Chem Sci Trans., 2012, **1(1),** 121-133
DOI:10.7598/cst2012.135

Chemical Science Transactions
ISSN: 2278-3458

RESEARCH ARTICLE

Microwave Synthesis, Reactivity, Spectral and Thermal Analysis of Some Binary/Mixed Ligand Oxovanadium(IV) Complexes

A. P. MISHRA, L.R. PANDEY and RAJENDRA K JAIN*

Synthetic Inorganic & Coordination Chemistry Laboratories, Department of Chemistry,
Dr. H.S. Gour Central University, Sagar (M.P.)-470 003, India
jainrajchem@gmail.com

Received 7 May 2012 / Accepted 17 May 2012

Abstract: Microwave-assisted synthesis is a branch of green chemistry. The salient features of microwave approach are shorter reaction times, simple reaction conditions and enhancements in yields. Vanadium containing compounds have their utility in various physicochemicals, biochemical physiological, enzymatic and catalytic processes. Novel six binary/mixed ligand oxovanadium(IV) complexes [VO(deb)(H_2O)] **(I),** [VO(deb)(hq)(H_2O)] **(II),** [VO(dpeda)$_2$].SO_4.H_2O **(III),** [VO(dndsa)(H_2O)$_2$].SO_4.3H_2O **(IV),** [VO(tcne)].(VO_3)$_2$.H_2O **(V),** [VO(dnph)$_2$(VO_3)$_2$].H_2O **(VI)** have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analyses, thermal data, FAB mass, FT-IR, molar conductance, electronic spectra, ESR and magnetic measurements. FAB mass and Thermal data show degradation pattern of the complexes. The thermal behavior of complexes shows that the hydrated complexes lose water molecules of hydration in the first step; followed by decomposition of ligand molecules in the subsequent steps. The reactivity and substitution behaviour of the synthesized complexes have also been studied.

Keywords: Microwave synthesis, Oxovanadium(IV), Binary/mixed ligand, Thermal analyses

Introduction

The coordination chemistry of oxovanadium(IV) with multidentate ligand received attention of researchers due to its growing applications in catalysis and therapeutics. Vanadium has multiple biological roles as essentiality in traces, therapeutic effect in small doses and toxicity in excess. V(V)-V(IV)/V(IV)-V(III) redox systems are very significant from reactivity view point. Vanadium compounds have been utilized in various homogenous/heterogenous catalytic processes, where they exhibited good synthetic potential. Doped vanadium compounds have been used in synthesizing nanoparticles. Distortion in geometry of oxovanadium(IV) complexes from trigonal bipyramidal, square pyramidal to octahedral is also a subject of interest for structural studies[1, 2]. 2,3-dihydro-4-nitro-2,3-dioxo-9,10-secostrychnidin-10-oic acid (cacotheline) is a nitro derivative of brucine. It is a CNS stimulant and also used for separating racemic mixtures and as reversible redox indicator. Sodium 5,5-diethyl barbiturate (sodium barbitone) is well known sedative-hypnotic drug, shows effect on CNS. *N,N'*-diphenyl ethanediamide (oxanilide) is an oxalic acid dianilide, common in use a starting material for the manufacture of various medicine, dyes and industrial products. A chelating agent, 8-hydroxy quinoline (oxine) has also been used as antiseptic and fungistatic agent. 1,1,2,2-Tetracyano ethene (TCNE) is well in ESR as marker because of its structural peculiarity. It is also used in the synthesis of spiro compounds and as aromatizing agent. 2,4-Dinitro phenylhydrazine is popular in analytical chemistry for the tests of aldehyde and ketone[3-6].

The application of microwave-assisted synthesis in organic, organometallic and coordination chemistry continues to develop at an astonishing pace. Microwave irradiated reactions under solvent free or less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling[7-11]. Reports on the synthesis of metal complexes by microwave methods have been comparatively less.

Considering the relevance and significance of the work, we have synthesized and characterized six binary/mixed ligand oxovanadium(IV) complexes $[VO(deb)(H_2O)]$ **(I),** $[VO(deb)(hq)(H_2O)]$ **(II),** $[VO(dpeda)_2].SO_4.\ H_2O$ **(III),** $[VO(dndsa)(H_2O)_2].\ SO_4.3H_2O$ **(IV),** $[VO(tcne)].(VO_3)_2.H_2O$ **(V),** $[VO(dnph)_2(VO_3)_2].H_2O$ **(VI),** where deb=5,5-diethyl barbiturate ion, hq=8-hydroxy quinoline ion, dpeda=N,N'-diphenyl ethanediamide, dndsa=2, 3-dihydro-4-nitro-2,3-dioxo-9,10-secostrychnidin-10-oic acid, tcne=1,1,2,2-tetracyano ethene and dnph=2,4-dinitro phenylhydrazine.

