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Vanadium(IV) and (V) complexes of 2-formylpyridinethiosemicarbazone and its N(4)-ethyl and N(4)-phenyl derivatives

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ABSTRACT

The new complexes [VO(L^1/L^3)(acac)],[VO(HL^2)(H_2O)(SO_4)], [{VO_2(L^1)}$_2$] and cis-[VO_2(L^2/L^3)] [Hacac = acetylacetonate; HL = 2-formylpyridine thiosemicarbazone ligand or its derivatives N(4)-ethyl(HL^2) and N(4)-phenyl (HL^3)] have been prepared and characterized by spectroscopy. Their redox behaviour was studied by cyclic voltammetry. They effectively and selectively catalyze the oxidation of primary and secondary alcohol into their corresponding aldehyde and ketone, respectively.

KEYWORDS

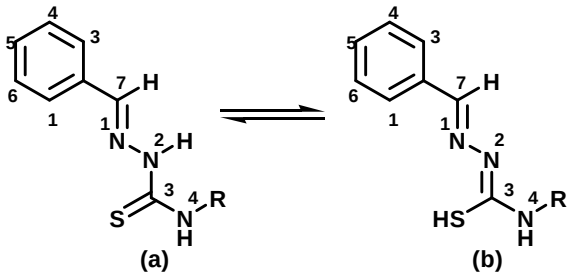
Vanadium(IV)/(V);
2-formylpyridinethiosemicarbazones;
Spectral properties;
Cyclic voltammetry;
Catalytic oxidation.

INTRODUCTION

Biological properties of thiosemicarbazones (TSCs) have been extensively studied owing to their wide variety of biological activities[1]. The members of one of the most famous families of TSCs have a tridentate ligands derived from 2-formyplyridine which show antitumour activity due to their ability to inhibit the biosynthesis of DNA[2,3]. Thiosemicarbazones are considered to be mixed hard-soft chelating agents as they contain both N and S atoms. This dual character gives them the ability to bind metal ions in either a neutral or anionic manner[4]. In most cases these TSCs act as a tridentate ligands that coordinate to metal ion through N,N,S-centres and their coordination behaviour depends on the nature of metal ions concerned[5].

In recent years the medicinal applications of oxovanadium(IV) and dioxovanadium(V) complexes with N-, O- and S- donor ligands have been reported for their potential insulin-mimetic effects[6-8] and anticancer activities[9].

As a continuation of our research on N,N,S-donor ligand of 2-pyridine thiosemicarbazone (Hptsc) with different transition metal ions[10], it is of interest to describe the preparation, spectral characterization and redox properties of the oxovanadium(IV) complexes [VO(acac)(ptsc)], [VO(acac)(pptsc)], [{VO_2(ptsc)}$_2$]



HL^1 : R = H, 2-formylpyridine thiosemicarbazone(Hptsc)
HL^2 : R = C_2H_5, 2-formylpyridine-N(4)-ethyl thiosemicarbazone (Hpetsc)
HL^3 : R = Ph, 2-formylpyridine-N(4)-phenyl thiosemicarbazone (Hpptsc)

Scheme 1 : Structure and tautomerism of 2-formylpyridine-*N*(4)-substituted thiosemicarbazone(HL)

and [VO(Hpetsc)(SO_4)(H_2O)] as well as the cis-dioxovanadium(V) complexes; cis-[VO_2(petsc)] and cis-[VO_2(pptsc)] which involve the thiosemicarbazone derivatives; 2-formylpyridine-N(4)-ethylthiosemicarbazone (Hpetsc), 2-formylpyridine-N(4)-phenylthiosemicarbazone (Hpptsc). The reactivity of the complex cis-[VO_2(petsc)] towards catalytic oxidations of alcohols in presence of excess H_2O_2 or t-butylhydroperoxide as co-oxidants has also been reported in comparison with our previous work on catalytic oxidations by ruthenium(II) and (III) complexes[11,12].

EXPERIMENTAL

Instrumentation

IR spectra were measured on a JASCO 410 FT-IR spectrometer (4000-400 cm^{-1}) as KBr discs. ^1H NMR spectra were measured on a Varian Gemini WM-200 spectrometer (Laser Centre, Cairo University). Electronic spectra in DMF were recorded using a Perkin-Elmer Lambda 2S. ESR spectra were recorded with a Bruker EMX spectrometer (Radiation Technology Centre, Cairo). Cyclic voltammetric studies were carried out on an electroanalyzer CHI 610A, the three electrode cell comprised a reference Ag wire, Pt auxiliary and working electrode, the complexes (10^{-3}M) in 0.1 M (n-Bu_4N)PF_6 as supporting electrolyte were used. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility balance.

Analysis

Carbon, hydrogen and nitrogen were determined by microanalytical unit of Cairo University. The vanadium content of each of the complexes was determined[13] after decomposition by gentle heating using conc. HNO_3 (three times) and complete drying. The orange mass (V_2O_5) obtained was dissolved in dilute H_2SO_4 and sodium sulphite or ethanol with heating are used to reduce vanadium(V) into vanadium(IV) and then titration against standard $KMnO_4$ is performed. Satisfactory vanadium analytical data for complexes are consistent with their formula.

