		(13.02)			
[VO(ohacpnol)Cl] (**8**)	Light green	400	53.90	4.80	6.82	8.80	11.49	945	Dia	12.22
$C_{19}H_{20}ClN_2O_4V$		(426.77)	(53.47)	(4.72)	(6.56)	(8.31)	(11.94)			
[VO(dampnol)Py] (**9**)	Greenish-brown	386	48.22	5.62	17.80	–	12.88	930	1.78	14.00
$C_{16}H_{23}N_5O_4V$		(400.33)	(48.00)	(5.79)	(17.49)		(12.72)			
[VO(acacpnol)Py] (**10**)	Brown	370	54.62	6.28	10.95	–	12.68	920	1.75	15.06
$C_{18}H_{25}N_3O_4V$		(398.36)	(54.27)	(6.32)	(10.55)		(12.79)			
[VO(salpnol)Py] (**11**)	Light brown	429	59.26	4.89	9.91	–	11.98	950	1.79	14.82
$C_{22}H_{21}N_3O_4V$		(442.37)	(59.73)	(4.78)	(9.50)		(11.51)			
[VO(ohacpnol)Py] (**12**)	Brown	492	61.08	5.67	8.70	–	10.98	950	1.77	14.00
$C_{24}H_{25}N_3O_4V$		(470.42)	(61.28)	(5.36)	(8.93)		(10.83)			
[V(dampnol)Cl$_2$] (**13**)	Bluish-green	358	35.67	4.99	14.70	18.90	13.68	–	1.73	d
$C_{11}H_{18}Cl_2N_4O_3V$		(376.14)	(35.12)	(4.82)	(14.89)	(18.85)	(13.54)			
[V(acacpnol)Cl$_2$] (**14**)	Greenish-blue	362	41.68	5.77	7.90	18.75	13.75	–	1.75	d
$C_{13}H_{20}Cl_2N_2O_3V$		(374.16)	(41.73)	(5.39)	(7.49)	(18.95)	(13.61)			
[V(salpnol)Cl$_2$] (**15**)	Greenish-blue	388	48.72	3.78	6.90	16.80	12.60	–	1.77	d
$C_{17}H_{16}Cl_2N_2O_3V$		(418.17)	(48.83)	(3.86)	(6.70)	(16.96)	(12.18)			
[V(ohacpnol)Cl$_2$] (**16**)	Bluish-green	462	51.00	4.62	6.70	15.72	11.68	–	1.78	d
$C_{19}H_{20}Cl_2N_2O_3V$		(446.23)	(51.14)	(4.52)	(6.28)	(15.89)	(11.41)			

(Continued)

Table 1. Continued.

Compound	Colour	Mol. wt found (Calcd)	Analyses found (Calcd) %					ν(V=O) (cm^{-1})	μ_{eff}[a] (B.M.)	Λ_M[b] (Ω^{-1} cm^2 mol^{-1})
			C	H	N	Cl	V			
[(salpnol)V(C_6H_5)$_2$]CH_3OH (**17**)	Brown	521	67.00	5.92	5.44	–	9.92	–	1.76	d
$C_{30}H_{30}N_2O_4V$		(533.52)	(67.54)	(5.67)	(5.25)		(9.55)			
[(ohacpnol)V(C_6H_5)$_2$]CH_3OH (**18**)	Brown	541	68.28	6.40	4.71	–	9.82	–	1.78	d
$C_{32}H_{34}N_2O_4V$		(561.57)	(68.44)	(6.10)	(4.99)		(9.07)			
[(salpnol)V(CH_2Ph)$_2$]CH_3OH (**19**)	Brown	548	68.62	6.77	4.79	–	9.28	–	1.75	d
$C_{32}H_{34}N_2O_4V$		(561.57)	(68.44)	(6.10)	(4.99)		(9.07)			
[(ohacpnol)V(CH_2Ph)$_2$]CH_3OH (**20**)	Brown	605	69.70	6.66	4.29	–	8.90	–	1.76	d
$C_{34}H_{38}N_2O_4V$		(589.63)	(69.26)	(6.50)	(4.75)		(8.64)			
[{(salpnol)VO}$_2$(*p*-C_6H_4)] (**21**)	Reddish-brown	788	59.66	4.72	6.82	–	12.88	960	Dia	e
$C_{40}H_{36}N_4O_8V_2$		(802.63)	(59.86)	(4.52)	(6.98)		(12.69)			
[{(ohacpnol)VO}$_2$(*p*-C_6H_4)] (**22**)	Brown	818	61.77	5.42	6.79	–	11.98	965	Dia	e
$C_{44}H_{44}N_4O_8V_2$		(858.74)	(61.54)	(5.16)	(6.52)		(11.86)			
[{(salpnol)VO}$_2$(*p*-$CH_2C_6H_4CH_2$)] (**23**)	Light brown	800	60.58	4.67	6.99	–	12.39	965	Dia	e
$C_{42}H_{40}N_4O_8V_2$		(830.68)	(60.73)	(4.85)	(6.74)		(12.26)			
[{(ohacpnol)VO}$_2$(*p*-$CH_2C_6H_4CH_2$)] (**24**)	Brown	869	62.49	5.92	6.09	–	11.98	970	Dia	e
$C_{46}H_{48}N_4O_8V_2$		(886.79)	(62.30)	(5.46)	(6.32)		(11.49)			