Experimental

All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation were obtained from Sigma Aldrich and Loba Chemie. Elemental analysis was carried out using a Heraeus elemental analyser at SAIF, CDRI, Lucknow. The complexes were analysed for vanadium and sulphate contents by the standard methods. FAB-mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Magnetic measurement was made by Gouy's method. Electronic spectra (10^{-3} M in methanol) were recorded on Perkin Elmer Lambca-2B-spectrophotometer. Molar conductance (10^{-3} M in methanol) was measured on Elico-CM 185 Conductivity Bridge at room temperature. FT-IR spectra (in KBr pellet) were recorded on Perkin Elmer RX-I spectrophotometer at SAIF, Panjab University Chandigarh. Thermogravimetric analysis was done on a Perkin Elmer thermal analyser in the temperature range 30-800 °C at heating rate 10 °C/min (in air) at Institute Instrumentation Centre, IIT Roorkee. The solid state electrical conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at room temperature. Microwave assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800 W and microwave frequency 2450 MHz. A thermocouple used to monitor the temperature inside the vessel of the microwave. The microwave reactions were performed using on/off cycling to control the temperature.

Conventional preparation of binary/mixed ligand complexes (I-VI)

*5,5-Diethylbarbiturate oxovanadium(IV) binary complex (**I**)*

An aqueous solution (75 mL) of $VOSO_4.5H_2O$ (2.53 g, 0.01 mole) was added to an aqueous solution (75 mL) of the ligand sodium-5,5-diethyl barbiturate (4.12 g 0.02 mole) in 1:2

molar ratio. The resulting mixture was refluxed for 6 hours at 80-90 °C. A dirty green product appears on concentrating the solution. It was filtered and washed three times with 50% ethanolic water. Finally complex was washed with petroleum ether and recrystallised twice with 50% ethanolic water. The complex was dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator and further dried in an electric oven at 60–75 °C. The complex is air stable non-hygroscopic and soluble in water, methanol and acetone (yield: 65%).

*5,5-Diethyl barbiturate and 8-hydroxyquinoline mixed ligand oxovanadium(IV) complex (**II**)*

The complex has been prepared by mixing aqueous solution (50 mL) of $VOSO_{4.}$ $5H_2O$ (2.53 g, 0.01 mole) to the aqueous solution (50 mL) of sodium-5,5-diethyl barbiturate (2.06 g, 0.01mole) and aqueous solution of (50 mL) 8-hydroxy quinoline (1.45 g, 0.01 mole) in 1:1:1 molar ratio. The reaction mixture was refluxed for 7 hours at 85-90 °C. A black precipitate appeared on concentrating the solution. It was filtered and washed four times with 50% ethanolic water. Finally, complex was washed with petroleum ether and recrystallized twice with 50% ethanolic water. The complex was dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator and also further dried in an electric oven at 60–75 °C. The complex is air stable, non-hydroscopic and soluble in water, methanol and acetone (yield: 66%).

*N,N'-Diphenyl ethanediamide oxovanadium(IV) binary complex (**III**)*

A methanolic solution (50 mL) of $VOSO_4.5H_2O$ (2.53 g 0.01 mole) was added to a methanolic suspension (100 mL) of the ligand *N*, *N*'-diphenyl ethanediamide (4.8 g, 0.02 mole) in 1:2 molar ratio. The reaction mixture was refluxed on a water bath for 10 h. The resulting dark green precipitate of the complex was washed five times with ethanol and finally washed with petroleum ether. It was recrystallized twice with ethanol and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The complex is air stable, non-hygroscopic and partially soluble in methanol and acetone (yield: 60%).

*2,3-Dihydro-4-nitro-2,3-dioxo-9, 10-secostrychnidin-10-oic acid oxovanadium(IV) binary complex (**IV**)*

An aqueous solution (50 mL) of $VOSO_{4.}5H_2O$ (2.53 g, 0.01 mole) was added to aqueous solution (50 mL) of 2,3-dihydro-4-nitro-2,3-dioxo-9, 10 secostrychnidin-10-oic acid (4.27 g, 0.01 mole) in 1:1 molar ratio. The reaction mixture was refluxed for 5 hours at 80-90 °C. The solution so obtained was concentrated and allowed to stand overnight. The dark brown precipitate was filtered and washed four times with 50% ethanolic water. The complex was finally washed with petroleum ether, recrystallized twice with ethanol and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The complex was further dried in an electric oven at 70-80 °C. The complex is air-stable and soluble in methanol, acetone and water (yield: 73%).

Oxovanadium(IV) metavanadate

Oxovanadium(IV) metavanadate has been prepared by adding aqueous solution (75 mL) of $VOSO_4.5H_2O$ (2.53g, 0.01 mole) with the aqueous solution (50 mL) of ammonium metavanadate (2.34 g, 0.02 mole) in 1:2 molar ratio. The dark green precipitate of oxovanadium(IV) metavanadate was obtained on standing the solution. It was filtered and washed with 50% ethanolic water. Finally, oxovanadium(IV) metavanadate was washed with petroleum ether recrystallized with 50% ethanolic water and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. It was further dried in an electric oven at 70-80 °C. The oxovanadium(IV) metavanadate is air stable, non-hygroscopic and partially soluble in methanol.

*1,1,2,2-Tetra cyanoethene oxovanadum(IV) metavanadate complex (**V**)*

A methanolic solution (100 mL) of oxovanadium(IV) metavanadate (2.65 g, 0.01 mole) was added to a methanolic solution (50 mL) of the ligand of 1,1,2,2-tetracyanoethene (1.28 g, 0.01 mole) in 1:1 molar ratio. The reaction mixture was refluxed on a water bath for 9 hours. A black precipitate appears on standing and cooling the refluxate. It was filtered and washed four times with ethanol. The complex was finally washed with petroleum ether, recrystallized twice with ethanol and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The complex was further dried in an electric oven at 50-60 °C. The complex is air-stable, non-hygroscopic and soluble in methanol and acetone (yield: 70%).