Preparation of ligands

The ligands Hptsc(HL^1), Hpetsc(HL^2) and Hpptsc (HL^3) were prepared by refluxing an equimolecular amounts (10 mmol) of thiosemicarbazide (or its N(4)-substituted derivatives) and 2-formylpyridine (10 mmol) in methanol or 5:1 methanol-water mixture if appropriate for dissolution of the thiosemicarbazide. Condensation by reflux (3-4 h) was performed on water bath where white or pale yellow crystalline products of the ligands were obtained (Yield, > 70%).

Preparation of complexes

[VO(acac)(L^1)] (1)

Solutions of the complex [$VO(acac)_2$][14] (0.13 g, 0.5 mmol) and the ligand HL^1(0.09 g, 0.5 mmol) were prepared separately in minimal amounts of MeCN and then mixed. The mixture was then refluxed (65°C 30 min on a water bath, during which a dark green precipitate was formed, filtered off, washed with hot MeCN, Et_2O and dried in vacuo over P_2O_5 . Increase time of reflux to 3 h gave the same compound and yield (~70%).

[{$VO_2(L^1)$}$_2$] (2)

To the solution of the ligand HL^1(0.11 g, 0.6 mmol) in EtOH (15 cm^3) was added grinded NH_4VO_3 (0.06 g, 0.5 mmol) in an open round flask (25 cm^3) and the mixture was heated (65^{0}C) with stirring on water bath (2-2.5 h) where an evolution of ammonia observed and a yellow precipitate generated during the reaction. The nice yellow precipitate was filtered while hot washed with EtOH and Et_2O and dried in vacuo (yield 90%).

[VO(HL^2)(SO_4)(H_2O)] (3)

The ligand HL^2 (0.104 g, 0.5 mmol) in 10 cm^3 MeOH was added to a solution of vanadyl sulphate $VOSO_4.H_2O$ (0.09 g, 0.5 mmol) in 10 cm^3 MeOH and the mixture refluxed for 0.5 h on a water bath, during which a pale green precipitate was filtered off, washed with hot MeOH, Et_2O and dried in vacuo over P_2O_5 (yield 75%).

cis-[$VO_2(L^2)$] (4)

Method 1

Solutions of the complex [$VO(acac)_2$] (0.13 g, 0.5 mmol) and the ligand HL^2 (0.104 g, 0.5 mmol) were prepared separately in MeCN and then mixed. The mixture was refluxed (65°C) for 10 h on a water bath during which a green solution changed into a yellow precipitate

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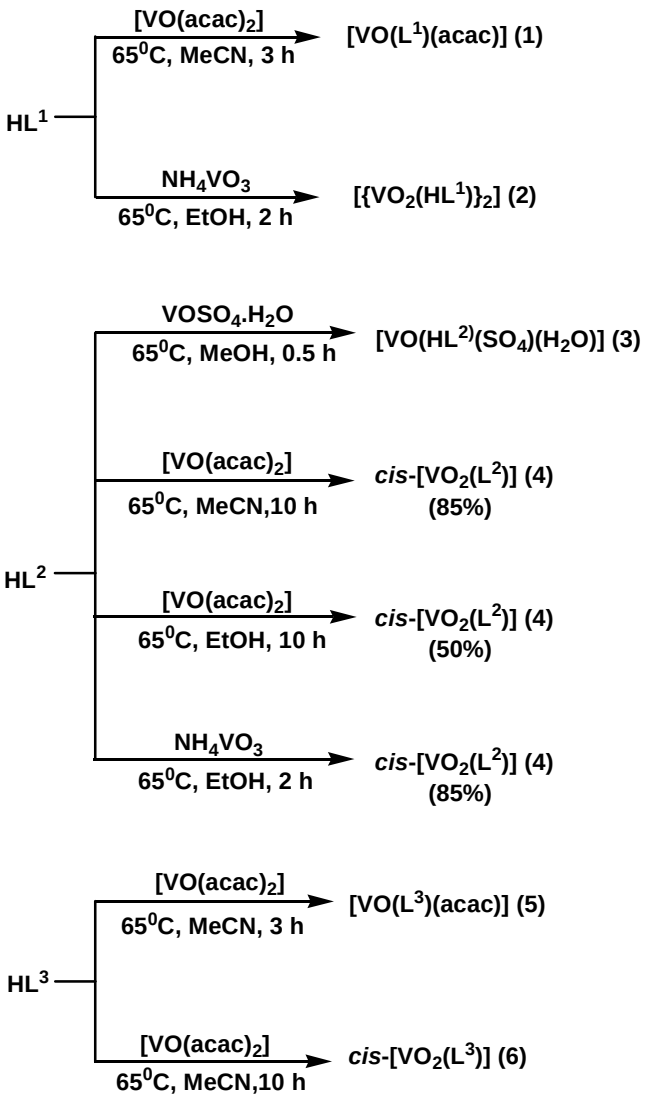

