

Vanadyl Binary Schiff Base Complexes Containing N₂O₂ Coordination Sphere: Synthesis, Ab Initio Calculations and Thermodynamic Properties

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ABSTRACT. Some vanadyl complexes were synthesized by treating a methanolic solution of the appropriate Schiff base ligand and one equivalent of VO(SO₄)₂ to yield [(VOL₂¹⁻¹⁴)](L=Salicylaldehyde's derivatives, Schemes 1, 2). These oxovanadium (IV) complexes were characterized based on their FT-IR, UV-Vis spectroscopy and elemental analysis. The IR spectra suggest that coordination takes place through azomethine nitrogen and phenolate oxygen. In addition, the formation constants of the oxovanadium (IV) binary complexes were determined in methanolic medium. The ab initio calculations were also carried out to determine the structural and the geometrical properties of one of the complexes and its calculated vibrational frequencies were investigated.

Key words: Oxovanadium (IV), Formation constants, Thermodynamics, Ab initio calculations

INTRODUCTION

Schiff base ligands are considered “privileged ligands” because they are easily prepared by condensation between aldehydes and primary amines. Schiff base ligands are able to coordinate with many different metals,¹⁻⁵ and to stabilize them in various oxidation states. The Schiff base complexes have been used in catalytic reactions⁶ and as models for biological systems.^{7,8} It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complex. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors.^{9,10} The interest in the coordination chemistry of vanadium complexes has grown enormously over the last few decades due to the role of vanadium in several biological processes, such as haloperoxidation,¹¹ phosphorylation,¹² glycogen metabolism,^{13,14} and insulin mimicking.^{15,16} More recently, vanadium(IV) coordination compounds have been shown to catalyze selective oxidation of alkenes by molecular oxygen.¹⁷⁻²¹

In view of recent interest in the energetics of the metal ligand bonding in metal chelates involving N, O donor ligands,²²⁻³⁰ we tried to synthesize Schiff base complexes derived from ligands involving N₂O₂ donor sphere. So, the aim of the present work was to support and evaluate

the chelation behavior of this class of ligands having C=N and OH groups, towards VO(IV) metal ion and to evaluate their thermodynamic properties. Also, the conformational stability of the bis(5-bromo-salicylideneanilinato) oxovanadium (IV) molecule was investigated through quantum mechanical calculations. Geometry optimizations of *cis* and *trans* conformers were performed, and the corresponding relative energies were compared. A complete vibrational analysis of the complex was performed by infrared data with quantum mechanical calculations. Infrared spectroscopy is among the traditional methods of analysis, and particularly powerful for nondestructive characterization of substances including living and drug materials.³¹ The calculated vibrational spectra were analyzed based on each vibrational mode, which allowed us to obtain a quantitative as well as qualitative interpretation of the infrared spectrum.

EXPERIMENTAL

Materials

All solvents and chemicals were purchased from Merck, Fluka or Aldrich and used without further purification.

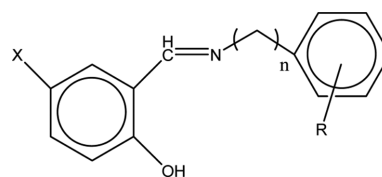
Apparatus and Techniques

The infrared spectra of all ligands and their complexes were recorded in the range 4000–400 cm⁻¹ using a Shi-

madzu FTIR–8300 spectrophotometer applying the KBr disc technique. The UV-Visible absorption spectra were recorded using Perkin-Elmer Lambda 2 spectrophotometer at room temperature. The Elemental analysis was carried out by Thermo Finnigan-Flash-1200. The NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer.

Synthesis of the Ligands

The Schiff bases were prepared by mixing equimolecular amounts of 5-Br-salicylaldehyde or 5-MeO-salicylaldehyde and aniline or substituted anilines in the 3- and 4-positions by methoxy, hydroxy, chloro, bromo, nitro and cyano groups in 10 mL absolute ethanol in a round bottomed flask equipped with a condenser. The mixture was brought into reflux for 4 h. The products obtained after cooling were filtered off and crystallized from absolute ethanol. The product's solids were dried under vacuum and kept dry in a desiccator over anhydrous calcium chloride. Melting points were measured and elemental analysis for the prepared Schiff bases was done. The results obtained were in good agreement with the calculated values.

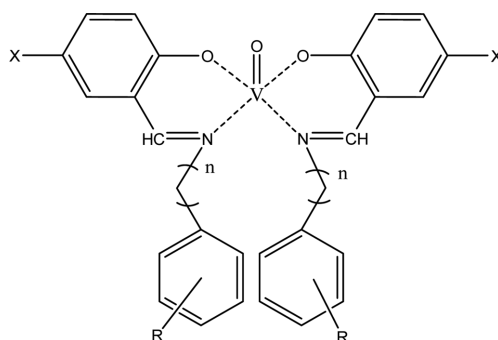


Scheme 1. The structural formula of the Schiff bases.

The prepared Schiff bases have the structural formula shown in *Scheme 1*.

