Synthesis, characterization, *ab initio* calculations, thermal behaviour and thermodynamics of some oxovanadium(IV) complexes involving O,O- and *N,N*-donor moieties

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Abstract. Some oxovanadium(IV) complexes, namely *bis*(1,1,1-trifluro-2,4-pentanedionato-*O,O'*) oxovanadium (IV), [VO(tfac)$_2$(H$_2$O)], *bis*(1-phenyl-2,4-pentanedionato-*O,O'*)oxovanadium(IV), [VO (phac)$_2$(H$_2$O)], *bis*(1,3-diphenyl-2,4-pentanedionato-*O,O'*)oxovanadium(IV), [VO(dphac)$_2$ (H$_2$O)], of the type [VO(O$_4$)] and *bis*(pyrolidineaniline)oxovanadium(IV), [VO(pyran)$_2$(H$_2$O)], *bis*(*p*-hydroxy-pyrolidineaniline)oxovanadium(IV), [VO(*p*-hydroxypyran)$_2$(H$_2$O)], *bis*(*p*-methoxypyrolidineaniline) oxovanadium(IV), [VO(*p*-MeOpyran)$_2$ (H$_2$O)], *bis*(*p*-chloropyrolidineaniline)oxovanadium(IV), [VO(*p*-chloropyran)$_2$(H$_2$O)], *bis*(*p*-bromopyrolidineaniline)oxovanadium(IV), [VO(*p*-bromopyran)$_2$(H$_2$O)], *bis* (*p*-cyano pyrolidineaniline)oxovanadium(IV), [VO(*p*-cyanopyran)$_2$(H$_2$O)], and *bis*(pyrolidinebenzyl-amine)oxovanadium(IV), [VO(pyrbz)$_2$(H$_2$O)], of the type [VO(N$_4$)] were synthesized and characterized by IR, UV−Vis, mass spectrometry, elemental analysis, magnetic moment and thermogravimetry in order to evaluate their thermal stability and thermal decomposition pathways. The number of steps and, in particular, the starting temperature of decomposition of these complexes depends on the equatorial ligand. Also, formation constants of the complexes have been determined by UV-Vis absorption spectroscopy through titration of the ligands with the metal ions at constant ionic strength (0·1 M NaClO$_4$) and at 25°C. According to the thermodynamic studies, as the steric character of the ligand increases, the complexation tendency to VO(IV) center decreases. Also, the *ab initio* calculations were carried out to determine the structural and the geometrical properties of the complexes.

Keywords. Oxovanadium(IV); formation constants; thermodynamic; *ab initio* calculations.

1. Introduction

In recent years, vanadium chemistry has attracted attention due to its interesting structural features and biological relevance.[1–7] Vanadium oxide (vanadyl) complexes, in particular, have come under close scrutiny because of their utility as insulin mimetics.[2] Peroxovanadium complexes[8–12] and *bis*-(maltolato) oxovanadium(IV)[13,14] (VO(malto)$_2$) have been found to be more effective than the simple vanadium(IV) and -(V) salts, both in cell cultures and in animal studies. Furthermore, a bis(maltolato)oxovanadium (IV) derivative (KP-102) has now entered phase I clinical trials in humans. A related compound, *bis*(2,4-pentanedionato-*O,O'*)oxovanadium(IV) (VO (acac)$_2$) was also found to have insulin-mimetic

properties superior to those of VOSO$_4$ in cell culture studies.[15]

Since the first published account of the synthesis of VO(acac)$_2$ in 1914,[16] the complex has been used extensively as a reagent in organic synthesis.[17–19] The physical properties of VO(acac)$_2$ have been examined by numerous workers,[20–22] and the crystal structure was published in 1962.[23] In the solid state, VO(acac)$_2$-type complexes are five-coordinate; however, upon dissolution in organic solvents, the vanadium coordinates a donor ligand in the vacant site, generating products expressed as [VO(acac)$_2$L] (where L = coordinated ligand and acac is 2,4-pentanedionato or corresponding acac- derivatives).

In view of importance of vanadium compounds, and also extending the search for more efficacious compounds, this study is undertaken of the synthesis and coordination chemistry of some oxovana-

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dium(IV) complexes of the type $[VO(O_4)]$ and $[VO(N_4)]$ involving some diketone and some pyrrolecarbaldehyde derivatives.

The resulting complexes have been characterized on the basis of elemental analysis (C, H, N), infrared, mass and electronic spectral techniques. Thermal stability is an important feature of the complexes in their potential applications as catalysts, so the differences observed in the thermal behaviour of $[VO(O_4)]$-type complexes is described by using thermogravimetry (TG). Also the formation constants of the complexes were determined spectrophotometrically at 25°C in methanol.

In addition to the importance of the experimental studies, it is crucial to investigate the theoretical behaviour of target complexes to find their structural characteristics and the way that these structures affect the other properties of the complexes. The structure of a complex can be studied by the *ab initio* methods to find the stable structure electronically by solving the wave function of the molecule. The theoretical goal of this study focuses on these features of the chemistry.

2. Experimental

2.1 Reagents

Diketones, aniline and its derivatives were purchased from Aldrich and were used as received. All other solvents and reagents with analytical grade (PA) were obtained commercially and used without further purification.