*2,4-Dinitrophenylhydrazine oxovanadium(IV) metavanadate complex (**VI**)*

A methanolic solution (100 mL) of oxovanadium(IV) metavanadate (2.65 g, 0.01 mole) was added to a methanolic solution (50 mL) of the ligand 2,4 –dinitro phenylhydrazine (3.96 g, 0.02 mole) in 1:2 molar ratio. The resulting mixture was refluxed on a water bath for 9–10 h. A black precipitate of the complex appears on cooling, which was filtered and washed four times with ethanol. The complex was finally washed with ether, recrystallized twice with ethanol and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. It was further dried in an electric oven at 50–60 °C. The complex is air-stable, non-hygroscopic and soluble in methanol and acetone (yield: 71%).

*Microwave synthesis of binary/mixed ligand complexes (**I-VI**)*

The ligands and the metal salts were mixed in appropriate ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-5 mL solvent. The reaction was completed in a short time (10-15 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 79-87%).

Results and Discussion

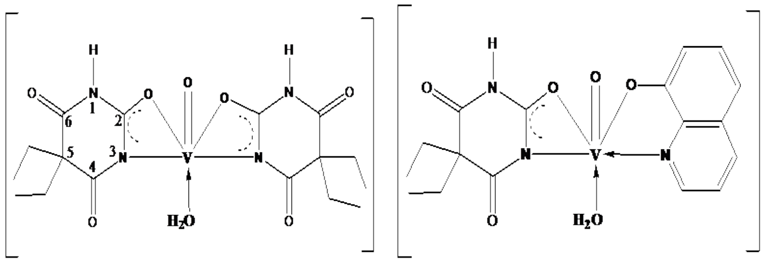
As a result of microwave assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method. In the microwave method homogeneity of reaction mixture was increased by the rotating of reaction platform tray. The confirming of the results was also checked by the repeating of the synthesis process. All the oxovanadium(IV) (Figure 1) complexes (**I-VI**) are coloured solid, stable towards air and moisture at room temperature and more or less soluble in common organic solvents. Some complexes (I, II, IV and V) are also soluble in water. The comparative results of conventional and microwave methods and analytical data of the compounds, together with their physical properties are consistent with proposed molecular formula and magnetic moment values are given in Table 1. The oxovanadium(IV) complexes exhibit 1:1 (complexes IV and V), 1:2 (complexes I, III and VI) and 1:1:1 (complex II) metal to organic ligand stoichiometry. The representative equations are shown below -

$$VOSO_4.5H_2O + 2Nadeb \rightarrow [VO(deb)_2(H_2O)] + Na_2SO_4 \textbf{ (Complex I)}$$
$$VOSO_4.5H_2O + Nadeb + Hhq \rightarrow [VO(deb)(hq)(H_2O)] + NaHSO_4 \textbf{ (Complex II)}$$
$$VOSO_4.5H_2O + 2dpeda \rightarrow [VO(dpeda)_2].SO_4.H_2O \textbf{ (Complex III)}$$
$$VOSO_4.5H_2O + dndsa \rightarrow [VO(dndsa)(H_2Ol_2].SO_4.3H_2O \textbf{ (Complex IV)}$$
$$VOSO_4.5H_2O + 2NH_4VO_3 \rightarrow VO(VO_3)_2.xH_2O + (NH_4)_2 SO_4$$
$$VO(VO_3)_2.xH_2O + tcne \rightarrow [VO(tcne)].(VO_3)_2 H_2O \textbf{ (Complex V)}$$
$$VO(VO_3)_2.xH_2O + 2dnph \rightarrow [VO(dnph)_2(VO_3)_2].H_2O \textbf{ (Complex VI)}$$

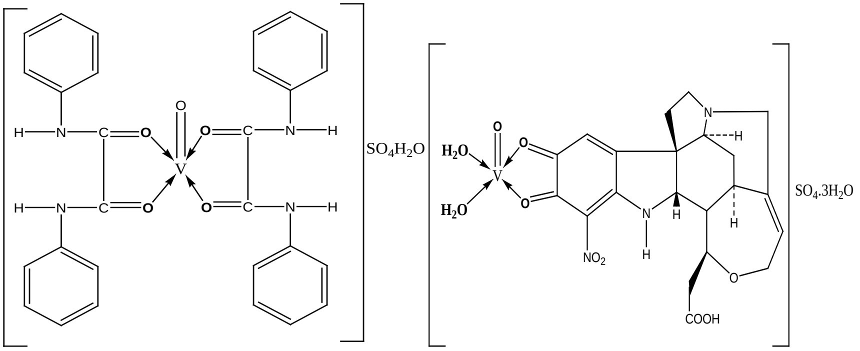
Table 1. The comparative results of conventional and microwave methods, analytical and physical data of Oxovanadium(IV) complexes