Synthesis of the Complexes

A methanolic solution (10 mL) of vanadyl sulfate $\text{VO}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ (0.25 mmol) was added dropwise to a stirred solution of the Schiff base (0.5 mmol) in a mixture of degassed MeOH (10 mL) and NEt_3 (1 mmol). The reaction mixture was refluxed for 2 h under N_2 , and then cooled to room temperature (RT), affording a greenish-grey solid product which was isolated by vacuum filtration, washed with cold methanol, and then dried overnight in vacuo at RT.³² The prepared Schiff base complexes have the structural formula shown in *Scheme 2*.



Schiff bases	R	X	
$[\text{VO}(\text{L}^1)_2]^a$	Bis(5-bromo-salicylideneanilinato)oxovanadium(IV)	H	Br
$[\text{VO}(\text{L}^2)_2]^a$	Bis(5-bromo-salicylidene-4-methoxyanilinato)oxovanadium(IV)	4-OCH ₃	Br
$[\text{VO}(\text{L}^3)_2]^a$	Bis(5-bromo-salicylidene-4-bromoanilinato)oxovanadium(IV)	4-Br	Br
$[\text{VO}(\text{L}^4)_2]^a$	Bis(5-bromo-salicylidene-3-chloroanilinato)oxovanadium(IV)	3-Cl	Br
$[\text{VO}(\text{L}^5)_2]^a$	Bis(5-bromo-salicylidene-4-chloroanilinato)oxovanadium(IV)	4-Cl	Br
$[\text{VO}(\text{L}^6)_2]^a$	Bis(5-bromo-salicylidene-3-cyanoanilinato)oxovanadium(IV)	3-CN	Br
$[\text{VO}(\text{L}^7)_2]^a$	Bis(5-bromo-salicylidene-4-cyanoanilinato)oxovanadium(IV)	4-CN	Br
$[\text{VO}(\text{L}^8)_2]^a$	Bis(5-bromo-salicylidene-3-nitroanilinato)oxovanadium(IV)	3-NO ₂	Br
$[\text{VO}(\text{L}^9)_2]^a$	Bis(5-methoxy-salicylidene-4-methoxyanilinato)oxovanadium(IV)	4-OCH ₃	OCH ₃
$[\text{VO}(\text{L}^{10})_2]^a$	Bis(5-methoxy-salicylidene-4-hydroxyanilinato)oxovanadium(IV)	4-OH	OCH ₃
$[\text{VO}(\text{L}^{11})_2]^a$	Bis(5-methoxy-salicylidene-4-bromoanilinato)oxovanadium(IV)	4-Br	OCH ₃
$[\text{VO}(\text{L}^{12})_2]^a$	Bis(5-methoxy-salicylidene-4-chloroanilinato)oxovanadium(IV)	4-Cl	OCH ₃
$[\text{VO}(\text{L}^{13})_2]^a$	Bis(5-methoxy-salicylidene-4-cyanoanilinato)oxovanadium(IV)	4-CN	OCH ₃
$[\text{VO}(\text{L}^{14})_2]^b$	Bis(5-bromo-salicylidenebenzylaminato)oxovanadium(IV)	H	Br

^an=0, ^bn=1

Scheme 2. The structural formula of the Schiff base complexes.

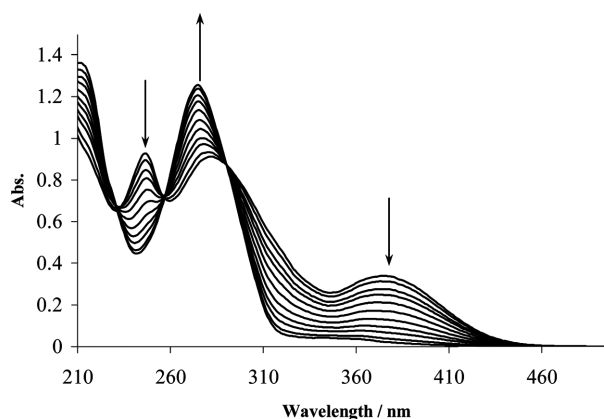
Table 1. The physical properties of the prepared compounds

Compounds	mp (°C)	Color
HL ¹	125	Orange
HL ²	160	Yellow
HL ³	180	Yellow
HL ⁴	130	Yellow orange
HL ⁵	160	Yellow
HL ⁶	164	Orange
HL ⁷	190	Orange
HL ⁸	190	Pale yellow
HL ⁹	160	Yellow
HL ¹⁰	167	Orange
HL ¹¹	130	Orange
HL ¹²	110	Orange
HL ¹³	160	Yellow
HL ¹⁴	90	Yellow
[VO(L ¹) ₂]	>250	Olive green
[VO(L ²) ₂]	250	Olive green
[VO(L ³) ₂]	250	Green
[VO(L ⁴) ₂]	>250	Light green
[VO(L ⁵) ₂]	>250	Green
[VO(L ⁶) ₂]	>250	Light green
[VO(L ⁷) ₂]	>250	Light green
[VO(L ⁸) ₂]	>250	Pale green
[VO(L ⁹) ₂]	>250	Green
[VO(L ¹⁰) ₂]	250	Pale green
[VO(L ¹¹) ₂]	>250	Olive green
[VO(L ¹²) ₂]	>250	Pale green
[VO(L ¹³) ₂]	>250	Green
[VO(L ¹⁴) ₂]	>250	Green