Scheme 2 : Preparation of complexes

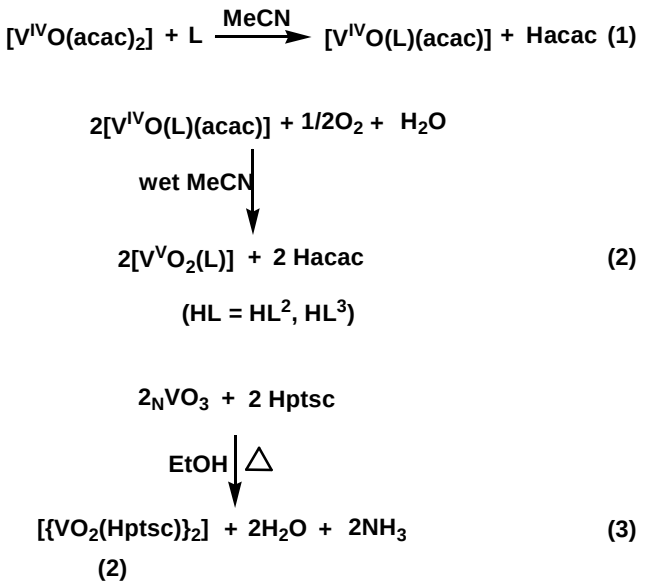

TABLE 1 : Analytical and magnetic moments data for thiosemicarbazone complexes

Compound		Color	Yield (%)	Found C	(Calc.)% H	N	μ_{eff} (B.M)[a]
Hpytsc (HL^1)		White	75	46.6(46.7)	4.5(4.4)	31.2(31.1)	
$[VO(L^1)(acac)]$	(1)	Dark green	80	41.6(41.7)	4.2(4.1)	16.0(16.2)	1.65
$[\{VO_2(L^1)\}_2]$	(2)	Yellow	75	32.3(32.1)	2.5(2.7)	21.3(21.4)	Dia
Hpyetsc (HL^2)		Yellow	80	51.8(51.9)	5.7(5.8)	26.6(26.9)	
$[VO(HL^2)(H_2O)(SO_4)]$	(3)	Pale green	75	27.7(27.8)	3.6(3.6)	14.2(14.4)	1.70
$[VO_2(L^2)]$	(4)	Yellow	60	37.0(37.2)	3.5(3.8)	19.1(19.3)	Dia
Hpyptsc(HL^3)		Pale yellow	85	61.0(60.9)	4.5(4.7)	21.7(21.9)	
$[VO(L^3)(acac)]$	(5)	Dark green	75	51.0(51.3)	4.0(4.3)	13.1(13.3)	1.67
$[VO_2(L^3)]$	(6)	Orange	65	46.0(46.2)	3.0(3.2)	16.3(16.6)	Dia

[a]**Dia = Diamagnetic**

which was filtered off, washed with hot MeCN, Et_2O and dried in vacuo over P_2O_5 (yield 85%).

The same reaction was carried out but in EtOH or MeOH solvent instead of MeCN, the comound **(4)** was also obtained but with smaller yields (45 - 50%).

Method 2

Complex **(4)** was prepared as described for **(2)** by replacing HL^2 for HL^1 (yield 85%).

[VO(L³)(acac)] (5)

Similar procedure for preparation of the complex **(1)** is used in which the ligand HL^3 (0.128 g, 0.5 mmol) replaces HL^1 (yield 65%).

cis-[$VO_2(L^3)$] (6)

This complex was prepared by following similar procedure (method 1) for complex **(4)** using the HL^3 (0.128 g, 0.5 mmol) instead of HL^2.

Catalytic oxidation by cis-[$VO_2(L^2)$] (4)

(1) H_2O_2 as co-oxidant

The oxidation of p-methoxybenzyl alcohol is typical. To a solution of the alcohol (10 mmol) in dichloroethane 10 cm^3, complex **(4)** (10^{-2} mmol) and aliquat 336(1mmol) were added. The mixture was heated to 70-80°C with stirring, then 30% H_2O_2 (3.5 cm^3, 30 mmol) were added dropwise at constant rate over 40 min. The reaction continued for further 80 min., then the reaction solution was extracted with CH_2Cl_2 (3×10 cm^3). The extracts were combined, dried over anhydrous Na_2SO_4 and evaporated to dryness. The aldehyde content was quantified as its 2,4-dinitro-

TABLE 2 : IR spectral data of thiosemicarbazone ligands and their vanadium complexes (cm^{-1})