Compd. No.	Molecular formula of the complex (Mol. Wt.) Colour	M. P. /Dec. °C	Reaction period		Yield %		Elemental analysis% found (calcd.)				*Λ_m* Scm^2mol^{-1}
			CM, h	MM, min	CM	MM	C	H	N	V	
I	$[VO(C_8H_{11}N_2O_3)_2(H_2O)]$ (451.4) Dark Green	230	6.2	10.4	80	65	43.12 (42.53)	5.45 (5.31)	12.57 (12.40)	11.33 (11.29)	22.4
II	$[VO(C_8H_{11}N_2O_3)(C_9H_7NO)(H_2O)]$ (413.2) Black	243	7.0	12.1	82	66	57.68 (58.08)	4.93 (4.84)	10.22 (10.16)	12.49 (12.34)	20.6
III	$[VO(C_{14}H_{12}N_2O_3)_2].SO_4.H_2O$ (661.5) Light Green	200	10.1	15.0	79	60	50.12 (50.83)	4.02 (3.93)	8.55 (8.47)	7.86 (7.71)	120.5
IV	$[VO(C_{12}H_{21}N_3O_7)(H_2O)_2].SO_4.3H_2O$ (680.4) Dark Brown	202	5.1	11.2	86	73	37.25 (37.03)	4.58 (4.55)	8.15 (7.93)	7.67 (7.49)	145.9
V	$[VO(C_6N_8)].(VO_3)_2.H_2O$ (411.1) Dark Brown	290	9.0	14.3	81	70	17.93 (17.15)	0.52 (0.48)	13.86 (13.62)	37.55 (37.22)	150.8
VI	$[VO(C_6H_6N_4O_4)_2(VO_3)_2].H_2O$ (679.3) Black	250	9.6	13.9	87	71	21.66 (21.20)	2.17 (2.06)	16.66 (16.49)	22.98 (22.53)	18.5

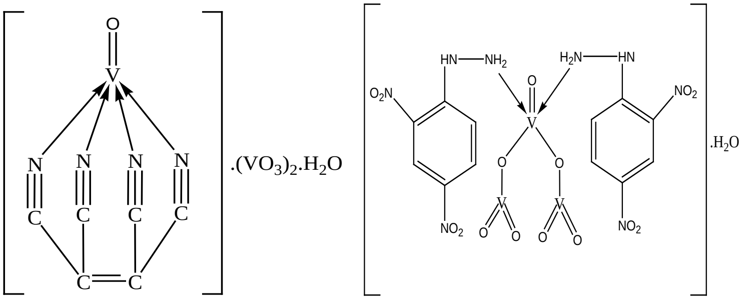
CM = Conventional Method time in hours; MM = Microwave Method time in minutes



$[VO(deb)_2(H_2O)]$ **Complex (I)** $[VO(deb)(hq)(H_2O)]$ (**Complex II**)



$[VO(dpeda)_2].SO_4.H_2O$ (**Complex III**) $[VO(dndsa)(H_2Ol_2].SO_4.3H_2O$ (**Complex IV**)



$[VO(tcne)].(VO_3)_2.H_2O$ (**Complex V**) $[VO(dnph)_2(VO_3)_2].H_2O$ (**Complex VI**)

Figure 1. Proposed structures of binary/mixed ligand oxovanadium(IV) complexes

Molar conductance

Low molar conductance (10^{-3} M in MeOH) values of **I, II** and **VI** complexes show that these three complexes are non-electrolytic in nature. The Molar conductance values of complexes **III-V** suggest that the complexes **III** and **IV** are 2:2 electrolytic in nature while complex **V** is 2:1 electrolytic nature. The ionic nature of metavanadate ion (in complex **V**) has been inferred from conductance data and chemical tests. Low molar conductance value and chemical tests for complex **VI** suggest unidentate coordinating nature of metavanadate ion in this complex.

Reactivity

For the study of reactivity and substitution behaviour of the synthesized complexes, 0.005 M solution (in 50% methanolic water) of reacting complex was prepared. 0.01 M aqueous solution of reactants *viz.* hydrochloric acid sodium hydroxide, aqueous ammonia, potassium thiocyanate, barium chloride and copper sulphate were also made. For observing the reactivity, a little amount of the above reactant was added to the solution of the complex.

The ionic nature of the sulphate and vanadate ions in the complexes has been tested by reacting, the complexes with aqueous solution of barium chloride and copper sulphate. Reaction was monitored by observing any change in colour or precipitation at room temperature (1 h) as such and also after heating[12].

Reaction with dil. aq. NH_3

VO-deb/dpeda complexes do not react on keeping for 1 hour at room temperature, but VO-tcne complex reacts slowly and VO-deb-hq/dndsa/dnph complexes react fast under similar conditions. On heating also VO-deb/dpeda complexes do not react while VO-deb-hq/dndsa/tcne/dnph complexes react well.

Reaction of dil. aq. HCl

VO-deb/dpeda complexes do not react at room temperature (1 h), but VO-tcne complex reacts slowly and VO-deb-hq/dndsa/dnph complexes react fast under similar conditions. On heating also VO-deb-hq/dndsa/tcne/dnph complexes react well.

Reaction of dil. aq. NaOH

VO-deb/dpeda complexes do not react even on retaining for 1 hour at room temperature, but VO-tcne complex reacts slowly and VO-deb-hq/dndsa/dnph complexes react quickly under similar conditions. On heating VO-deb-ng/dndsa/tcne/dnph complexes react well.