2.2 Physical measurements

All of the scanning UV-Vis spectra were recorded on Perkin-Elmer Lambda 2 spectrophotometer. FT–IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. Mass spectra were obtained with Shimadzu LCMS–2010EV. The Elemental analysis was carried out by Thermo Finnigan-Flash-1200. The NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer.

2.3 Preparation of the vanadyl complexes

2.3a *[VO(O₄)]-type:* $[VO(dphac)_2(H_2O)]$, $[VO(phac)_2(H_2O)]$, $[VO(tfac)_2(H_2O)]$, were prepared by the same general procedure.[24] Vanadyl sulphate tri-

hydrate (0·163 g, 1 mmol) was dissolved in 10 ml 10% H_2SO_4. Then diketone was dissolved in 10 ml methanol and added. The resulting solution was pH adjusted with 10% sodium bicarbonate solution to pH 4·0. A green precipitate began to form and was collected by filtration. These materials were purified by dissolving the complexes in chloroform, as neither the vanadyl hydroxide nor sodium bicarbonate is soluble in this solvent. The solid compound was obtained by evaporation of the solvent to dryness. Structural representations of the complexes with their abbreviations are given in figure 1.

2.3b *[VO(N₄)]-type:* 1 mmol of pyrrol-2-carbaldehyde was mixed with 10 ml of ethanol and then added to the ethanolic solution of 1 mmol aniline derivatives (1 M), magnetically stirred with the addition of 2 to 3 drops of concentrated triethylamine, refluxed for 2 h and left overnight at room temperature. The solid product formed was filtered, washed with ethanol and ether consecutively. It was dried at room temperature and recrystallized with hot ethanol to give the required Schiff base. Table 1 shows the analytical data of the prepared compounds.

2.3c *Synthesis of the Schiff base complexes:* To a 2 mmol *p*-pyrolidineaniline in 10 ml of ethanol was added 1 mmol of $VOSO_4 \cdot 5H_2O$ in 10 ml of water, when coloured solid precipitated immediately. After refluxing the mixture for approximately 1 h, the solid mass was filtered by suction and repeatedly washed with 1 : 1 ethanol–water mixture and dried in vacuum.

2.4 Computational details

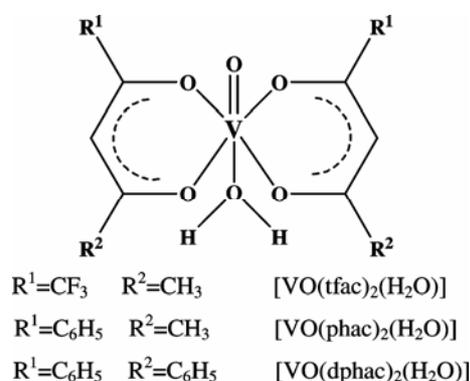The relative stability and molecular properties of the structures under investigation were determined by

$R^1 = CF_3$	$R^2 = CH_3$	$[VO(tfac)_2(H_2O)]$
$R^1 = C_6H_5$	$R^2 = CH_3$	$[VO(phac)_2(H_2O)]$
$R^1 = C_6H_5$	$R^2 = C_6H_5$	$[VO(dphac)_2(H_2O)]$

Figure 1. The structural representations of the complexes of $VO(O_4)$ type.
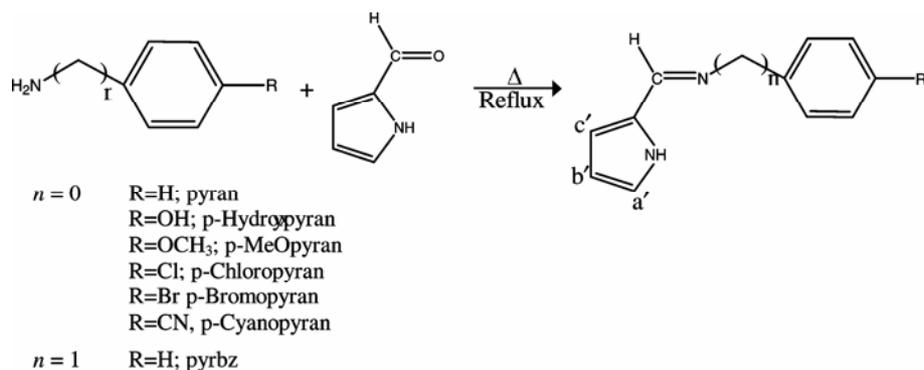
Figure 2. The structural representations of the pyrolidineaniline ligands.

Table 1. Physicoanalytical properties.

Compound	m.p. (°C)	Colour	Yield %
[VO(tfac)$_2$(H$_2$O)]	230	Green	55
[VO(phac)$_2$(H$_2$O)]	220	Green	52
[VO(dphac)$_2$(H$_2$O)]	250	Green	58
Pyran	98	Pale brown	61
p-Hydroxypyran	192	Brownish-yellow	61
p-MeOpyran	98	Pale-brown	65
p-Chloropyran	95	Pale-brown	71
p-Bromopyran	82	Brown	60
p-Cyanopyran	110	Pale-brown	67
Pyrbz	105	Brown	63
[VO(pyran)$_2$(H$_2$O)]	>250	Olive-green	58
[VO(*p*-Hydroxypyran)$_2$(H$_2$O)]	>250	Green	50
[VO(*p*-MeOpyran)$_2$(H$_2$O)]	>250	Green	55
[VO(*p*-Chloropyran)$_2$(H$_2$O)]	>250	Green	58
[VO(*p*-Bromopyran)$_2$(H$_2$O)]	>250	Brownish-green	52
[VO(*p*-Cyanopyran)$_2$(H$_2$O)]	>250	Green	48
[VO(pyrbz)$_2$(H$_2$O)]	>250	Brownish-green	60

molecular mechanics and Hartree–Fock (HF) quantum methods. The standard 6–311g basis set was used in conjunction with the HF method. All the calculations were performed by using GAUSSIAN03 program package.[25]