Thermodynamic Studies of Complex Formation

The formation constants, K_f , of the VO(IV) complexes were determined by spectrophotometric titration of a fixed concentration of the ligands (5×10^{-5} M) with various concentrations of the metal sulfate (1×10^{-5} – 1.7×10^{-4} M) at 25 °C and at constant ionic strength (0.1 M NaClO₄). The interaction of NaClO₄ 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 (± 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 μ L syringe to the ligand. The absorption measurements were carried out at various wavelengths where the difference in 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

**Fig. 1.** The variation of the electronic spectra of H₂L¹³ titrated with VO(SO₄).nH₂O at 25 °C in 96% methanol.

H₂L¹³, titrated with various concentrations of VO (SO₄) · nH₂O at 25 °C in MeOH is shown in Fig. 1. The same procedure was followed for all other systems. The electronic spectra of the formed complexes at the end of titration were the same as the electronic spectra of the separately synthesized complexes.

RESULTS AND DISCUSSION

Physico-chemical Characterizations and Geometrical Configuration of the Complexes

VO(IV) salt reacts with Schiff base ligands in 1:2 molar ratio in alcoholic medium to afford greenish-grey complexes. The ligand and its complexes are stable at room temperature and are nonhygroscopic. The synthesized ligands and their complexes were characterized by spectral techniques and elemental analysis. Apart from this, thermodynamic properties of the complexes were studied and the optimized geometry of one of the newly synthesized compounds has been elucidated by ab initio calculations.

IR analysis

The IR spectra provide valuable information regarding the nature of functional groups attached to the metal atom. The ligands and the metal complexes were characterized mainly using the azomethine band. The main infrared bands and their assignments are listed in Table 2. The vanadyl complex shows a band at ~ 940 cm⁻¹ attributed to V=O frequency.³³ In addition the spectra of the ligands show –C=N band in the region 1608–1620 cm⁻¹, which is shifted to lower frequencies (1606–1612 cm⁻¹) through complex formation indicating the involvement of the –C=N nitrogen in the metal ion coordination.^{34,35} Assignment of the proposed coordination sites is further supported by the appearance

Table 2. IR Spectral data (cm^{-1}) of the compounds

Compounds	$\nu_{\text{O-H}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	$\nu_{\text{M-N}}$	$\nu_{\text{V=O}}$	$\nu_{\text{C=N}}$
HL ¹	3463	2920	1612	1558			
HL ²	3463	2939	1618	1562			
HL ³	3441	2827	1612	1554			
HL ⁴	3433	2943	1616	1558			
HL ⁵	3433	2989	1612	1554			
HL ⁶	3433	3055	1620	1566			2225
HL ⁷	3444	3085	1620	1558			2221
HL ⁸	3440	3093	1620	1566			
HL ⁹	3456	2825	1612	1573			
HL ¹⁰	3242	2942	1614	1598			
HL ¹¹	3427	2921	1614	1589			
HL ¹²	3436	2921	1620	1591			
HL ¹³	3427	2950	1620	1573			2223
HL ¹⁴	3440	2984	1631	1569			
[VO(L ¹) ₂]		2895	1608	1589	455	983	
[VO(L ²) ₂].0.25H ₂ O	3413	2835	1612	1531	474	987	
[VO(L ³) ₂].0.01H ₂ O	3421	2931	1604	1577	435	973	
[VO(L ⁴) ₂].0.01H ₂ O	3444	2930	1604	1581	424	987	
[VO(L ⁵) ₂].0.01H ₂ O	3444	2910	1604	1581	443	983	
[VO(L ⁶) ₂].0.2H ₂ O	3444	2860	1608	1542	416	975	2229
[VO(L ⁷) ₂]		2923	1608	1593	466	975	2225
[VO(L ⁸) ₂]		2896	1612	1593	420	925	
[VO(L ⁹) ₂]		2921	1604	1544	480	979	
[VO(L ¹⁰) ₂].0.1H ₂ O	3332	2815	1604	1598	493	956	
[VO(L ¹¹) ₂]		2897	1602	1544	476	977	
[VO(L ¹²) ₂]		2920	1610	1546	478	979	
[VO(L ¹³) ₂]		3087	1604	1575	434	987	2225
[VO(L ¹⁴) ₂].0.5H ₂ O	3345	2954	1612	1532	458	988	

of medium bands at $400\text{--}450\text{ cm}^{-1}$ and $450\text{--}500\text{ cm}^{-1}$ which could be attributed to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively.^{36,37} Thus the oxovanadium (IV) complexes have the general structure which were shown in *Scheme 2*.