Reaction of dil. aq. NH_3

VO-deb/dpeda/tcne/dnph complexes do not react on keeping for 1 h at room temperature while VO-deb-hq complex reacts slowly and VO-dndsa complex react rapidly under similar conditions. On heating-VO-deb/dpeda/tcne/dnph complexes do not react but VO-debhq/dndsa complexes react well.

Reaction of dil. aq. $BaCl_2$

VO-deb/deb-hq/dnph complexes do not give any precipitate when allowed to react with dil.aq.barium chloride at room temperature while, VO-dpeda-dndsa and tcne complexes quickly give white and yellow precipitate, this support the ionic nature of sulphate and metavanadote in VO-dpeda/dndsa and VO-tcne complexes.

Reaction of dil. aq. $CuSO_4$

VO-dnph complexes do not give any precipitate while VO-tcne complex give green precipitate indicating presence of metavanadate ion out from coordination sphere in VO-tcne complex.

FAB mass spectum

The FAB mass spectra of complex II have been studied as one of the representative case. The peaks of appreciable intensity have been observed at *m/z* value 410, 390, 180, 140 and 107 amu which suggest the proposed molecular formula and fragmentation pattern. The *m/z* value 410 corresponds to nearest composition $[VO(C_8H_{11}N_2O_3)(C_8H_7NO)(H_2O)]$, 390 to $[VO\ (C_8H_{11}N_2O_3)(C_8H_7NO)]$, 80 to ligand diethyl barbiturate, 140 to ligand 8-hydroxy quinoline and 107 to VO with some chelated O/N ligand moiety. This further indicate that oxovanadium(IV) at the centre of complex is coordinated with one aquo and two O,N-donor anionic bidentate ligands and also the resulting complex is monomeric[13].

FT-IR spectra

The important infrared spectra bands and most probable assignments for the ligands and oxovanadium(IV) complexes are given in Table 2. A careful comparison (position, intensity and shape wise) of the spectra of ligands with their complexes give information regarding coordination through various groups. All the oxovanadium(IV) complexes exhibit a strong band at 979-1006 cm^{-1}, due to υ(V=O). Discussion of individual metal ligand systems involving coordinating groups only, are being given herein.

The IR spectrum of the ligand deb **(I)** exhibits bands at 1697, 1668 1549, 1461, 1413, 1315 and 1266 cm^{-1}, in the pyrimidine ring. On coordination with metal ion these bands appear as merged at 1636, 1401, 1232 cm^{-1} with low intensity. This reflects bidentate behaviour of diethyl barbiturate ligand, coordinating through N(3)- O(2) sites. A characteristic non-ligand sharp band at 1006 cm^{-1} in the spectra of complex has been assigned to υ(V=O). In spectrum of complex a broad band around at 3397 cm^{-1} and a new band of medium intensity at 750 cm^{-1} have been assigned to be due to coordinated water molecule in complex. New weak bands at 554 and 512 cm^{-1} have been assigned to υ(V-O) and υ(V-N) modes, respectively.

The uncoordinated ligand Hhq **(II)** exhibits IR bands at 1597 cm^{-1}, 1315 cm^{-1} and 1237 cm^{-1} due to C=N quinoline ring, phenolic-OH (deformation) and phenolic C-O group, respectively. The change in position of C=N (1575 merged), disappearance of phenolic–OH and upward shift of phenolic C-O (1270 cm^{-1}) in mixed ligand complex suggests deprotonation and coordination through C=N nitrogen and phenolic oxygen. In the mixed ligand complex both the ligands (deb and Hhq) coordinate with oxovanadium ion in bidentate manner; above free ligand bands appear as changed, shifted and merged giving positions at 1625, 1575, 1498, 1466, 1377 and 1270 cm^{-1}. These bands appear as intense due to overlap. Shift in band positions and change in shape, help in deciding the coordination sites. A broad band around at 3428 cm^{-1} and a new band of medium intensity at 716 cm^{-1} have been assigned to be due to coordinated water in mixed ligand complex. New weak bands at 500 and 567 cm^{-1} have been assigned to υ(V-N) and υ(V-O) respectively.

The ligand dpeda **(III)** exhibits a strong IR band at 1732 cm^{-1} due to υ(C=O). This band shifts to the lower frequency side (1668 cm^{-1}) in the spectrum of complex indicating its participation in chelation. No change has been observed in υ(C-N) {1204 cm^{-1}} suggesting non-involvement of secondary nitrogen in complexation. A characteristic non-ligand sharp and at 1001 cm^{-1} in the spectrum of complex has been assigned to υ(V=O). The new band of medium intensity at 526 cm^{-1} in the spectrum of complex has been assigned to υ(V-O). A broad band around 3250-3300 cm^{-1} is due to lattice water[14-20].

The IR spectrum of ligand dndsa **(IV)** shows a strong band at 1691 cm^{-1} due to υ(C=O) {ketonic group}. This band shifts down side (1632 cm^{-1}) in VO-dndsa complex due to reduction of electron density between C=O; suggesting coordination of metal ion with ketonic oxygen. Bands due to carboxylic acid group {υ(C=O) , υ(O-H) and υ(C-O)} present in ligand spectrum at 1740, 1384 and 1225 cm^{-1} remain almost unchanged and unshifted in complex spectrum, suggesting non-participation in chelation. Some other ligand bands also remain unchanged in complex spectrum. A hump at around 3393 cm^{-1} and a medium intensity band at 740 cm^{-1} (rocking) in complex spectrum are due to lattice and coordinated water. A characteristic non-ligand sharp band at 979 cm^{-1} in spectra of complex has been assigned to υ(V=O). The new weak band at 543 cm^{-1} in the spectra of complex is assignable to υ(V-O).