[a]Solid state at room temperature, [b]10^{-3} M solution in DMSO at room temperature, [c]diamagnetic, [d]Λ_M changes with time in DMSO solutions, solvent may exchange with Cl^-, $C_6H_5^-$ or $C_6H_5CH_2^-$, etc., [e]not measured.

values of the complexes **13–20** in DMSO solution changed with time; suggesting possible exchange of DMSO with Cl^-, $C_6H_5^-$ or $C_6H_5CH_2$. No pure compounds, however, could be isolated from such solutions.

3.4. *Infrared spectra*

The infrared spectra of the Schiff base ligands H_2dampnol, H_2acacpnol, H_2salpnol and H_2ohacpnol show medium to strong bands in the region 3000–3400 cm^{-1} assignable to ν(OH) (oxime) in the case of ligand H_2dampnol and medium to strong bands in the region 3250–3350 cm^{-1} assignable to ν(OH) [$=C(CH_3)OH$] in the case of H_2acacpnol. The ν(OH) (phenolic) are possibly submerged in this region. A band around 3400 cm^{-1} has demonstrated the presence of secondary alcoholic OH group in these ligands. The broad nature of the bands suggests hydrogen bonding [15]. The ν(C=N) (azomethine) in H_2dampnol, H_2acacpnol, H_2salpnol and H_2ohacpnol appeared in the range 1610–1620 cm^{-1} as a very strong band. The ν(C=N) (oxime linkage) mode in the free ligand H_2dampnol is possibly submerged by a strong band at around 1615 cm^{-1}. The ν(N–O) mode H_2dampnol was observed as a strong band at 940 cm^{-1}. The ν(C–O) (secondary alcohol) appeared around 1350 cm^{-1} in the free ligands and remained unchanged in the metal complexes demonstrating non-involvement of this group in bonding [16]. The ν(C–O) (phenolic) of H_2salpnol and H_2ohacpnol observed around 1510 cm^{-1} shifted to 1560 cm^{-1} in the metal complexes. This, along with the disappearance of bands for ν(O–H) (phenolic), suggests deprotonation and complexation of phenolic oxygen during complex formation [23]. Disappearance of bands around 3000–3300 cm^{-1} suggests deprotonation of oxime OH (of H_2dampnol) and alcoholic OH [$=C(CH_3)OH$ of H_2acacpnol] allowing these ligands to function as dibasic tetradentate as seen in the case of H_2salpnol and H_2ohacpnol above. However, presence of a broad band around 3400 cm^{-1} (secondary alcoholic group) complicates this interpretation. The bands due to ν(C=N) (both azomethine and oxime) shift to lower frequencies by about 20–30 cm^{-1} compared to the free ligand values, indicating bonding through four nitrogen atoms (involving ligand H_2dampnol) and two nitrogen and two oxygen atoms (involving ligands H_2acacpnol, H_2salpnol and H_2ohacpnol). These lower ν(C=N) values suggest stronger V–N bonding in the complexes. Despite complications due to the appearance of several bands in the infrared spectra of the ligands in the region 500–300 cm^{-1}, the presence of ν(V–Cl) in (**2**), (**4**), (**6**) and (**8**) can be identified around 360 cm^{-1} by careful comparison of the IR spectra of the free ligand and metal complexes. On the other hand, complexes **13–16** exhibit a peak at 320 cm^{-1}, which may be assigned to ν(V–Cl) stretching. All the complexes show bands at ~480–500 cm^{-1} and at ~380–400 cm^{-1} indicating the presence of V–O and V–N bonds, respectively. Presence of bonded pyridine [24] in (**9**)–(**12**) is supported by the appearance of characteristic bands in the regions 420–440 cm^{-1}.