Elemental Analysis

The stoichiometry of the ligands and vanadyl complexes were confirmed by their elemental analysis. The metal/ligand ratio was found to be 1:2 has been arrived at by estimating the carbon, hydrogen, and nitrogen contents of the complexes. Elemental analysis of ligands and their VO (IV) complexes show good agreement with the proposed structures of the ligands and their complexes (*Table 3*).

UV-Vis Analysis

The ligands show two absorption bands at UV-Visible region. A $n\text{-}\pi^*$ transition band at $326\text{--}410\text{ nm}$ and a $\pi\text{-}\pi^*$ transition band at $240\text{--}297\text{ nm}$ are shown in the ligands. These absorption bands show a slight shift to higher energy

in the complexes that is evident for unalteration of the structure of ligands upon complexation (*Table 3*).

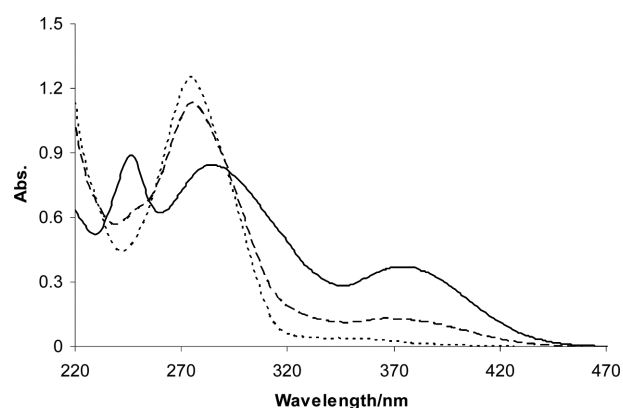
All the vanadyl (IV) complexes have a band at $340\text{--}470\text{ nm}$ in methanol corresponding to a d-d transition band. This band is not always observed, being often buried beneath a high intensity charge transfer band (or more accurately the low energy tail of that band), and when it is observed it is generally a shoulder (*Table 3*). UV-Vis spectra of HL¹³ and its oxovanadium (IV) are shown in *Fig. 2*.

¹H NMR

In the ¹H NMR spectral data of the salicylideneaniline ligands, the hydroxy proton is in the range $10\text{--}13\text{ ppm}$. The spectral data of the ligands show a singlet (1H) signal at $\sim 8.5\text{ ppm}$ which can be assigned to the azomethine proton group. The signals of the hydrogens of the phenyl group are appeared at $\delta = 6.3\text{--}8\text{ ppm}$. The signal appeared as a singlet at 4.45 ppm . The protons of the methoxy groups show a signal at $\sim 3.8\text{ ppm}$.^{38,39}

Table 3. UV-Vis^a and elemental analysis data of the compounds

Compounds	λ_{\max} (nm)	Elemental analysis (%; Found)		
		C	H	N
HL ¹	226, 268, 349	56.55 (56.20)	3.65 (3.69)	5.07 (5.14)
HL ²	229, 271, 355	54.92 (55.21)	3.95 (4.00)	4.57 (4.56)
HL ³	231, 270, 352	43.98 (44.05)	2.56 (2.30)	3.95 (3.85)
HL ⁴	231, 270, 353	50.28 (49.88)	2.92 (3.00)	4.51 (4.61)
HL ⁵	230, 270, 350	50.28 (50.64)	2.92 (2.69)	4.51 (4.46)
HL ⁶	224, 269, 350	55.84 (55.85)	3.01 (2.87)	9.30 (9.14)
HL ⁷	230, 275, 354	55.84 (56.15)	3.01 (2.82)	9.30 (9.25)
HL ⁸	229, 267, 351	48.62 (48.37)	2.82 (2.63)	8.72 (9.00)
HL ⁹	271, 330, 365	70.02 (70.12)	5.88 (5.55)	5.44 (5.55)
HL ¹⁰	272, 335, 365	69.12 (69.43)	5.39 (5.76)	5.76 (6.02)
HL ¹¹	275, 309, 367	54.92 (55.03)	3.95 (3.75)	4.57 (4.95)
HL ¹²	275, 309, 366	64.25 (64.51)	4.62 (4.62)	5.35 (5.69)
HL ¹³	245, 284, 375	71.42 (71.73)	4.79 (4.55)	11.10 (11.02)
HL ¹⁴	269, 324, 411	57.95 (58.05)	4.17 (4.30)	4.83 (4.85)
[VO(L ¹) ₂]	218, 286(sh)	50.60 (50.20)	2.94 (2.74)	4.54 (4.17)
[VO(L ²) ₂].025H ₂ O	216, 358(sh)	49.33 (49.59)	3.33(3.13)	4.11 (4.08)
[VO(L ³) ₂].01H ₂ O	216, 288(sh)	40.20 (39.83)	2.10 (1.96)	3.61 (3.66)
[VO(L ⁴) ₂].01H ₂ O	283, 371(sh)	45.40 (45.44)	2.37 (2.45)	4.07 (4.20)
[VO(L ⁵) ₂].01H ₂ O	273, 354(sh)	45.40 (45.65)	2.37 (2.19)	4.07 (4.09)
[VO(L ⁶) ₂].0.2H ₂ O	211, 258(sh)	50.13 (50.52)	2.46 (2.32)	8.35 (8.39)
[VO(L ⁷) ₂]	215, 288(sh)	50.41 (50.80)	2.42 (2.44)	8.40 (8.17)
[VO(L ⁸) ₂]	283, 380(sh)	44.16 (44.43)	2.28 (2.05)	7.92 (7.96)
[VO(L ⁹) ₂]	360, 424	62.18 (62.40)	4.87 (4.68)	4.83 (4.54)
[VO(L ¹⁰) ₂].0.1H ₂ O	365, 429	60.79 (60.40)	4.41 (4.68)	5.06 (4.74)
[VO(L ¹¹) ₂]	272, 367	49.66 (50.02)	3.27 (3.15)	4.14 (4.50)
[VO(L ¹²) ₂]	269, 366	57.16 (57.29)	3.77 (3.74)	4.76 (5.10)
[VO(L ¹³) ₂]	211(sh), 273	63.27 (62.90)	3.89 (4.24)	9.84 (9.44)
[VO(L ¹⁴) ₂].0.5H ₂ O		51.40 (51.26)	3.54 (3.93)	4.28 (3.93)