Optimized geometries and relative stabilities of three conformers of gaseous [VO(phac)$_2$(H$_2$O)] and two conformers of [VO(pyran)$_2$(H$_2$O)] have been determined at MM//HF/6-311g level of theory. The atomic charges in addition to the structural analyses have been employed to interpret the difference among the conformers of the electronic structure and the origin of their relative stabilities. The results of the structural calculations have been used in order to compute the quantitative structure activity relationships (QSAR)[26,27] properties involving Van der Waals and solvent-accessible surface areas,[28]

hydration energy,[29] solvent-accessible surface-bounded molecular volume, log P (the log of the complex-water partition coefficient),[30] a measure of hydrophobicity, molar refractivity[30,31] and polarizability.

Quantitative structure activity relationships (QSAR) are attempts to correlate molecular structure, or properties derived from molecular structure, with a particular kind of chemical or biochemical activity. The kind of activity is a function of the interest of the user: QSAR is widely used in pharmaceutical, environmental, and agricultural chemistry in the search for particular properties. The molecular properties used in the correlations relate as directly as possible to the key physical or chemical processes taking place in the target activity.

Table 2. UV-Vis[a], mass spectral, elemental analysis and magnetic moments data of the compounds.

Compounds	λ_{max} (nm)	Mass spectra (m/z)	Elemental analysis (%, Found)			M_{eff} B.M. (298 K)
			C	H	N	
[VO(tfac)$_2$(H$_2$O)]^a	296	373, 218, 150	30·71 (30·60)	2·58 (2·21)		1·65
[VO(phac)$_2$(H$_2$O)]^a	326	389, 228, 161	58·98 (59·36)	4·95 (4·57)		1·68
[VO(dphac)$_2$(H$_2$O)]^a	356	513, 289, 223	67·80 (67·88)	4·55 (4·39)		1·66
pyran^b	320	170	71·91 (72·10)	6·31 (6·02)	15·25 (15·65)	
p-Hydroxypyran^b	295 (*sh*), 335	187, 170	70·27 (70·39)	5·47 (5·50)	14·90 (14·70)	
p-MeOpyran^b	297 (*sh*), 332	200, 170	71·98 (71·82)	6·04 (6·04)	13·99 (13·97)	
p-Chloropyran^b	326	204, 170	62·36 (62·10)	4·66 (4·32)	13·22 (12·88)	
p-Bromopyran^b	271, 343	249, 170	73·15 (72·81)	4·71 (5·01)	21·33 (21·10)	
p-Cyanopyran^b	326	195, 170	70·57 (70·68)	4·94 (5·08)	20·57 (21·11)	
pyrbz^b	280	184	74·58 (74·65)	6·78 (7·01)	14·50 (14·10)	
[VO(pyran)$_2$(H$_2$O)].0.25H$_2$O^b	237, 364	405,236,169	61·76 (61·44)	4·83 (4·52)	13·09 (13·33)	1·65
[VO(p-Hydroxypyran)$_2$(H$_2$O)]^b	300, 380	437 ,252, 186	58·03 (58·10)	4·43 (4·60)	12·30 (12·26)	1·67
[VO(p-MeOpyran)$_2$(H$_2$O)]^b	381	465, 265, 200	59·63 (59·95)	5·00 (5·04)	11·59 (11·31)	1·63
[VO(p-Chloropyran)$_2$(H$_2$O)]^b	243, 370	473, 268, 204	53·68 (53·85)	3·69 (4·10)	11·38 (11·46)	1·70
[VO(p-Bromopyran)$_2$(H$_2$O)]^b	211, 271	560, 314, 247	45·47 (45·12)	3·12 (3·12)	9·64 (9·46)	1·69
[VO(p-Cyanopyran)$_2$(H$_2$O)]^b	242, 371	455, 261, 194	60·89 (60·82)	3·83 (3·98)	17·75 (17·88)	1·66
[VO(pyrbz)$_2$(H$_2$O)]0·5H$_2$O^b	240, 326	433, 250, 183	62·61 (62·22)	5·47 (5·80)	12·17 (12·48)	1·64

^{a}Solvent is CH$_3$OH. ^{b}Solvent is CH$_3$CN

3. Results and discussion

3.1 *Characterization of the compounds*

The compounds were synthesized and characterized by ^{1}HNMR, IR, magnetic moment, mass, UV-Vis spectroscopy and elemental analysis.

3.1a *Magnetic moments and electronic spectra:* The effective magnetic moment was measured using a Gouy balance. Data were corrected for diamagnetic contributions using the Pascal's constants.[32] Oxovanadium(1V) complexes show magnetic moment values in the range of 1·64–1·70 BM, which are in accordance with the values reported for oxovanadium(IV) complexes with one unpaired electron[33] (table 2) indicating that the complexes are monomeric. This is in agreement with the ν(V=O) obtained.