The infrared spectra of oxovanadium(IV) complexes (**1**), (**3**), (**5**) and (**7**) exhibit a very low V=O stretching frequency (nujol mull) in the 880–890 cm^{-1} range (table 2) compared to a value of ~990 cm^{-1} for the corresponding 1,2-diamine complexes [24]. Comparison of the infrared spectra of the copper(II) complexes of the present ligands with those of the infrared spectra of (**1**), (**3**), (**5**) and (**7**) helped us to assign the ν(V=O) band. These low values of ν(V=O) for the present oxovanadium(IV) complexes suggests the presence of bridging VO in these compounds. Electronic spectra of these complexes

Table 2. The V=O stretching frequencies (cm^{-1}) for the oxovanadium(IV) complexes (**1**), (**3**), (**5**) and (**7**) in different solvents.

Complex	Nujol mull	$CHCl_3$	Pyridine
[VO(dampnol)] (**1**)	890	992	970
[VO(acacpnol)] (**3**)	888	993	968
[VO(salpnol)] (**5**)	880	986	960
[VO(ohacpnol)] (**7**)	890	980	965

support this conclusion (see later discussion). In chloroform solution, the V=O stretching frequencies of **1**, **3**, **5** and **7** are shifted from 800–890 cm^{-1} to 980–993 cm^{-1} (table 2). This latter value is similar to the values of ν(V=O) observed for five-coordinate tetradentate salicylaldimine [22] and β-ketimine [22, 25] complexes derived from 1,2-diamine. In coordinating solvents (table 2), the ν(V=O) for the present complexes occurs at 960–970 cm^{-1}, similar to the change in the V=O stretching frequency of $VO(acac)_2$ upon addition of a ligand into the sixth position [26].

The oxovanadium(IV) complexes (**9**)–(**12**) show ν(V=O) stretching frequencies in the range 950–960 cm^{-1}, supporting their formulations as six coordinate complexes. Such observations are also made earlier [27]. On the other hand, the V=O stretching frequencies in the oxovanadium(V) complexes (**2**), (**4**), (**6**) and (**8**) are observed in the region 940–945 cm^{-1}. Meaningful interpretation of these lower values in comparison with those obtained for oxovanadium(IV) complexes (mentioned above) are not possible due to difference in oxidation states of these two types of complexes. Infrared spectra of the organovanadium(IV) and organovanadium(V) (**17**)–(**24**) exhibit some typical bands in the range 650–900 cm^{-1}. A monosubstituted benzene ring is expected to show two bands in this region while a disubstituted ring would exhibit only one band. These absorptions are ring C–H out-of-plane bands. We observed several bands in this region. The bands at 700–740 cm^{-1} indicate the presence of the phenyl substituent groups. These bands are comparable to those at 705 and 743 cm^{-1} of the yellow organic byproduct, Ph_2CH_2. The band at ~765 cm^{-1} may be due to the disubstituted benzene ring in the ligands, observed at 770 cm^{-1} in spectra of complexes (**1**)–(**16**). Complexes **21**–**24** exhibit another band at 758 cm^{-1}, from the bridging *p*-diphenyl and *p*-dibenzyl chromophores.

Evidence that the ligands are intact in the organoderivatives and that the phenyl group must be bound to the vanadium atom comes from observation of the C=N stretching frequency of the ligand in the complexes (see above discussion). Complexes **13**–**20** do not show any infrared band in the vanadyl region, while the organoderivatives of oxovanadium(V) ion exhibit V–O stretching bands in the region 960–970 cm^{-1}.

3.5. ^{1}*H NMR spectra*

The ^{1}H NMR spectral data of the free Schiff base H_2salpnol and a diamagnetic complex of VO (**6**) have been measured in DMSO-d_6. The broad signals for the hydrogen bonded phenolic OH in the free ligand at about δ 12.2 ppm disappeared in (**6**). The chemical shifts of the signals (sightly broadened) for HC=N (δ 8.58 ppm) and NCH_2 (δ 3.96 ppm) protons in the free ligands appear as singlets (also slightly broad) at slightly lower field in the complex. The signal for secondary alcoholic proton of the free ligand (δ 4.08 ppm, slightly broad) remained almost unchanged in the complex. These data support the conclusion drawn from the infrared spectral data (see above). Thus, it may be tentatively suggested that H$_2$salpnol functions as dibasic tetradentate N$_2$O$_2$ donor [28, 29], with secondary alcoholic groups remaining free in the complex. Similar conclusions may be drawn on the ligational behaviour of the other Schiff bases under study.