The IR spectrum the ligand tcne **(V)** shows a strong stretching band at 2203 cm^{-1} due to υ(C≡N). In the spectrum of VO-tcne complex, this band shifts higher side (2218 cm^{-1}). This increase in electron density has been accounted to coordination of tcne ligand with oxovanadium(IV) ion. The new medium intensity band at 508 cm^{-1} in complex spectrum has been assigned to υ(V-N) mode. Some other bands of appreciable intensity between 1000-500 cm^{-1} in complex spectrum are assignable to oxovanadium(IV) and free metavanadate ions *i.e.* υ(V=O), υ(VO_3) and υ(V-O)[14-20].

Table 2. Selected IR frequencies (cm^{-1}) of ligands and their oxovanadium(IV) Complexes

Compd. No.	Compounds (Abbr. Name)	ν(C=O)	ν(O-H) Phenolic	ν(C-O)	ν(N-N)	ν(V=O)	$\nu(VO_3)$	H_2O (Rocking)	ν(V-O)	ν(V-N)
L	Nadeb	-	-	-	-	-	-	-	-	-
I	$[VO(deb)_2H_2O]$	-	-	-	-	1006	-	750	554	512
L	Hhq	-	1315	1237	-	-	-	-	-	-
II	$[VO(deb)(hq)H_2O]$	-	-	1270	-	952	-	716	567	500
L	dpeda	1732	-	-	-	-	-	-	-	-
III	$[VO(dpeda)_2].SO_4.H_2O$	1668	-	-	-	1001	-	-	526	-
L	dndsa	1691	-	-	-	-	-	-	-	-
IV	$[VO(dndsa)(H_2O)_2].SO_4.3H_2O$	1632	-	-	-	979	-	740	543	-
L	tcne	-	-	-	-	-	-	-	-	-
V	$[VO(tcne)](VO_3)_2H_2O$	-	-	-	-	981	780, 650	-	-	508
L	dnph	-	-	-	1017	-	-	-	-	-
VI	$[VO(dnph)_2(VO_3)_2].H_2O$	-	-	-	1043	987	750		550	510

The ligand dnph **(VI)** exhibits a medium intensity band at 1017 cm^{-1} due to υ(N-N). This shifts higher in the spectrum of complex (1043 cm^{-1}) suggesting coordination through nitrogen of –NH_2 group. A non-ligand sharp band at 987 cm^{-1} in the spectra of complex has been assigned to υ(V=O). Characteristic absorption bands observed at 750 cm^{-1} in this complex are due to coordination of metavanadate ion through oxygen. This supported by some new bands at 550 cm^{-1} and 510 cm^{-1} in the complex spectrum have tentatively been assigned to υ(V-O) and υ(V-N)[14-20].

Electronic absorption spectra

The assignments of electronic absorption spectra of complexes **(I-VI)** have been summarised in Table 3. All the oxovanadium(IV) complexes exhibit bands in regions: 12900-14000 cm^{-1}, 15800-18100 cm^{-1} and 21000-23020 cm^{-1} which are assignable to $^2B_2$-^2E, $^2B_2$-$^2B_1$ and $^2B_2$-$^2A_1$ transitions, respectively. Atleast minimum two bands have been observed clearly in each complex. Octahedral geometry has been suggested for six coordinated complexes (**I-II**). The geometry of five coordinated complexes **(III-VI)** can be described in terms of trigonal bipyramidal or square pyramidal. In the octahedral complexes due to the presence of sixth donor ligand (H_2O), trans to terminal V=O bond, has a direct influence on ligand field so the d-d transitions here are slight higher shifted compared to the corresponding positions in trigonal bipyramidal or square pyramidal complexes[21-23].

Magnetism

Oxovanadium(IV) complexes are magnetically straight forward. The observed values of magnetic moment for complexes **(I-VI)** at room temperature 298 K are given in Table 3. The magnetic moment values lie in the range 1.72-1.77 B.M. which is in accord with the spin only value for a simple $^1S=½$ system. The values are well suited for oxovanadium(IV) monomeric complexes with one unpaired electron[24-26].