The ligands show two absorption bands at UV-Visible region. A $n - \pi^*$ transition band at 326–410 nm and a $\pi-\pi^*$ transition band at 240–297 nm are shown in the ligands. These absorption bands show a slight shift to higher energy in the complexes that is evident for unalteration structure of ligands in complexation (table 2).

All the vanadyl(IV) complexes have a band at 340–470 nm in solvent corresponding to a *d–d* transition band. This band is not always observed, being often buried beneath a high intensity charge transfer band (or more accurately the low energy tail of that band), and when it is observed it is generally a shoulder (table 2). UV–Vis spectra of pyrbz and its oxovanadium(IV) are shown in figure S1.

3.1b *Mass spectra:* The mass spectra of the ligands show intense molecular ion peaks m/z $M^+/(M + H)^+$ (table 2). The mass spectra of the vanadium(IV) chelates show intense peaks including [VOL$_2$] and [VOL$_2$ + H]$^+$ that confirmed a structure of stoichiometry of 2 : 1 for ligands to vanadium(IV). The spectra of the vanadyl(IV) complexes, also show some peaks corresponding to [VOL]$^+$ and L$^+$ fragments (table 2).

3.1c *Infrared spectra:* The solid state properties of the ligands and the vanadyl complexes were examined by infrared spectroscopy. For each of these compounds, the characteristic ν(V=O) stretching at 920–995 cm^{-1} was observed, as reported for other oxovanadium(IV) derivatives[34] and is not present in the spectrum of the free ligands (table S1).

IR spectra of the ligand (table S1) showed the absence of bands at ~ 1735 and 3315 cm^{-1} due to the carbonyl ν(C=O) and ν(NH$_2$) stretching vibrations and a strong new band appeared at 1612–1633 cm^{-1} assigned to azomethine ν(HC=N) linkage, showing that amino and aldehyde moieties of the starting

Table 3. ^{1}HNMR spectroscopic data of the compounds (δ in ppm).

Compounds	Pyrrol-H	H–C=N	Ar–H	–CH$_2$–	OH	CH$_3$
Pyran[a]	6·3[b'] 6·6[a'] 6·8[c']	8·59	6·93–7·93			
p-Hydroxypyran[b]	6·1[b'] 6·5[a'] 6·7[c']	8·26	6·69–7·05		11·7	
p-MeOpyran[a]	6·3[b'] 6·7[a'] 6·9[c']	8·3	6·9–7·5			3·8
p-Chloropyran[a]	6·3[b'] 6·7[a'] 6·9[c']	8·2	6·9–7·3			
p-Bromopyran[a]	6·4[b'] 6·8[a'] 7·1[c']	8·2	7·2–7·6			
p-Cyanopyran[b]	6·1[b'] 6·2[a'] 6·7[c']	9·4	6·5–7·3			
pyrbz[a]	6·1[b'] 6·4[a'] 6·7[c']	8·1	7·0–7·2	4·64		

^{a}Solvent is CDCl$_3$. ^{b}Solvent is DMSO-d_6

material are absent and have been converted into the ligand, i.e. *p*-pyrrolidineaniline.

The comparison of IR spectra of the ligand and its vanadyl complexes indicated that the ligand is principally coordinated to the metal ion in 2 ways, thus acting as a bidentate ligand. The band appearing at ~ 1630 cm^{-1} due to azomethine was shifted to a lower frequency by ~ 1–15 cm^{-1} in both complexes, indicating participation of azomethine nitrogen in the interaction with the metal ion. The band appearing at 3153–3300 cm^{-1} assigned to the ν(NH) in the ligand was no longer found in the spectra of the metal complexes indicating deprotonation and coordination of the nitrogen with the metal ion.

3.1d *^{1}HNMR spectra:* ^{1}H NMR spectral data of pyrrolidineaniline ligands show a singlet (1H) signal at $\delta = 10 \cdot 5$–12 ppm which can be assigned to the N–H of the pyrrol rings. The pyrrol ring proton signals resolved into three groups in the range $\delta = 6 \cdot 2$–7·4 ppm as a triplet and doublet that are related to the protons in position b and (a, c). The signals of the hydrogen of the phenyl group are appeared at $\delta = 6 \cdot 6$–8 ppm. A singlet signal at $\delta = 3 \cdot 8$ ppm is assigned to those compounds that have OMe group. The ^{1}HNMR spectra of the ligands provide compel-

ling evidence of the presence of one azomethine proton group at $\sim 8 \cdot 0$ ppm.

3.2 *Geometry and energy*

The theoretical calculation mainly focuses on the geometries and the relative stability of the possible conformers of [VO(pyran)$_2$(H$_2$O)] and [VO(phac)$_2$(H$_2$O)]. The results of the methods conventionally assumed to explain the relative stability of the complexes. All calculations have been consistent in predicting that the conformer *cis* is more stable than the *trans* one in [VO(pyran)$_2$(H$_2$O)] complex while the most stable form among all the supposed structures for [VO(phac)$_2$(H$_2$O)] is the *trans* conformer. We have proposed two conformers for the *trans*, the first one is a conformer with the phenyl groups in the *trans* position and the other one is that the oxygen atoms connected to the vanadium are in the *trans* position.