3.6. *Electronic spectra*

The electronic spectra of oxovanadium(IV), vanadium(IV) and oxovanadium(V) complexes in different solvents have been measured and data of some representative complexes are given in table 3. The spectra of the oxovanadium(IV) complexes (**1**), (**3**), (**5**), and (**7**) in chloroform exhibit a single band at around 17,000 cm^{-1} with additional inflections at around 14,000 and 21,000 cm^{-1}. These data are comparable with data reported for five-coordinate square-pyramidal oxovanadium(IV) complexes synthesized with 1,2-diamine tetradentate β-ketimine [22] and salicylaldimine [22, 30] which are reported to show solvent-independent electronic spectra. Unlike the 1,2-diamine analogs, the present oxovanadium(IV) complexes with 1,3-diamine backbone chelates exhibit different d → d spectra in coordinating solvents. In the presence of an additional donor molecule (electronic spectra in pyridine), the spectra of the present oxovanadium(IV) complexes (**1**), (**3**), (**5**), and (**7**) consist of an absorption band around 13,000 cm^{-1} and a pronounced shoulder or inflection at 19,000 cm^{-1}. Similar changes in the electronic spectra of five-coordinate oxovanadium(IV) complexes occur upon axial coordination [22]. From the above observations of the V=O stretching

Table 3. Electronic spectral data of some oxovanadium(IV), oxovanadium(V) and vanadium(IV) complexes.

Complex	Solvent or Phase	ν (cm^{-1}) ($\varepsilon_{\max}$)
[VO(dampnol)] (**1**)	Nujol	11,340^{a} (I); 19,900^{b} (II)
	CHCl$_3$	13,400^{c} (40) (I); 16,980 (75) (II); 21,200^{c} (110) (III), 28,000 (9000)
	Pyridine	13,010^{b} (I); 19,200^{c} (90) (II); 27,550 (8350)
[VO(dampnol)Cl] (**2**)	Nujol	~12,300; ~15,000^{b}; ~18,000^{b}; 19,500^{c}; 23,500^{b}, 26,000
	Pyridine	A broad band ranging from 11,000 to 18,000 cm^{-1}; 28,000 (highly intense but broad).
[VO(acacpnol)] (**3**)	Nujol	11,240 (I); 19,000^{b} (II)
	CHCl$_3$	13,300^{c} (30) (I); 17,000 (68) (II); 21,000^{c} (1000) (III); 27,000 (8250)
	Pyridine	13,000^{b} (I); 19,1000^{c} (II); 27,030 (8700)
[VO(salpnol)] (**5**)	Nujol	11,250 (I); ~19,000^{b} (II)
	CHCl$_3$	13,160^{c} (I); 16,721 (70) (II); ~20,000^{c} (III)
	Pyridine	13,000^{b} (I); ~19,000^{c} (II); ~27,000 (8400)
[VO(ohacpnol)] (**7**)	Nujol	~11,000 (I); ~19,200^{b} (II)
	CHCl$_3$	13,160^{c} (34) (I); 16,000 (150) (II); 21,250^{b} (III); 27,780 (6800)
	Pyridine	A broad band ranging from 12,000 to 15,000 cm^{-1}; ~28,000 (6500)
[VO(dampnol)Py] (**9**)	Nujol	~13,000^{b} (I); 16,6000 (II); 21800^{c} (III); ~29,000
	Pyridine	12,900 (40) (I); 19,250^{c} (90) (II); 27,030 (8400)

^{a}Numbering to the low energy bands, ^{b}shoulders, ^{c}inflections.

frequencies and the electronic spectra of (**1**), (**3**), (**5**), and (**7**), we may conclude that these complexes have a six-coordinate structure in the solid state (achieved by V–O–V bridging) and a six-coordinate structure in donor solvents (achieved by coordination of a solvent molecule) but exhibit a five-coordinate square-pyramidal structure in non-coordinating solvents. Reactions of pyridine with **1**, **3**, **5**, and **7** leading to the isolation of six-coordinate **9**–**12** (see table 1) and their characterization support the above conclusion.

The oxovanadium(IV) complexes (**1**), (**3**), (**5**), and (**7**) in pyridine exhibit three bands in 10,000–21,000 cm^{-1} region: a band maximum at $\sim$13,000 cm^{-1} (I) and inflections/shoulders at $\sim$19,000 cm^{-1} (II) and 21,000 cm^{-1} (III) (see table 3). A comparison of the solid-state reflectance spectra with the donor solution spectra (table 3) reveals that band I is shifted to higher energy with a change from the solid state to coordinating solutions. The observed spectral shifts reflect the changes caused by the replacement of a polymeric V–O–V species by a monomeric complex containing an axially-coordinating solvent molecule.