Table 3. Electronic spectral and magnetic values of the oxovanadium(IV) complexes

Comp. No.	Complexes (Abbr. name)	Transitions/Band, cm^{-1}			μ_{eff} (B.M.)
		$^2B_2$-^2E	$^2B_2$-$^2B_1$	$^2B_2$-$^2A_1$	
I	$[VO(deb)_2(H_2O)]$	13900	17400	22900	1.72
II	$[VO(deb)(hq)H_2O]$	14000	18100	23020	1.73
III	$[VO(dpeda)_2].SO_4.H_2O$	13190	17500	21400	1.76
IV	$[VO(dndsa)(H_2O)_2].SO_4.3H_2O$	13510	15900	21500	1.77
V	$[VO(tcne)].(VO_3)_2.H_2O$	12900	15800	21000	1.75
VI	$[VO(dnph)(VO_3)_2].H_2O$	13100	17100	22000	1.74

Electron spin resonance

The X-band EPR spectra of Oxovanadium(IV) (d^1, $^{51}V_,$ I = 7/2) complexes are not so resolved at room temperature (298K) to exhibit all eight hyperfine lines. The calculated values of $g_{\perp,}$ $g_{||\,,}$ g_{av} and Δg for all the complexes **(I-VI)** are summarised in Table 3. Here $g_{av} = 1/3\ [2g_\perp + g_{||}]$. The values are typical of the spectra displayed by octahedral, tbp or sp complexes with one unpaired electron in an orbital of mostly dxy character. The g_{av} values determined from the spectra are nearer to spin only; a slight variation may be accounted to spin-orbital coupling. In square pyramidal complexes (**III-VI**) with C_{4V} symmetry, the V=O bond is along z axis and the other four donor atoms ($O_4/N_4/O_2N_2$) are along x, y axes. An anisotropic EPR spectrum is expected exhibiling two g values ($g_z = g_{||} < g_\perp = g_x = g_y$) in such cases[27, 28].

Table 4. ESR parameters of the oxovanadium(IV) complexes

Comp. No.	Complexes (Abbr. Name)	ESR Parameters			
		$g_{\|\|}$	$g_{\perp}$	g_{av}	Δg
I	$[VO(deb)_2(H_2O)]$	1.9057	1.9904	1.9621	0.0847
II	$[VO(deb)(hq)H_2O]$	1.9085	1.9935	1.9651	0.0850
III	$[VO(dpeda)_2].SO_4.H_2O$	1.9001	1.9723	1.9482	0.0722
IV	$[VO(dndsa)(H_2O)_2].SO_4.3H_2O$	1.8945	1.9693	1.9443	0.0748
V	$[VO(tcne)].(VO_3)_2.H_2O$	1.8808	1.9663	1.9378	0.0855
VI	$[VO(dnph)(VO_3)_2].H_2O$	1.8835	1.9711	1.9419	0.0876

Thermogravimetric analysis

*5,5-Diethyl barbiturate and 8-hydroxyquinoline mixed ligand Oxovanadium(IV) Complex (**II**)*

It is observed from TG curve that there is no weight loss upto 140 °C indicating absence of any lattice water. A weight loss corresponding to one coordinated water molecule has been observed between the temperature 140-243 °C (Remaining wt%, obs./cal 95.16/96.01). After 243 °C chelated ligands starts decomposing and the pyrolysis curve shows that the decomposition occurs mainly in two steps – first step between 243-434 °C (with slow rate) and the second from 434-482 °C (with fast rate). A weight loss corresponding to four side group of diethyl barbiturate ligand appeard in first decomposition step (Remaining wt%, obs./cal 70.5/73.84) while the remaining ring structures break and decompose faster as second step giving the intermediate $VO(O_2)$ (N_2) moiety at 482 °C (Remaining wt% obs./cal 30.79/30.75). An almost horizontal thermal curve has been observed after 482 °C giving the ultimate pyrolysis product vanadium pentaoxide in oxygenated atmosphere after 510 °C alongwith some carbon ashes. (Remaining wt% obs./cal. 28.26/22.08)[29,30].

*N ,N' – Diphenyl ethanediamide oxovanadium(IV) complex (**III**)*

The thermogram of $[VO(dpeda)].SO_4.H_2O$ complex exhibit a minor weight loss between 50-120 °C corresponding to one lattice water molecule (Remaining wt% obs./cal. 97.25/97.27). The complex does not show any loss in weight between 130-190 °C. Further decomposition of complex occurs between 200-300 °C at a faster rate. Indicating the loss of major part of ligand *N,N'*-dipphenyl ethane diamide) in this step (Remaining wt% obs./cal., 29.10/24.65). The decomposition remaining oxovanadum (IV) sulphate moiety may be occurring between 300 -500 °C. After 500 °C a horizontal thermal curve has been obtained corresponding to vanadium pentaoxide as an ultimate pyrolysis product (Remaining wt% obs./cal.13.13/13.75).

*2,3-Dihydro-4-nitro-2,3-dioxo-9,10-secostrychnidin-10-oic acid Oxovanadium(IV) Binary Complex (**IV**)*

Tharmogram of $[VO(dndsa)(H_2O)_2].SO_4.3H_2O$ complex display a weight loss at around 100 °C which corresponds to three lattice water molecules present in complex (Remaining wt. % obs./cal. 92.00/92.05). Between 125-200 °C, the loss in weight correspond to two coordinated water molecules (Remaining wt. % obs./cal. 86.44/86.77). Beyond 200 °C a gradual weight loss occurs up to 386 °C which becomes fast between 386-434 °C. This is due to the thermal degradation of the bulky ligand. In the oxygenated atmosphere, the V_2O_5 has been inferred to be the ultimate pyrolysis product. (Remaining wt % obs./cal. 13.53/13.37) [29,30].