The results of the computation reported in table S2 demonstrates the HF energy for each complex in atomic units. The energy difference is 13·6261 eV for the conformers of the [VO(pyran)$_2$(H$_2$O)] complex. This energy difference value in the conformers
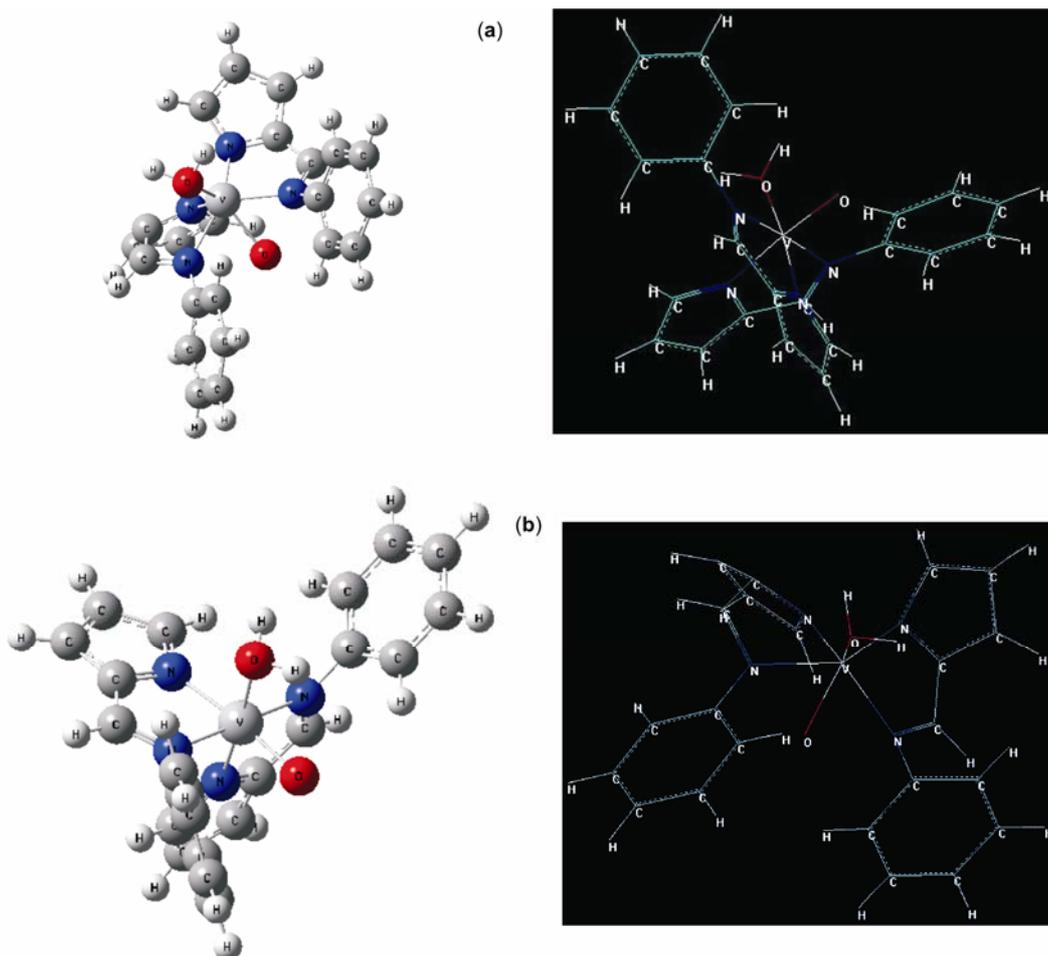
Figure 3. The structure of the (**a**) *cis*-[VO(pyran)$_2$(H$_2$O)] complex and (**b**) *trans*-[VO(pyran)$_2$(H$_2$O)] complex.

of the [VO(phac)$_2$(H$_2$O)] is 0·2685 and 5·6061 eV, respectively, for the *cis* and the *trans* conformers relative to the most stable conformer. The value of the energies suggests that the lowest-energy form of the [VO(phac)$_2$(H$_2$O)] complex in the gas is the *trans* conformer with a planar structure and having oxygen atoms in the two sides of the molecule plane. However, the trend of stability and the structures of the conformers depend upon the level of the theory. Figure 3 shows the structures of the [VO(pyran)$_2$(H$_2$O)]. The structures of the conformers of the [VO(phac)$_2$(H$_2$O)] complex are presented in the appendix 1.

3.3 *Thermal analysis*

The thermal decomposition of the [VO(O$_4$)]-type complexes studied in this work presented characteristic pathways, depending on the nature of the ligands, as can be seen from the TG/DTG curves in figure S2.

The hydrated water molecules are associated with the complex formation and found outside the coordination sphere formed around the central metal ion. The dehydration of this type of water takes place in the temperature range of 25–220°C. On the other hand, the coordinated water molecules are eliminated at higher temperatures than the water molecules of hydration. The water of coordination is usually eliminated[35] in the temperature range of 100–316°C. The organic part of the complexes may decompose in one or more steps with the possibility of the formation of one or two intermediates. These intermediates may include the metal ion with a part of the Schiff base in case of 1 : 1 or 1 : 2 complexes. These intermediates may finally decompose to stable metal oxides.

The thermogravimetric curve of [VO(tfac)$_2$(H$_2$O)] shows a weight loss of 81·1% in the temperature

range of 150–230°C with a residue of 19·8% (calcd. weight loss for 1 mol of H_2O and 2 mol of tfac: 82·1%) corresponding to the elimination of one molecule of the coordinated water and 2 tfac groups. According to the DTG curve, the decomposition involves one step (figure S2, curve a).