The infrared spectral data discussed above show that the V=O bond order increases when the V–O–V bonded polymeric complexes (**1**), (**3**), (**5**), and (**7**) are dissolved in coordinating solvent (table 2). In terms of the Ballhausen and Gray (BG) molecular orbital scheme [31], this observation suggests that π boding between the $3d_{xz}$, $3d_{yz}$ orbitals of vanadium and $2p_x$ and $2p_y$ orbitals of oxygen in the VO moiety is enhanced in coordinating solvents relative to the solid-state. Increased axial π bonding would result in an increase in the energy of the $^2B_2\ (d_{xy}) \rightarrow {}^2E(\mathrm{I})\ (d_{xz}, d_{yz})$ transition (BG scheme) in solutions of coordinating solvents compared to the solid-state. Band I exhibit this type of behaviour and therefore is assigned to the $^2B_2 \rightarrow {}^2E(\mathrm{I})$ transition. Support for this interpretation can be obtained from solution studies [32] and the polarized crystal spectra of VO $(acac)_2$.

The ν(V=O) of the present complexes **1**, **3**, **5**, and **7** is shifted approximately 25 cm^{-1} towards higher energy (table 2) compared to ν(V=O) of the complexes found in pyridine solution. This indicates five-coordinate complexes with an additional increase in axial V=O π bonding for the chelates in non-coordinating solvents compared to coordinating solvents. On the basis of these observations, the $^2B_2\ (d_{xy}) \rightarrow {}^2E(\mathrm{I})\ (d_{xz}, d_{yz})$ and $^2B_2(d_{xy}) \rightarrow {}^2B_1(\mathrm{II})\ (d_{x^2-y^2})$ transitions would be expected to shift to higher and lower energies, respectively, in non-coordinating solvents compared to coordinating solvents.

The electronic spectra of (**1**), (**3**), (**5**), and (**7**) in chloroform are characterized by a single maximum about 16,700 cm^{-1} (II) with inflections/shoulders at about 13,255 cm^{-1} (I) and 20,865 cm^{-1} (III). Comparison with those obtained in coordinating solvents indicates that band I shifts to higher energy and band II to lower energy upon going from coordinating solvent to chloroform. These shifts support the assignment of the lowest energy bands to the $^2B_2 \rightarrow {}^2E(\mathrm{l})$ and $^2B_2 \rightarrow {}^2B_1$ transitions, respectively [24, 27]. The band around 20,865 cm^{-1}, found in the present complexes, may tentatively be assigned to $^2B_2 \rightarrow {}^2A_1$ transitions, as discussed elsewhere [24, 27]. The other high-energy bands may originate from charge transfer transitions [24, 27].

3.7. *ESR spectra*

The g_o and A_o values of **1**, **3**, **5**, and **7**, obtained from ESR spectra are in agreement with previously published data for similar oxovanadium(IV) complexes with tetradentate Schiff bases [22]. A_o values are decreased in donor solvents relative to chloroform

Table 4. Isotropic ESR data for the oxovanadium(IV) complexes in different solvents.

Complex	Solvent	A_o, [a]G	g_o[b]
[VO(dampnol)] (**1**)	$CHCl_3$	96.5	1.973
	Pyridine	94.6	1.973
[VO(acacpnol)] (**3**)	$CHCl_3$	95.8	1.973
	Pyridine	93.7	1.972
[VO(salpnol)] (**5**)	$CHCl_3$	98.2	1.973
	Pyridine	95.1	1.974
[VO(ohacpnol)] (**7**)	$CHCl_3$	98.6	1.973
	Pyridine	96.2	1.974

[a]Deviation ± 0.5 G, [b]deviation ± 0.001.

solutions (table 4). A similar trend was observed in similar Schiff base complexes of oxovanadium(IV) [22]. Beside the effect of axial coordination, other factors such as hydrogen bonding and dielectric constant effects may also influence these reductions of A_o values on going from non-donor solvents to donor solvents [22].

4. Conclusion

New oxovanadium(IV), vanadium(IV) and oxovanadium(V) complexes with dibasic tetradentate Schiff bases have been synthesized and characterized. New routes have been suggested for the synthesis of vanadium-carbon bonded compounds. Some of the complexes might show important biological activities, yet to be investigated. The X-ray crystal structure of some of the complexes might reveal supramolecular assembly, thus the studies of the solid-state properties of such compounds might focus on their use as valuable materials.

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