Compound	$\nu(N^4\text{-}H)$	$\nu(N^2\text{-}H)$	$\nu(C{=}N^1)$	$\nu(C{=}S)$/ $\nu(C\text{-}S)$	$\nu(N\text{-}N)$	py(ip)[a]/ (op)	$\nu(V\text{-}N)$	Other bands	Assignments
Hpytsc (HL^1)	3435s 3260s	3160vs	1608s	820m -	1060s	620m 420m	-	-	-
$[VO(L^1)(acac)]$	3375s 3290s	-	1635s	- 802m	1022m	621m 410w	536m	937vs 1515vs 1376vs	$\nu(V{=}O)$ $\nu^{as}(C\cdots O)$ $\nu^{s}(C\cdots O)$
$[\{VO_2(HL^1)\}_2]$	3348m 3286m	-	1620s,b	700w	1061m 1030w	624m 425w	505w 462m	933vs 895s	$\nu^{as}(VO_2)$ $\nu^{s}(VO_2)$
Hpyetsc (HL^2)	3282s	3132m,b	1585s	802m	1058m	620m 403w	-	-	-
$[VO(HL^2)(H_2O)(SO_4)]$	3210m,b	2970s,b	1640sh 1595s	880m	1120s	650m 430m	480w	3400b 970s 1110sh, 520m	ν(O-H) $\nu(V{=}O)$ $\nu(SO_4)$ unidendate
cis-$[VO_2(L^2)]$	3259s	-	1610m 1574s	- 690m	1057m	635m 408w	482w	937vs 891s	$\nu^{as}(VO_2)$ $\nu^{s}(VO_2)$
Hpyptsc(HL^3)	3300s	3120s,b	1600vs	820m	1080s	620m 400w	-	-	-
$[VO(L^3)(acac)]$	3372m	-	1603vs	- 700w	1023m	640m 430w	480w	1515s 1395s 951vs	$\nu^{as}(C\cdots O)$ $\nu^{s}(C\cdots O)$ $\nu(V{=}O)$
cis-$[VO_2(L^3)]$	3370m 3215m,b	-	1607w 1591s	- 735w	1109m	630w 470w	500w	935vs 898s	$\nu^{as}(VO_2)$ $\nu^{s}(VO_2)$

[a]ip = in- plane bending, op = out-of plane bending

TABLE 3 : ^{1}HNMR data of ligands and their vanadium(V) complexes

Compound	HN(4)	HN(2)	H(C=N)	HC(6)	HC(5)	HC(4)	HC(3)	solvent	Other signals	Assignments
Hpytsc(HL^1)	8.18s 8.36s	11.64s	8.08s	8.55 d	7.38t	7.80t	8.35d	d_6-DMSO	-	-
$[\{VO_2(HL^1)\}_2]$ **(2)**	8.13s, 8.30s 7.97s, 7.90s -	-	8.47s(1H) 8.08s(1H) 8.45s(1H) 8.07s(1H)	8.60d (2H) 8.56m (2H)	7.57t(1H) 7.37t(1H) 7.57t(1H) 7.37t(1H)	7.81t(2H) 7.81t(2H)	8.27d(2H) 8.20d(2H)	d_6-DMSO d_6-DMSO /D_2O	-	-
Hpyetsc (HL^2)	8.66s	11.60s	8.09s	8.56d	7.36t	7.80t	8.25d	d_6-DMSO	3.63q(2H) 1.16t(3H)	$-CH_2$ $-CH_3$
cis-$[VO_2(L^2)]$ **(4)**	8.56s	-	8.09s	8.58d	7.58t	7.86d	8.24d	d_6-DMSO	3.37q(2H) 1.15t(3H)	$-CH_2$ $-CH_3$
Hpyptsc(HL^3)	10.23s	12.00s	8.20s	8.59d	7.24t	7.85t	8.44d	d_6-DMSO	7.56d (2H) 7.39t(3H)	Phenyl ring protons
cis-$[VO_2(L^3)]$ **(6)**	10.33s	-	8.88s	8.76d	7.17t	8.37t	8.03d	d_6-DMSO	7.80,d (2H) 7.40t, (3H)	Phenyl ring protons

TABLE 4 : UV-Vis spectral and cyclic voltammetric data for complexes

Compound	λ_{max} (ε, $M^{-1}cm^{-1}$)[a]	E_{pa}(V)	E_{pc}(V)	Solvent
$[VO(L^1)(acac)]$ **(1)**	290(22690), 340(20850), 420(23610), 600(215), 755(80)	+ 0.85		DMF
$[\{VO_2(HL^1)\}_2]$ **(2)**	305(21850), 337(15810), 438(23360)		- 0.8	MeCN
$[VO(HL^2)(H_2O)(SO_4)]$ **(3)**	270(9000), 310(21000), 420(2500), 678(40)	-[b]	-	DMF
$[VO_2(L^2)]$ **(4)**	306(9175), 438(12240)		- 0.39	MeCN
$[VO(L^3)(acac)]$ **(5)**	350(26190), 378(32570), 427(50530), 586(155), 748(60)	+ 0.77		MeCN
$[VO_2(L^3)]$ **(6)**	295(15730), 315(10810), 440(18078)		- 0.77	DMF

[a]In DMF solution [b]ill – defined peak

phenylhydrazone derivative.

(2) t-BuOOH as co-oxidant

To the alcohol (10 mmol), complex **(4)** (10^{-2} mmol) and) t-BuOOH (2.5 M) in dry benzene (25 mmol) were added. The mixture was stirred at RT for 2 h, then evaporated to dryness and extracted with Et_2O (3×20 cm^3). The extracts combined, evaporated and the al-

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dehyde product was quantified as above using 2,4-dinitrophenylhydrazone.

RESULTS AND DISCUSSION

Synthesis of complexes

Both analytical (TABLE 1) and spectroscopic data of IR and ^{1}HNMR (TABLE 2 and 3) are consistent with the structure of the ligands (Scheme 1a).

Preparation of oxo- and dioxovanadium complexes described in experimental section can be summarized in scheme 2.