The thermal decomposition of $[VO(phac)_2(H_2O)]$ occurs in two steps. The first mass loss (observed 36·6%), can be seen between 190 and 307°C (calcd. weight loss for 1mol of H_2O and 1 mol of phac: 42·1%) corresponding to the elimination of one molecule of coordinated water and 1 phac group. The decomposition continues with the gradual weight loss, and it ceases at about 480°C. This weight loss in the temperature range of 370–480°C (observed 32·6%) (calcd. 38·1%), assuming weight removal of the other coordinated phac group. The final residue with attaining a constant weight (observed 37%) roughly corresponds to V_2O_5 (calcd. 42%) (figure S2, curve b).

The $[VO(dphac)_2(H_2O)]$ decomposes in two steps. The first step occurs between 188 and 310°C is probably a partial decomposition of the ligand and elimination of one molecule of the coordinated water (observed 42·6%) (calcd. weight loss for 1 mol of H_2O and 1 mol of phac: 45·0%). The second step of the thermal decomposition, which occurs in the range of 360–458°C, was assigned to the loss of the second ligand (observed 35·3%) (calcd. 40·7%) with the formation of V_2O_5 (observed 30%) (calcd. 35·0%) (figure S2, curve c).

The thermal studies performed suggest that $[VO(tfac)_2(H_2O)]$ is less stable than the other complexes because of the lower degradation temperature (approximately 150°C). The presence of the phenyl group in the coordination sphere of the two other complexes may enhance their stability.

3.4 Thermodynamic studies of complex formation

The formation constants, K_f, of the complexation were determined by spectrophotometric titration of a fixed concentration of the ligands (5×10^{-5} M) with various concentrations of the metal sulphate ($2·5 \times 10^{-6} – 9·75 \times 10^{-5}$ M) at 25°C and at constant ionic strength (0·1 M $NaClO_4$). The interaction of $NaClO_4$ with the ligands was negligible. In a typical titration 2·5 mL of the ligand solution was transferred into the thermostated cell compartment of the UV–Visible instrument, which was kept at constant temperature ($\pm 0·1$°C) by circulating water, and was titrated by the metal ion solution.

The titration was performed by adding aliquots of the metal ion with a Hamilton μL syringe to the ligand. The absorption measurements were carried out at various wavelengths where the difference in
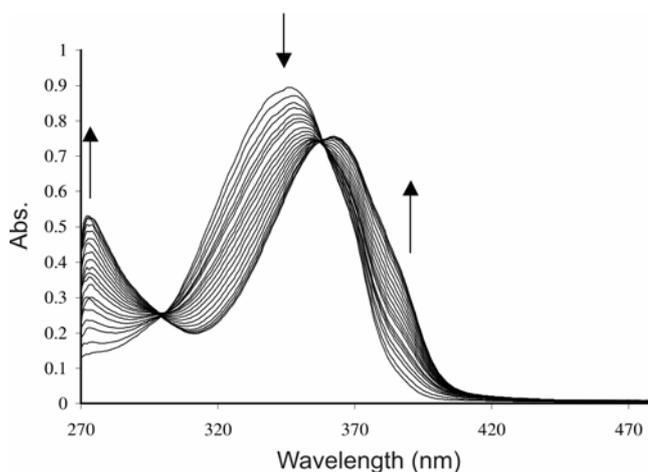

Figure 4. The variation of the electronic spectra of dphac titrared with $VO(SO_4) \cdot nH_2O$ at 25°C in 96% methanol.

Table 4. The formation constants, log K_f, for the complexes at 25°C.

Ligand	log K_f	$\Delta G°$ (kJ mol^{-1})
tfac[a]	8·97 ± 0·07	−51·18 ± 0·11
phac[a]	8·00 ± 0·01	−45·63 ± 0·70
dphac[a]	7·48 ± 0·06	−42·66 ± 0·19
pyran[b]	10·18 ± 0·14	−58·06 ± 0·07
p-Hydroxypyran[b]	10·94 ± 0·22	−62·39 ± 0·09
p-MeOpyran[b]	9·00 ± 0·06	−51·33 ± 0·32
p-Chloropyran[b]	8·48 ± 0·06	−48·36 ± 0·19
p-Bromopyran[b]	8·22 ± 0·43	−46·88 ± 0·37
p-Cyanopyran[b]	8·00 ± 0·05	−42·63 ± 0·44
pyrbz[b]	8·41 ± 0·08	−47·96 ± 0·19