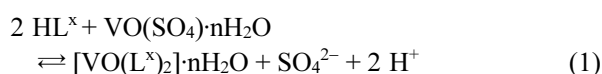
^aIn methanol.**Fig. 2.** UV-Vis spectra of the HL¹³ ligand (—), VO(L¹³)₂ complex separately synthesized (.....), and the product at the end of titration (-----).**Table 4.** ¹H NMR spectroscopic data of the compounds (δ in ppm)

Compounds	H-C=N	Ar-H	OH	-CH ₂ -	OCH ₃
^a HL ¹	8.56	6.91–7.52	13.28		
^a HL ²	8.53	6.89–7.49	13.44		3.81
^a HL ³	8.54	6.69–7.67	10.94		
^a HL ⁴	8.54	6.93–7.67	10.93		
^a HL ⁵	8.53	6.69–7.61	10.94		
^a HL ⁶	8.54	6.93–7.65	10.93		
^a HL ⁷	8.53	6.90–7.62	10.94		
^a HL ⁸	8.53	6.69–7.61	10.94		
^a HL ⁹	8.57	6.87–7.29	10.42		3.51, 4.12
^b HL ¹⁰	8.83	6.79–7.29	12.75		3.72
^a HL ¹¹	8.56	6.90–7.56	10.65		3.83
^a HL ¹²	8.58	6.86–7.46	10.65		3.86
^a HL ¹³	8.56	6.90–7.74	10.65		3.83
^a HL ¹⁴	8.41	6.32–7.74	11.39	4.45	

^aIn CDCl₃, ^bIn d₆-DMSO.

Thermodynamic Studies

To study the effect of the steric and the electronic parameters of the ligands on the formation constants and the thermodynamic free energy of complexation, the interaction of the ligands as donors and VO (IV) as acceptor was carried out. The formation constants, K_f , were calculated using SQUAD computer program,^{40,41} designed to calculate the best values for the formation constants of the proposed reaction model (reaction 1) by employing a non-linear, least-squares approach. The free energy change ΔG° values of the formed complexes were calculated from $\Delta G^\circ = -RT \ln K_f$ at 25 °C (See Table 5).



As the results show, in the para substituted Schiff base ligands, the formation constants ($\log K_f$) varies as can be expected from the electronic effects of the substituents at positions 4,4. Thus, the formation constants decrease according to the sequence OH > OCH₃ > H > Br > Cl > CN. In fact,

Table 5. The formation constants, $\log K_f$, for the complexes at 25 °C in methanol

Ligand	$\log K_f$	ΔG° (kJmol ⁻¹)	σ_p
[VO(HL ¹) ₂]	8.04 ± 0.06	-45.88 ± 0.15	0
[VO(HL ²) ₂]	8.19 ± 0.06	-46.71 ± 0.15	-0.268
[VO(HL ³) ₂]	7.50 ± 0.09	-42.77 ± 0.22	0.232
[VO(HL ⁴) ₂]	6.97 ± 0.25	-39.75 ± 0.62	
[VO(HL ⁵) ₂]	7.11 ± 0.57	-40.55 ± 0.43	0.227
[VO(HL ⁶) ₂]	6.72 ± 0.46	-38.33 ± 0.41	
[VO(HL ⁷) ₂]	7.02 ± 0.13	-40.03 ± 0.32	0.660
[VO(HL ⁸) ₂]	6.05 ± 0.05	-34.50 ± 0.12	
[VO(HL ⁹) ₂]	9.62 ± 0.45	-54.86 ± 0.41	-0.268
[VO(HL ¹⁰) ₂]	10.47 ± 0.11	-59.71 ± 0.27	-0.370
[VO(HL ¹¹) ₂]	8.98 ± 0.51	-51.21 ± 0.47	0.232
[VO(HL ¹²) ₂]	8.74 ± 0.09	-49.84 ± 0.22	0.227
[VO(HL ¹³) ₂]	7.93 ± 0.30	-45.22 ± 0.74	0.660