In literature, similar oxovanadium complexes to that of $[VO(HL^2)(SO_4)(H_2O)]$ **(3)** (HL^2 = Hpetsc) for the ligands Hptsc (HL^1) and Hpptsc (HL^3) have been prepared under our similar conditions[15]. The complexes [VO(L)(acac)] **(A)** and cis-$[VO_2(L)]$ **(B)** (L = monoanions of 2-acetylpyridine thiosemicarbazones or its derivatives N(4)-methyl/phenyl thiosemicarbazone had been synthesized from the reaction of the ligands HL and $[VO(acac)_2]$ in MeCN at RT for a time of 15 min. and 5 days for the complexes **(A)** and **(B)**, respectively[16]. Our attempts to prepare analogue complex of **(B)** with the ligand Hptsc (HL^1) was unsuccessful under these reported conditions[16]. Reaction of $[VO(acac)_2]$ with HL^1 ligand in presence of Et_3N in MeOH and reflux gave only a very little brown precipitate of unidentified product.

Similar cis-dioxovanadium complexes to those of ours cis-$[VO_2(L^2/L^3)]$ **(4)** and **(6)** had also been obtained from the reaction of $[VO(acac)_2]$ and the ligands, 5-methyl-3-formyl pyrazol-N**(4)**-methyl/ethyl/dimethyl thiosemicarbazone in reflux (3 h) and standing the solutions at RT for a few dayes[17]. Other relavant oxo- and dioxovanadium complexes [VO(NNO)(acac)] and cis-$[VO_2(NNO)]$ [NNO = monoanion of N,N,O- tridentate donor ligand(-1)] had been isolated after reaction of the ligand, HNNO with $[VO(acac)_2]$ or KVO_3 in MeOH[18].

Reaction of equimolecular amounts of $[VO(acac)_2]$ and the ligand Hpptsc (HL^3) in refluxing MeCN yields [VO(pptsc)(acac)] **(5)**, but we could not isolate the analogue complex with Hpetsc (HL^2) ligand under these conditions. Here, as in the complexes **(4)** and **(6)**, the ligands HL^2 and HL^3 reacts out of its enolic toutomeric form (scheme 1b), i.e in N,N,S (-1) mode. On aerial oxidation in MeCN or MeOH the dioxovanadium(V) complexes cis-$[VO_2(L^2/L^3)]$ are obtained, a reaction which requires water. The intermediate green complexes $[VO(L^1/L^3)(acac)]$ **(1)** and **(5)** could be isolated from MeCN prior to aeration. Equations **(1)** and **(2)** represent the synthetic procedures as have been suggested for similar related complexes[18].

TABLE 5 : Catalytic oxidation of alcohols by cis- $[VO_2L^2]$ (4)

Substrate	prouduct[a]	H_2O_2 time (h)	Turnover[b]	t-BuOOH Time (h)	Turnover[b]
Benzyl alcohol	A	2	250	2.5	120
p-Methoxybenzyl alcohol	A	2	500	2.5	300
Cyclohexanol	K	2	220	3	160

[a]**A = corresponding aldehyde, K = corresponding ketone.**
[b]**Turnover = moles of product / moles of catalyst**

The dimmer dioxovanadium complex $[\{VO_2(ptsc)\}_2]$ **(2)** formed from reactions of NH_4VO_3 and the ligand Hptsc (HL^1) in reflux EtOH, is tentatively suggested to be obtained according equation **(3)**, supporting our observation for evolution of NH_3 during the reaction.

Analytical data of the complexes (TABLE 1) are in a good agreement with their composition. The solid complexes are air stable and partially soluble in MeCN but soluble in DMF and DMSO in which the molar conductivities of these complexes are non-electrolytes, as expected.

Magnetic properties and EPR spectra

Magnetic susceptibility measurements of the solid complexes were studied at room temperature. Complexes **(1)**, **(3)** and **(5)** are paramagnetic corresponding to one electron unpaired ($3d^1$) with values of μ_{eff} 1.65 - 1.70 BM, close to the spin-only value (1.73 BM) for one unpaired electron[19]. The other vanadium complexes **(2)**, **(4)** and **(6)** were found to be diamagnetic and are silent EPR which is consistent with the oxidation state of +5 ($3d^0$) for the vanadium centers[20].

The room temperature X-band EPR spectrum of the representative complex $[VO(L^1)(acac)]$ **(1)** was recorded for a powdered sample (Figure 1). Only one line is observed with g value = 1.96 (less than g_e of the free electron, g_e = 2.0023). This is similar to many other ESR spectra of powdered oxovanadium(IV) complexes[16,21,22], suggesting that the packing in solid state is accompanied by magnetic exchange interaction be-

tween neighbour molecules. This phenomenon is very known in Cu(II) amino acids peptides and other molecules compounds[23-27].