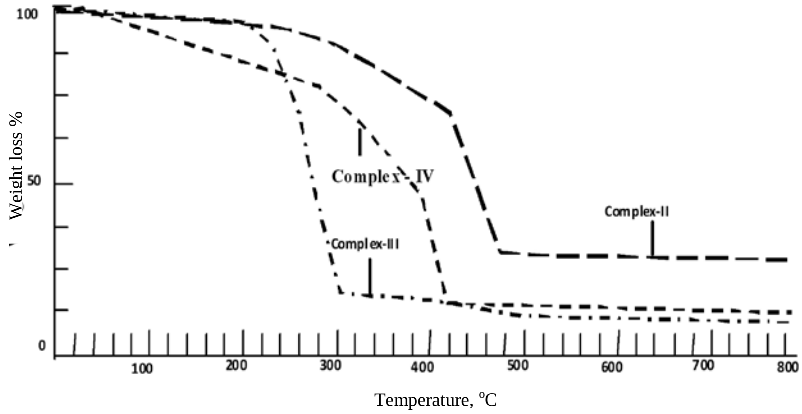


Figure 2. TGA Curves of Oxovanadium(IV) Complexes

Acknowledgement

We are thankful to I.I.T. Mumbai and I.I.T. Roorkee for ESR and thermal analysis, respectively. We also acknowledge SAIF, CDRI Lucknow for micro analysis and spectral analysis. Thanks are also due to the Head, Department of Chemistry and Physics Dr. Hari Singh Gour University, Sagar (M.P.) for Laboratory facilities.

References

1. Gup R and Kirkan B, *Spectrochim Acta A,* 2005, **62**, 1188-1195.
2. Masoud M S, Heiba A M and Ashmawy F M, *Trans Met Chem.*, **1983,** 8, 124-126.
3. Suksrichavalit T, Prachayasittikul S and Prachayasittikul V, *Molecules*, **2008,** 13, 3040-3056.
4. Masoud M S and Muhamed G B, *J Korean Chem Soc.*, 2002, **2**, 99-116.
5. Ikotun A A, Ojo Y, Obafemi C A and Egharevba G O, *African J Pure App Chem.,* **2011,** 5(5), 97-103.
6. Masoud M S, Soayed A A, Ali A.E. and Sharsherh O K, *J Coord Chem.,* 2003, **56** (8), 725–742.
7. Mahajan K, Fahmi N and Singh RV, *Indian J Chem.*, 2007, **46A**, 1221-1225.
8. Mahajan K, Swami M and Singh R V, *Russ J Coord Chem.,* 2009, **35,** 179-185.
9. Mohanan K, Kumari S and Rijulal G, *J Rare Earths,* 2008, **26**, 16-21.
10. Garg R, Saini M.K, Fahmi N. and Singh R V, *Trans Met Chem.*, 2006**, 31**, 362-367.
11. Sharma K, Singh R, Fahmi N and Singh R V, *Spectrochim Acta Part A,* 2010, **75A**, 422-427.
12. Mishra A P and Pandey L R, *Indian J Chem.,* 2005, **44A**, 1800-1805.
13. Dubey R K, Dubey U.K and Mishra C M, *Indian J Chem.*, 2008, **47A**, 1208-1212.
14. Hossain M B, Saidul Islam M, Hassan M N, Yousuf M A and Salam M A, *J Sci Tech.,* 2009, **4(1),** 57-59.
15. Mishra A P, Mishra R.K and Shrivastava S P, *J Serb Chem Soc.*, 2009, **74**, 523-535.
16. Kirkan B and Gup R, *Turk J Chem.,* 2008, **32**, 9–17.
17. ABD El-Wahab Z H, Mashaly M M and Faheim A A, *Turk J Chem.*, 2005, **59(1),** 25-36.
18. Nakamoto K., Infrared and Raman Spectra of Inorganic, Coordination Compounds, 5th Ed., John Wiley and Sons, Part A & B, New York, **1998**.
19. Patel R N, Gundla V L N and Patel D K, *Indian J Chem.,* 2008, **47A**, 353-360.

20. Patel R N, *Indian J Chem.*, 2009, **48A**, 1370-1377.
21. Jian-ning L I U, Bo-wan W U and Yongchun L I U, *Turk J Chem.*, 2006, **30**, 41-48.
22. Raman N, Raja S J, Joseph J and Raja J D, *J Chil Chem Soc.*, 2007**, 52**, 1138-1144.
23. Lever A B P, Inorganic Electronic Spectroscopy, 2nd Ed., Elsevier, New York, **1984**.
24. Mishra A P, Khare M and Gautam S K, *Synth React Inorg Met-Org Chem.,* 2002, **32**, 1485-1489.
25. Dutta R L and Syamal A, Elements of Magneto Chemistry, 2nd Ed., Affiliated East West Press, New Delhi, 1993.
26. Mishra A.P and Pandey L.R, *Indian J Chem.*, 2005, **44A**, 94-97.
27. Soliman A A and Mohamed G G, *Thermochim Acta,* 2004, **421**, 151-159.
28. Hathaway B J, In Comprehensive Coordination Chemistry, Ed., Wilkinson Pergamon Press (U.K.), 1987, **5**, 534.
29. Mohamed G G, Omar M M and Ibrahim A A, *Eur J Med Chem.*, 2009, **44**, 4801-4812.
30. Sujamol M S, Athira C J, Sindhu Y and Mohanan K, *Spectrochim Acta,* 2010, **75A,** 106-112.