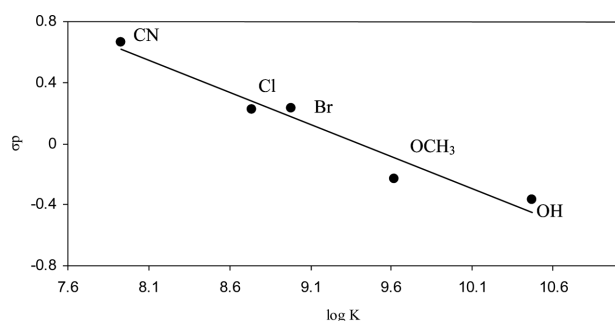


Fig. 3. Linear correlation between the para substituted constants, σ_p , and $\log K_f$ for the substituted salicylideneaniline Schiff bases with VO(SO₄)_nH₂O in methanol at 25 °C.

for the selected Schiff bases, Hammett type relationships were found between the $\log K_f$ values and σ_p , the para-substituent constant.⁴² Such correlations are shown in Fig. 3.

COMPUTATIONAL DETAILS

The electronic structure and the optimized geometries of the stable conformers of the complex bis (5-bromo-salicylideneanilinato)oxovanadium (IV) were computed by the Hartree-Fock (HF) method using the Gaussian 03 program⁴³ employing 6-311G basis set. The infrared absorption intensity was calculated in the harmonic approximation, at the same level of theory as in the geometry optimization to verify the adequacy of method and the basis set.

Optimized Geometries and Energies

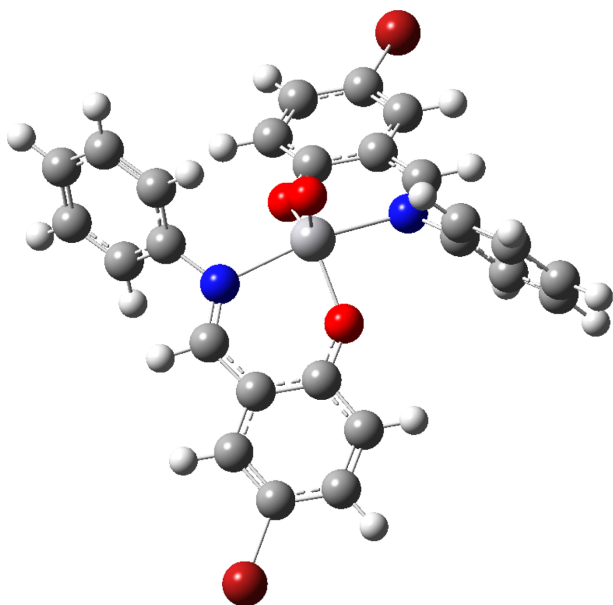
Geometry optimization was performed by HF/6-311G method on the two conformers of [VO(L¹)₂·H₂O] complexes. Comparison of the energies shows that the *trans* conformer is the more stable molecule. Careful examination of the conformer's structure indicates that the target complex does not involve water molecule coordinated to vanadium. This is evident by the fact that distances between the V and O atoms of the *cis* (2.354 Å) and *trans* (4.196 Å) conformers are larger than a V–O single bond (1.791 Å).⁴⁴ Therefore, it is adequate to continue the investigation on the stable *trans* conformer without water coordinated as it has been already confirmed experimentally.⁴⁵

The equilibrium geometry of the complex has been determined by the energy minimization with the same basis set, i.e., 6-311G. The relative energies, dipole moments, HOMO, LUMO, and the energy gaps for the two conformers are given in Table 6. The relative energies show that the *trans* conformer, shown in Fig. 4, is the stable structure of the target complex. The energy difference between conformers is 7.88 kJ/mol, which is larger by about three times of the thermal energy kT (at room temperature where k is Boltzmann constant). As a result, there is no possibility of coexistence of these two conformers at room temperature. From the other side of view, it can be found that (Table 6) the *cis* conformer having higher dipole moment and less stable HOMO electronic state is not favorable as the *trans* conformer.