[a]Solvent is CH_3OH. [b]Solvent is CH_3CN.
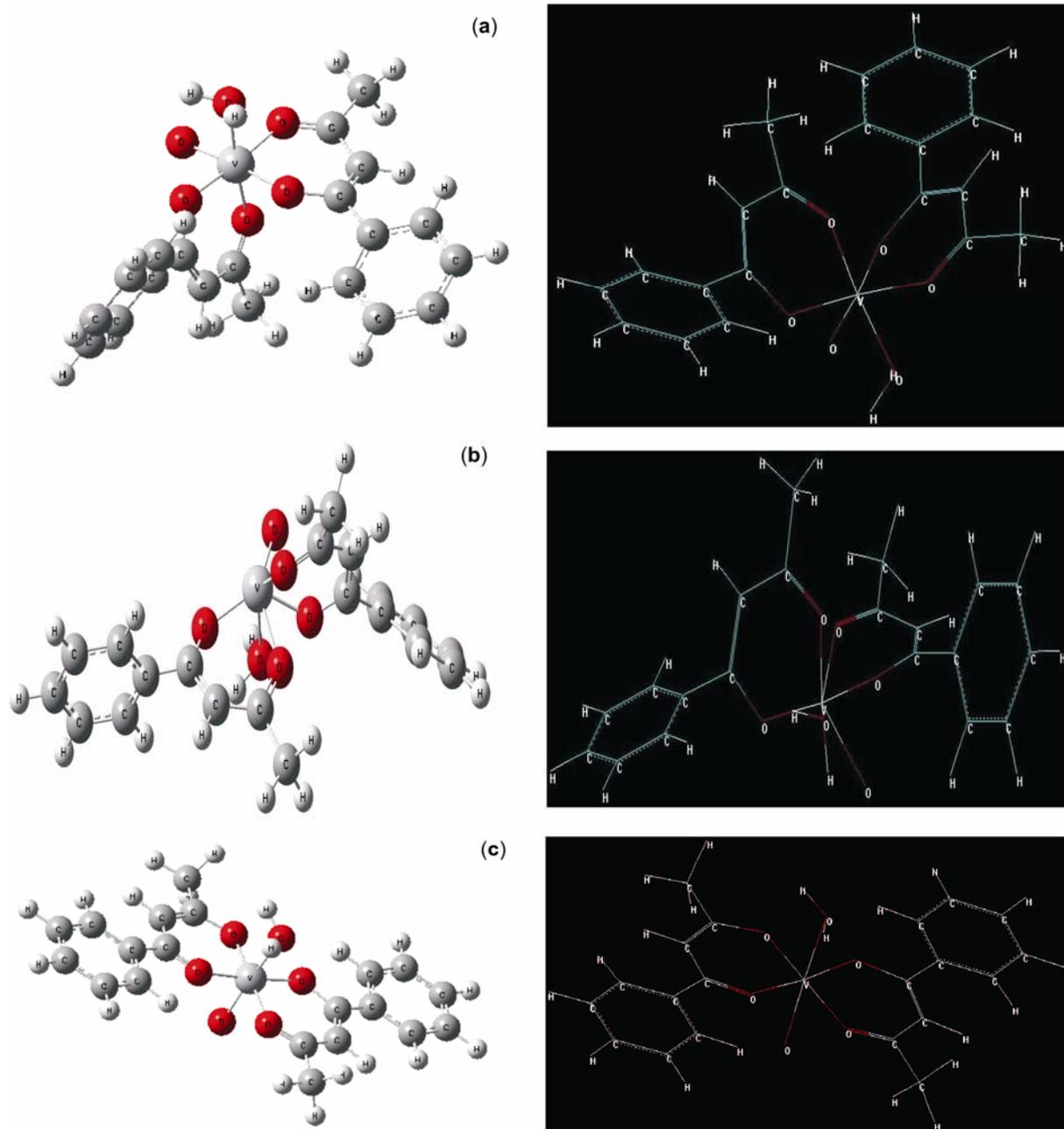
Appendix 1. The structure of the (**a**) *cis*-[VO(phac)$_2$(H$_2$O)] complex, (**b**) *trans*-[VO(phac)$_2$(H$_2$O)] complex and (**c**) *trans*-[VO(phac)$_2$(H$_2$O)] (O and H$_2$O) complex.

absorption was the maximum after equilibrium. The formed complex shows different absorption from the free ligand, while the metal ion solution shows no absorption at those wavelengths. As an example, the variation of the electronic spectra for dfac, titrated with various concentrations of VO(SO$_4$)·nH$_2$O at 25°C in MeOH is shown in figure 4. The same procedure was followed for all other systems. The electronic spectra of the formed complexes were the same as the electronic spectra of the separately synthesized complexes.

The formation constants, K_f, were calculated using SQUAD computer program,[36] designed to calculate the best values for the formation constants of the proposed equation model (1) by employing a non-linear, least-squares approach. Also, the free energy change $\Delta G°$ values of the formed complexes were calculated from $\Delta G° = -RT \ln K_f$ at 25°C (see table 4).

$$2HL + VO(SO_4) \cdot nH_2O \rightleftharpoons$$

$$[VO(L)_2] \cdot nH_2O + SO_4^{2-} + 2H^+. \quad (1)$$
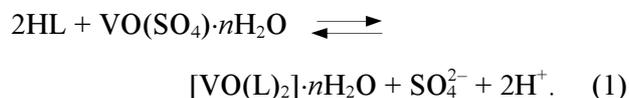
The results in table 4 show that for $VO(O)_4$-type complexes, the steric character of the ligands predominates the electronic factor toward VO(IV) center. Concerning this effect, tfac has more tendency to bind with VO(IV) center than phac and dphac.

As far as $VO(N)_4$-type complexes are concerned, the electron withdrawing functional groups such as bromo, chloro and cyano make the Schiff base as a poor donor ligand toward VO(IV) center. On the other hand, the electron donating groups such as hydroxy or methoxy make the ligand more potent donor toward the VO(IV) center, although the steric effect of the substitution cannot be ruled out. Therefore, *p*-Hydroxypyran, *p*-MeOpyran and pyran have the highest tendency toward VO(IV).