Infra red spectra

Selected diagnostic bands of the solid infrared spectra of the ligands and their complexes are shown in (TABLE 2) the IR spectra of the ligands exhibit a sharp bands at 3435, 3282 and 3300 cm^{-1} for HL^1, HL^2 and HL^3 ligands, respectively, assignable to v(N-H) of the terminal amino derivatives. These bands remain more or less unaltered in all complexes, implying the non-participation of the terminal nitrogen in coordination as similarly found for the complexes $[VO(L^1)X_2]$ (X = Cl, Br, ClO_4)[15]. The absence of $v(^2N\text{-}H)$ band is suggestive of deprotonation of a hydazinic $-N^2H$ proton in complexes via thioenolate form (Scheme 1b)[28,29]. The vibrations attributed to v(C=C) + v(C=N) at 1585-1608 cm^{-1} for the free thiosemicarbazone ligands are shifted to higher wave numbers in the corresponding complexes indicating the involvement of the azomethine nitrogen in complexation as similarly observed in Zn(II) thiosemicarbazone complexes[30]. The shift of the v(N-N) band in the IR spectra of the complexes compared to that in the ligand is a confirmation of the coordination through the azomethine nitrogen atom[31,32]. The spectra of the free ligands shows the thioamide bands which possesses a considerable contribution from v(C=S) near 800 cm^{-1}, these bands are shifted to lower energy at (690-733 cm^{-1}) on coordination of thiolate form[33-35]. with the appearance of new bands due to $v(^3C{=}N^2)$[36]. The oxovanadium complexes exhibit a strong v(V=O) mode in 940-970 cm^{-1} region. Two strong absorption bands in 900-940 cm^{-1} region corresponding to the anti-symmetric and symmetric stretching modes for the dioxovanadium complexes[35-37]. The lowering of $v^s(VO_2)$ is possibly due to the involvement of one of the oxygens in hydrogen bonding with other groups present in the complexes[35]. The out-of-plane and in-plane bending vibrations of the pyridine ring in the uncomplexed ligands near 405 and 620 cm^{-1} are shifted to higher frequencies on complexation, confirming the coordination of the ligands to the metal via the pyridine nitrogen as similarly observed in the copper(II) thiosemicarbazone complexes[38]. There are two absorption bands at 1515 and near 1385 cm^{-1} for the spectra of the complexes **(1)** and **(5)**, corresponding to $v^{as}(C\cdots O)$ and $v^s(C\cdots O)$ modes of acetylacetonate moiety. The bands at 1110 and 520 cm^{-1} are due to coordinated unidentate sulphate group[39]. The bands in 460-536 cm^{-1} can be attributed to v(V-N) modes while those for v(V-S) are expected below 400 cm^{-1}[10,31].

^{1}H NMR spectra

The ^{1}H NMR spectra of $[\{VO_2(ptsc)\}_2]$ **(2)**, cis-$[VO_2(petsc)]$ **(4)** and cis-$[VO_2(pptsc)]$ **(6)** in $(CD_3)_2SO$ solution are listed in TABLE 3 (Scheme 1a for atom numbering). The ^{1}H NMR spectra of the ligands shows N-**(2)**-H resonance at a downfield chemical shift near δ 11.6 ppm for ligands HL^1(Hptsc) and HL^2 (Hpetsc), and at δ 12.0 ppm for HL^3 (Hpptsc) ligand, indicating that this proton is involved in an intra- or inter-molecular hydrogen bond[30]. This N-**(2)**-H resonance is absent in the spectra of complexes according to deprotonation and formation of a thiol form. The resonance of pyridine ring hydrogen atoms in the complexes display resonances for the hydrogen protons at down or up field compared to that of the ligand itself. These show that N-pyridine atom involves in coordination by vanadium ion, similar to those found for cis-$[VO_2(L)]$ (HL = 2-acetylpyridine-N-**(4)**-methylphenylthiosemicarbazone)[16]. A down-field shift for the azomethine H(C^7=N) proton is observed in the complexes **(2)** and **(6)** which is attributed to participation of the azomethine nitrogen in coordination[16]. In complex **(4)** there is no change in the resonance of H-(C^7=N) proton, indicating non – involvement of azomethine nitrogen in bonding, the thioamide N^2-nitrogen unusually involve in bonding with vanadium ion, as in case of the complex cis-$[VO_2(L)]$ (L = monoanion of 5-methyl-3-pyrazole-N-**(4)**-methyl thiosemicarb- azone) which is characterized by the X-ray crystal structure[17].

The ^{1}H NMR spectrum of the dimeric complex $[\{VO_2(ptsc)\}]$ **(2)** in $(CD_3)_2SO$ (data listed in TABLE 3) showed resonances for fourteen protons, as expected; four broad singlets which disappeared using $(CD_3)_2SO$ / D_2O solvent, attributable to four non-equivalent protons of two terminal H_2N-**(4)** protons. A pair of non-equivalent two proton resonances for each of H(C^7=N) and H-C-**(5)** protons. The remaining six protons in pyridine rings H-C-**(3)**, H-C-**(4)** and H-C-**(6)** show resonance corresponding to a pair of protons