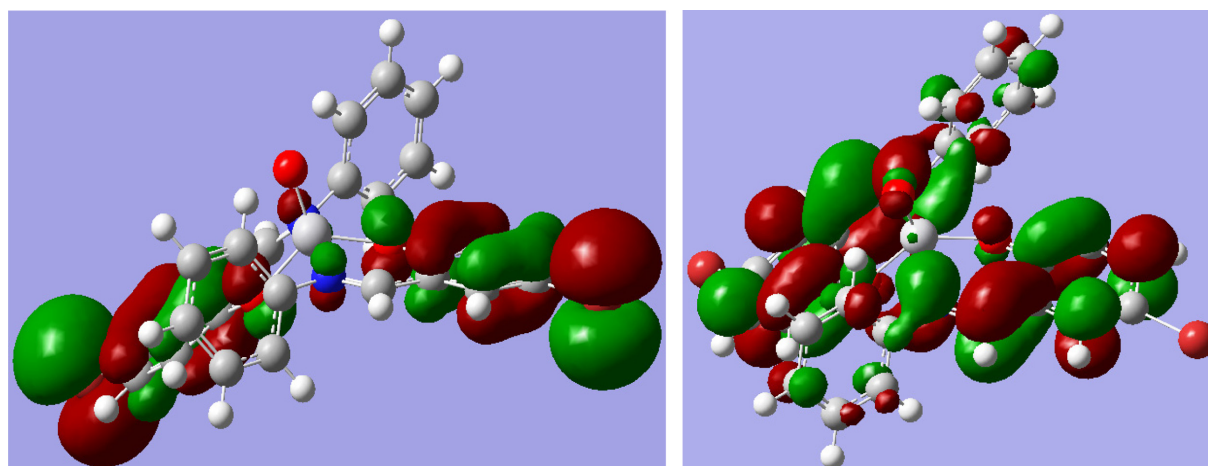
The calculated electron density on the rings containing Br indicates that the electron orbital of HOMO is localized over the rings having Br, while of the LUMO is distributed over the rings. As a result, the HOMO-LUMO energy gap of the *trans* complex increases. The stability of the *trans* conformer can be in part accounted by consid-

Table 6. Calculated properties for *cis* and *trans* conformers of the [VO(L¹)₂] complex at HF/6-311G level of theory

	Trans	Cis
E _{HF} (a. u.)	-7415.950	-7415.947
μ (Debye)	1.471	3.0217
point group	C1	C1
HOMO (a.u.)	-0.110	-0.108
LUMO (a.u.)	0.049	0.049
HOMO-LUMO gap (eV)	4.318	4.272

**Fig. 4.** The structure of the *trans* conformer of VO(L¹)₂.

ering that its electric dipole moment is less than that of the *cis*. Fig. 5 shows the distribution of the HOMO and LUMO orbitals over the stable conformer.

**Fig. 5.** HOMO (left) and LUMO (right) orbitals of the *trans* conformer of VO(L¹)₂ in vacuo.

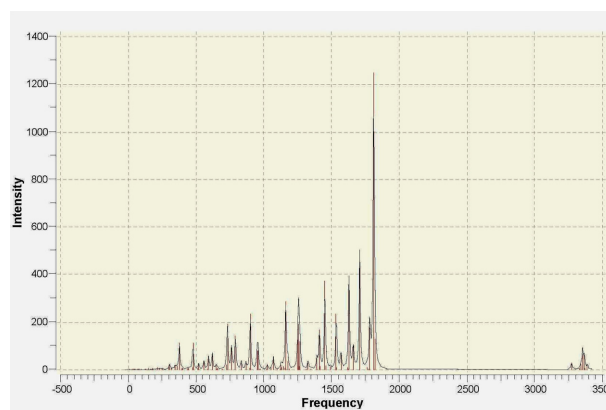
Vibrational Assignment

For the conformer [VO(L¹)₂] shown in Fig. 4, the number of normal mode is 150 [(3N-6), where N is the number of atoms N=52]. The conformation obtained from the geometry optimization exhibits no special molecular symmetries, and hence the molecule belongs to the C1 point group. Consequently, all the 150 fundamental vibrations of the gas phase molecule belong to the A irreducible representation and are both IR and Raman active.

Vibrational Frequencies

Comparison of the calculated frequencies at HF/6-311G level with experimental values (Table 2) reveals an overestimation of the wavenumber of the vibrational modes, which can be attributed to the neglect of the anharmonicity present in a real system. The calculated infrared absorption spectra are shown in Fig. 6.

The spectrum predicted by HF method shows the fin-

**Fig. 6.** Calculated infrared absorption spectra of the [VO(L¹)₂] complex versus frequency (cm⁻¹) in vacuo.

gerprint of the complex in the range of 400–1820 cm^{-1} and the C–H stretching can be seen around 1820 cm^{-1} .

C–X vibrations, X=O, C, H, N, Br

The predicted stretching modes at 1165 and 1451.71 cm^{-1} correspond to bands of the IR spectra. The C–O bond in this complex is located near the center of the molecule (vanadium). C=C stretching bands can be seen at 1253.93, 1783, 1779.59, and 1181.37 cm^{-1} . The C=C bond near the Br group vibrates at a lower frequency compared to the vibration of C=C bond on the ring in the farthest position to Br. The C=C stretching mode in the benzene ring is 1783 cm^{-1} , which occurs at a higher frequency relative to the C=C bond in the ring involving Br (1779.59 cm^{-1}).