4.   Conclusion

The structural, geometrical, thermal, and thermodynamic properties of the oxovanadium(IV) complexes have been investigated. According to the thermodynamic studies, the formation constants of the complexes depend upon the steric and the electronic characteristic of the ligands. But as the steric character predominating, the tendency to bind with VO(IV) center decrease. Moreover, the electrical feature of each complex has an important role on the thermodynamic and the thermal properties. It is evident that there is a close relationship between these various properties. Charge distribution and the geometry are effective factors affecting the properties of the different complexes. The way that thermal properties change is the same as the variation of the QSAR properties for $VO(O_4)$-type complexes.

Supplementary information

For supplementary information see www.ias.ac.in/chemsci website.

References

1. Mohammadi K, Thompson K H, Patrick B O, Storr T, Martins C, Polishchuk E, Yuen V G, McNeill J H and Orvig C 2005 *J. Inorg. Biochem.* **99** 2217
2. Crans D C 2000 *J. Inorg. Biochem.* **80** 123
3. Maurya R C and Rajput S 2004 *J. Molecular Struct.* **687** 34
4. Plass W 2003 *Coord. Chem. Rev.* **237** 205
5. Rehder D 2003 *Inorg. Chem. Commun.* **6** 604
6. Aranha P E, Souza. M, Romera S, Ramos L A, Santos M, Dockal E and Cavalheiro E T G 2007 *Thermochim. Acta* **453** 9
7. Ahmad S, Isab A A, Ali S and Al-Arfaj A R 2006 *Polyhedron* **25** 1633
8. Posner B I, Shaver A and Fantus I G 1990 in *New antidiabetic drugs* (eds) C J Bailey and P R Flatt (Gordon London S), p. 107
9. Posner B I, Faure R, Burgess J W, Bevan A P, Lachance D, Zhang-Sun G, Fantus I G, Hall D A, Lum B S and Shaver A 1994 *J. Biol. Chem.* **269** 4596
10. Shaver A, Hall D A, Ng J B, Lebuis A M, Hynes R C and Posner B I 1995 *Inorg. Chim. Acta* **229** 253
11. Shaver A, Ng J B, Hall D A, Soo Lum B and Posner B I 1993 *Inorg. Chem.* **32** 3109
12. Kadota S, Fantus I G, Deragon G, Guyda H J, Hersh B and Posner B I 1987 *Biochem. Biophys. Res. Commun.* **147** 259
13. McNeill J H, Yuen V G, Hoveyda H R and Orvig C 1992 *J. Med. Chem.* **35** 1489
14. Caravan P, Gelmini L, Glover N, Herring F G, Li H, McNeill J H, Rettig S J, Setyawati I A, Shuter E, Sun Y, Tracey A S, Yuen V G and Orvig C 1995 *J. Am. Chem. Soc.* **117** 12759
15. Li J, Elberg G, Crans D C and Shechter Y 1996 *Biochem.* **35** 8314
16. Morgan G T and Moss H W 1914 *J. Chem. Soc.* **103** 78
17. Kaneda K, Jitsukawa K, Itoh T and Teranishi S 1980 *J. Org. Chem.* **45** 3004
18. Hirao T 1997 *Chem. Rev.* **97** 2707
19. Wender P A, Rice K D and Schnute M E 1997 *J. Am. Chem. Soc.* **119** 7897
20. Taguchi H, Isobe K, Nakamura Y and Kawaguchi S 1975 *Chem. Lett.* 757
21. Selbin J, Manning H R and Cessac G 1963 *J. Inorg. Nucl. Chem.* **2** 1253
22. Atherton N M, Gibbon P J and Shohoji M C B 1982 *J. Chem. Soc. Dalton Trans* 2289
23. Dodge R P, Templeton D H and Zalkin A 1961 *J. Chem. Phys.* **35** 55
24. Amin S, Cryer K, Zhang B, Dutta S, Eaton S, Anderson O, Miller S and Crans D 2000 *Inorg. Chem.* **39** 406
25. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P,

Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2003 (Pittsburgh PA: Gaussian, Inc)

26. Ghose A K, Pritchett A and Crippen G M 1994 *J. Comput. Chem.* **9** 80
27. Rogers D and Hopfinger A J 1994 *J. Chem. Inf. Comput. Sci.* **34** 854
28. Bodor N, Gabanyi Z and Wong C 1989 *J. Am. Chem. Soc.* **111** 3783
29. Ooi T, Oobatake M, Nemethy G and Scheraga H A 1987 *Proc. Natl. Acad. Sci. USA* **84** 3086

30. Viswanadhan V N, Ghose A K, Revankar G N and Robins R K 1989 *J. Chem. Inf. Comput. Sci.* **29** 163
31. Ghose A K and Crippen GM 1987 *J. Chem. Inf. Comput. Sci.* **27** 21
32. Selwood P W 1956 *Magnetochemistry* (New York: Interscience)
33. Symal A 1975 *Coord. Chem. Rev.* **21** 309
34. Selbin J 1966 *Coord. Chem. Rev.* **1** 293
35. Abdel-Ghani N T and Sherif O E 1989 *Thermochim. Acta* **156** 69
36. Leggett D L 1985 *Computational methods for the determination of formation constant* (New York: Plenum Press)