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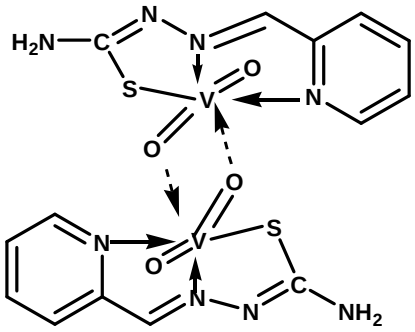
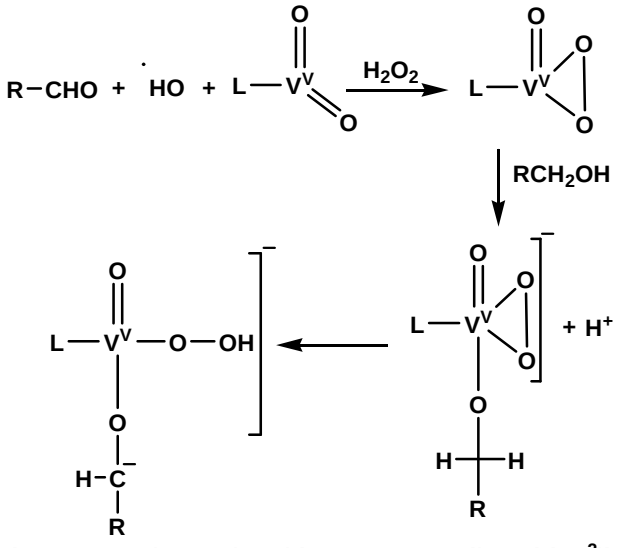


Scheme 3 : Suggested structure for the dinuclear complex (2)



(L = monoanion of the tridentate Hpetsc ligand (HL^2))

Scheme 4

for each in the complex **(2)**.

The non-equivalent protons in our dimmer complex [{VO_2(ptsc)}$_2$] **(2)** are expected due to a net of intermolecular hydrogen bonds. **(4)**-N-H···O=V, **(4)**-N-H….N-**(2)**, pyridine-C-H….O=V and probable **(1)**-N=C-H….O=V, as has been found by X-ray crystal structure for the monomer complexes cis-[VO_2(aptsc)] (Haptsc = 2-acetylpyridine thiosemicarbazone)[16] and cis-[VO_2(L/)] [L/ = N,N,O-tridentate donor ligand (-1)][37]. Our attempts to get suitable crystals from complex **(2)** for X-ray study were unsuccessful, however on the basis of analytical, spectroscopic data (IR and ^{1}H NMR), the suggested structure of the complex **(2)** can be formulated as below. Each vanadium ion is in a distorted octahedral N_2SO_3 coordination sphere as the dinuclear molecule **(2)** resembles two edge-shared octahedra. The complex provides a rare example of a di(μ-oxo)-bridged divanadium(V) species formed by dimerization of a dioxovanadium complex with tridentate ligand[40-43].

Electronic spectra

The electronic spectra of complexes were recorded in DMF and their results are summarized in TABLE 4. The spectra of complexes **(1)**, **(3)** and **(5)** show low intensity (ε, 40-215 $M^{-1}cm^{-1}$) ligand field transitions, characteristic of square pyramidal oxovanadium(IV) complexes[20,44,45]. On the basis of Balhausen and Gray model[46] the observed bands around 750 and 600 nm are due to $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz}, d_{yz})$ and $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x^2-y^2})$ transitions, respectively. While the expected third band of low intensity due to $^2B_2(d_{xz}) \rightarrow {}^2A_1(d_{z^2})$ may be obscured by charge-transfer band (LMCT) around 420 nm (ε, 2500-50530 $M^{-1}cm^{-1}$). The other high intensity bands around 350 nm are assigned to LMCT while the bands near 310 nm is due to intra-ligand ($\pi \rightarrow \pi^*$) transition[47].

The spectra of vanadium(V) complexes **(2)**, **(4)** and **(6)** (have a $3d^0$ configuration) showed no d-d transitions, as expected. The intense bands below 450 nm are similarly attributed to LMCT and intra-ligand transitions as those found above for vanadium(IV) complexes[36].

Redox properties

The electron transfer properties of oxovanadium(IV) and dioxovanadium(V) complexes were studied by cyclic voltammetry. Voltammetric data versus a silver electrode for DMF or MeCN solution of the complexes (10^{-3} M) in the presence of 0.1 M $(Bu^n_4N)PF_6$ as a supporting electrolyte are shown in TABLE 4 and figure 2 as a representative example, the $E_{1/2}$ for the ferrocene /ferrocinium (Fe/Fe^+) couple under the experimental conditions was 0.39 V (ΔE = 70 mV)[48]. The voltammograms of [$VO(L^1)$(acac)] **(1)** and [$VO(L^3)$(acac)] **(5)** show an irreversible oxidation peak near +0.80 V, attributed to V^{IV}/V^V oxidation as that observed for similar oxovanadium(IV) complexes[16,40]. The dimmer complex [{VO_2(ptsc)}$_2$] **(2)**, displays a broad reduction peak centered at - 0.8 V corresponding to V^V/V^{IV} reduction, similar to those found for di(μ-oxo)-bridged divanadium(V) complexes[40,43]. For cis-dioxovanadium(V) complexes **(4)** and **(6)**, also an irreversible reduction peak at - 0.39 and - 0.77 V were found, respectively, due to V^V/V^{IV} reduction as simi-