The bending vibration of C–H groups connected to the rings occurs at 1631 cm^{-1} . The C–H modes also depend upon the location of the bond. Near the electron acceptor bromide, it can be observed at 959.9, 1056.57, and 1260.52 cm^{-1} , while far from this electron acceptor, it can be found in a wide range from 970 cm^{-1} to 1300 cm^{-1} . In addition, the C–H bond near the nitrogen atom of the complex vibrates at 1570 cm^{-1} . The stretching mode of C=N bond is calculated to be at 1811.97 and 1820.38 cm^{-1} . The smaller wavenumbers at 96.95 and 165.95 cm^{-1} represent the torsional mode of C=N. The stretching vibration of CN group on the ring has the strongest band in the IR spectrum. The normal vibrational mode of C–Br in the bromobenzene ring was predicted to be at 1179.85 cm^{-1} .

V–Y vibrations, Y=O, N

The four modes of V=O vibrations can be identified by the bands at 593.04, 727.35, 732.69, and 1164 cm^{-1} . The first one corresponds to the bending motion and the second and the third ones to the symmetric and asymmetric stretchings, respectively. The fourth one could hardly be identified. The vibrational modes of the V–N bond are seen at 65.85, 378.52, and 5477.96 cm^{-1} of the IR spectra.

Lattice Vibrations

The lattice vibration can not be associated with any vibrational mode of the single molecule. Interestingly, the lattice vibrations are usually observed below 200 cm^{-1} . The lattice modes associated with the translations and librations of the whole molecule can be only observed by far infrared, dispersive Raman, or terahertz spectroscopy.⁴⁶ Since HF method overestimates these modes, the lattice vibrational mode in *trans* conformer of $[\text{VO}(\text{L}^1)_2]$ are observed at frequencies below 350 cm^{-1} .

Interaction Energy Between Complex and Water

To provide more insights into the nature of the interaction between $[\text{VO}(\text{L}^1)_2]$ complex and water molecule, a systematic approach was taken into account. The interaction energy of complex is defined as the difference between the energy of the complex with water ($E_{[\text{VO}(\text{L}^1)_2\text{H}_2\text{O}]}$) and the sum of the energies of the pure H_2O ($E_{\text{H}_2\text{O}}$) and $[\text{VO}(\text{L}^1)_2]$ ($E_{[\text{VO}(\text{L}^1)_2]}$) species:

$$E(\text{kJmol}^{-1}) = 2625.50[E_{[\text{VO}(\text{L}^1)_2\text{H}_2\text{O}]}(\text{a.u.}) - E_{\text{H}_2\text{O}}(\text{a.u.}) - E_{[\text{VO}(\text{L}^1)_2]}(\text{a.u.})] \quad (2)$$

For this purpose each isolated $[\text{VO}(\text{L}^1)_2\text{H}_2\text{O}]$ and its corresponding species ($[\text{VO}(\text{L}^1)_2]$ and H_2O) were optimized at HF/6-311g level of theory as mentioned above. The calculated interaction energies are –25.420 and –23.883 kJ/mol for the *trans* and the *cis* conformers, respectively. Since the interaction energy for the *trans* (–25.420 kJ/mol) and for the *cis* (–23.883 kJ/mol) conformers is small, it can be confirmed again that this complex does not contain water molecule coordinated to the vanadium.

Charge Distribution on the Complex

The atomic charges calculated by ab initio method at HF/6-311g level of theory by Natural Bond Orbital (NBO) for two conformers indicate that the most positive charge, +2.0216 C, is on the center of the *trans* complex (vanadium atom). This charge value may be one of the effective factors in determining the stability of *trans* conformer over the *cis* conformer.

CONCLUSIONS

The structural, geometrical and the thermodynamic properties of the oxovanadium(IV) complexes have been investigated. Geometry optimization on the *cis* and *trans* conformers shows that the *cis* conformer is less stable and the energy difference between these two conformers is 7.88 kJ/mol. Thus, calculations using HF method with 6-311g basis set show that the energy difference between the conformers is much larger than kT , such that there is no possibility of coexistence of conformers.

In conformer *trans*, there does not exist the possibility of intramolecular bond formation between V–O (the oxygen of the water) as indicated by the large distance between V and O atoms, e.g., 4.196 Å. This means that no water is coordinated to vanadium as confirmed by the calculated

interaction energy. Vibrational spectroscopy and computational chemistry have been applied for investigating the most stable conformer of bis(5-bromo-salicylideneanilinato) oxovanadium (IV). Infrared spectrum was recorded, and vibrational bands were assigned based on the HF calculations. In general, the calculated modes observed were overestimated. Using the elaborated method, which includes the correlations like DFT, shall improve the results.

A striking feature of the present work is the study of the interaction energy, which reveals small interaction between H₂O and [VO(L¹)₂] in [VO(L¹)₂.H₂O], e.g., -25.420 kJ/mol. This energy lies below a V–O bond energy and it can be concluded that bis(5-bromo-salicylideneanilinato)oxovanadium (IV) does not have a coordinated water. According to the thermodynamic studies, the formation constant of the complexes depends upon the steric and the electronic characteristic of the ligands. Moreover, the molecular electronic structure of each complex plays an important role on its thermodynamic properties. It is evident that there is a close relationship between these various properties.

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