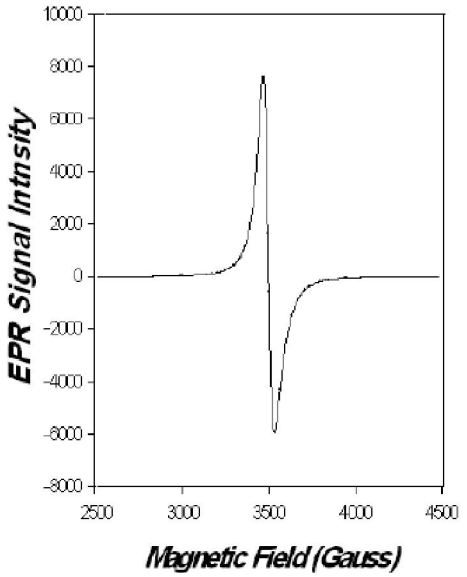


Figure 1 : ESR spectrum (X-band) for powdered [VO(L^1)(acac)] (1) at room temperature

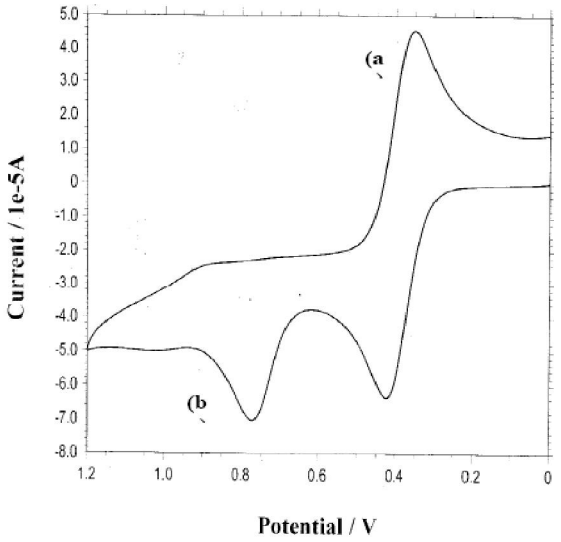


Figure 2 : Cyclic voltammogram in MeCN with 0.1 M (Bu^n_4N)PF_6, scan rate 50 mVS^{-1} for; (a) $[Fe(C_5H_5)_2]^{0/+}$, (b) ~ 10^{-3} M [VO(L^3)(acac)] (5)

larly observed for cis-dioxovanadium(V) complexes[17].

Catalytic oxidation

As a consequence of low radius/charge ratio of vanadium(V) centers, they are usually strong lewis acids, which makes them suitable for the activation of peroxidic reagents[49]. Accordingly, vanadium(V) complexes have been found to act as catalyst precursors in various oxidation reactions like epoxidation of alkenes and allylic alcohols, oxidations of sulphides to sulphoxides and sulphones, hydroxylations of alkanes and arenes, and oxidations of alcohols[50].

In the present work we have used cis-dioxovanadium(V) complex, cis-[$VO_2(L^2)$]**(4)** as a catalyst for selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, in the presence of hydrogen peroxide (H_2O_2) or t-butylhydroperoxide (t-BuOOH) as co-oxidants (TABLE 5). Slow dropwise addition of 30% H_2O_2 over 0.5 h to dichloroethane solution containing the vanadium catalyst **(4)** and aliquat 336 (as a phase transfere catalyst) at 75°C with stirring for 2 h, p-methoxybenzyl alcohol was oxidized selectively to the corresponding aldehyde and high turnover was obtained (ca 500), while half turnover (~250) found for benzyl alcohol similar to that found $RuCl_3/H_2O_2$ system[51]. Cyclohexanol was also oxidized to to cyclohexanone with turnover (220) higher than that for ruthenium(III)-bipyridine complexes under the same conditions[12]. No oxidation products were obtained in the absence of Aliquat 336, suggesting that the phase transfere catalyst brings both the vanadium catalyst and H_2O_2 into the organic layer where reaction occurs. Using t- BuOOH (2.5 M) in dry benzene as co-oxidant instead of H_2O_2 and without the phase transfer catalyst, the oxidations were carried out at room temperature. Primary alcohols were oxidized to the corresponding aldehydes and secondary alcohol to ketone with high turnovers (120-300) as shown in TABLE 5. Under similar reaction conditions carried out above for alcohol oxidations we have observed that ruthenium(II/III) bipyridine complexes[11,12] gave similar product yields and turnovers where it was suggested the oxoruthenium species of higher oxidation states (IV or VI) are the active intermediates responsible for the catalytic oxidations in the presence of t-BuOOH or H_2O_2 as co-oxidants[11,12,52,53].

In the presence of excess peroxide, oxovanadium(IV) and cis-dioxovanadium(V) complexes are converted to oxoperoxovanadium(V) complexes[32,50,54]. We suggest that oxidation by our cis-dioxovanadium(V) catalyst cis-[VO_2L^2] **(4)** in the presence of H_2O_2 or t-BuOOH as co-oxidants proceeds via the oxoperoxovanadium intermediate in which V(V)/V(IV) species occur. Vanadium monoperoxo complex can function as a 'catalytic pump' for the generation of hydroxyl radicals[55]. These are very reactive and strong oxidants species and promote other radical chains, e.g. by abstracting an H atom from an organic substrate[56]. The

mechanism for the catalytic oxidation of alcohol by the present cis-dioxo vanadium(V) catalyst **(4)** in the presence of excess peroxide e.g. H_2O_2 can be suggested[50] as follows below.

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