

Synthesis, *ab initio* Calculations, Thermal, Thermodynamic and Antioxidant Properties of Some Oxovanadium(IV) Complexes Containing N₂O₂ Set of Donor Atoms

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(Received 27 January 2010, Accepted 8 April 2010)

The formation constants of some oxovanadium(IV) binary complexes containing Schiff bases resulting from condensation of salicylaldehyde with aniline and with its derivatives were determined spectrophotometrically. The synthesized compounds were characterized by analytical and different physico-chemical techniques like ¹H NMR, IR, elemental analysis, mass and UV-Vis spectral studies. The IR spectra affirm that coordination takes place through azomethine nitrogen and phenolate oxygen. Three of the VO(IV) Schiff base complexes *i.e.* bis(salicylideneaniline)oxovanadium(IV), [VO(L¹)₂], bis(salicylidene-4-methoxyaniline)oxovanadium (IV), [VO(L²)₂] and bis(salicylidene-4-cyanoaniline)oxovanadium(IV), [VO(L¹⁰)₂], were studied by 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. The complexes screened for antioxidant activity and the *ab initio* calculations were carried out to determine the structural and the geometrical properties of a typical vanadyl salicylideneaniline complex, [VO(L¹)₂].

Keywords: Oxovanadium(IV), Formation constants, Thermodynamics, *Ab initio* calculations, Antioxidant

INTRODUCTION

Vanadium plays an unusual position among biometals as it may be available in both anionic and cationic forms. The most common ones being vanadate(V) and vanadyl(IV). Oxovanadium(IV) and (V) have particularly rich coordination chemistry [1,2] that have received much attention, for their use in oxidation and oxo-transfer catalysis, and for their potential therapeutic applications such as the treatment of diabetes [3-6] and as anticancer agents [7,8].

Particular attention has recently paid to the synthesis and study of the Schiff bases and their complexes. These complexes are known to be biologically important and serve as catalysts in various chemical and photochemical reactions

[9-10].

In view of recent interest in the energetic of the metal ligand bonding in metal chelates involving N, O donor ligand, we tried to study Schiff base complexes derived from ligands involving N₂O₂ donor atoms [11-18]. So, the aim of the present work was to support and evaluate the chelation behavior of these class of ligands having C=N and OH groups, towards VO(IV) metal ion and to evaluate their antioxidant properties and finally to present the optimized geometry of one representative sample of the complexes.

EXPERIMENTAL

Materials

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

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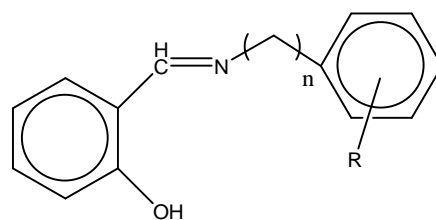
Apparatus and Techniques

The infrared spectra of all ligands and their complexes were recorded in the range 4000-400 cm^{-1} using a Shimadzu FTIR-8300 spectrophotometer applying the KBr disc technique. The infrared spectral vibration modes are listed in Table 2.

The UV-Vis absorption spectra were recorded using Perkin-Elmer Lambda 2 spectrophotometer at room temperature. Mass spectra were obtained with Shimadzu LCMS-2010EV. The Elemental analysis was carried out by Thermo Finnigan-Flash-1200.

Synthesis of the Ligands

The Schiff bases were prepared as in the literature. Melting points, the elemental composition and the spectral characterization such as IR, ^1H NMR, UV-Vis and mass

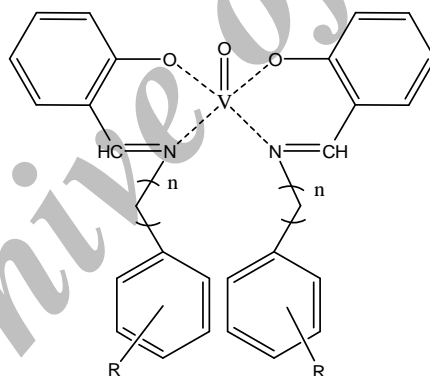


Scheme 1. The structural formula of the Schiff bases

spectroscopy for the prepared Schiff bases were determined and were in good agreement with the literature [19]. The prepared Schiff bases have the structural formula shown in Scheme 1.

Synthesis of the VO(IV) Complexes

The greenish-grey new complexes were prepared as in the literature [20]. The prepared Schiff base complexes have the structural formula shown in Scheme 2. The physical



Schiff bases		R
$[\text{VO}(\text{L}^1)_2]^a$	Bis(salicylideneaniline)oxovanadium(IV)	H
$[\text{VO}(\text{L}^2)_2]^a$	Bis(salicylidene-4-methoxyaniline)oxovanadium(IV)	4-OCH ₃
$[\text{VO}(\text{L}^3)_2]^a$	Bis(salicylidene-3-hydroxyaniline)oxovanadium(IV)	3-OH
$[\text{VO}(\text{L}^4)_2]^a$	Bis(salicylidene-4-hydroxyaniline)oxovanadium(IV)	4-OH
$[\text{VO}(\text{L}^5)_2]^a$	Bis(salicylidene-3-chloroaniline)oxovanadium(IV)	3-Cl
$[\text{VO}(\text{L}^6)_2]^a$	Bis(salicylidene-4-chloroaniline)oxovanadium(IV)	4-Cl
$[\text{VO}(\text{L}^7)_2]^a$	Bis(salicylidene-3-bromoaniline)oxovanadium(IV)	3-Br
$[\text{VO}(\text{L}^8)_2]^a$	Bis(salicylidene-4-bromoaniline)oxovanadium(IV)	4-Br
$[\text{VO}(\text{L}^9)_2]^a$	Bis(salicylidene-3-cyanoaniline)oxovanadium(IV)	3-CN
$[\text{VO}(\text{L}^{10})_2]^a$	Bis(salicylidene-4-cyanoaniline)oxovanadium(IV)	4-CN
$[\text{VO}(\text{L}^{11})_2]^a$	Bis(salicylidene-3-nitroaniline)oxovanadium(IV)	3-NO ₂
$[\text{VO}(\text{L}^{12})_2]^a$	Bis(salicylidene-4-nitroaniline)oxovanadium(IV)	4-NO ₂
$[\text{VO}(\text{L}^{13})_2]^b$	Bis(salicylidenebenzylamine)oxovanadium(IV)	H

^an = 0. ^bn = 1.

Scheme 2. The structural formula of the Schiff base complexes

Table 1. Physical Properties of the Prepared Complexes

Compounds	m.p. (°C)	Color
[VO(L ¹) ₂]	>250	Green
[VO(L ²) ₂]	238	Olive green
[VO(L ³) ₂]	>250	Dark green
[VO(L ⁴) ₂]	>250	Green
[VO(L ⁵) ₂]	240	Green
[VO(L ⁶) ₂]	250	Greenish-grey
[VO(L ⁷) ₂]	250	Brownish green
[VO(L ⁸) ₂]	250	Pale green
[VO(L ⁹) ₂]	250	Olive green
[VO(L ¹⁰) ₂]	250	Light green
[VO(L ¹¹) ₂]	>250	Green
[VO(L ¹²) ₂]	>250	Light green
[VO(L ¹³) ₂]	>250	Green

properties and spectral characterizations are shown in Tables 1, 2 and 3.

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 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-Vis 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 H₂L¹¹, 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.

RESULTS AND DISCUSSION

Physico-Chemical Characterizations and Geometrical Configuration of the Complexes

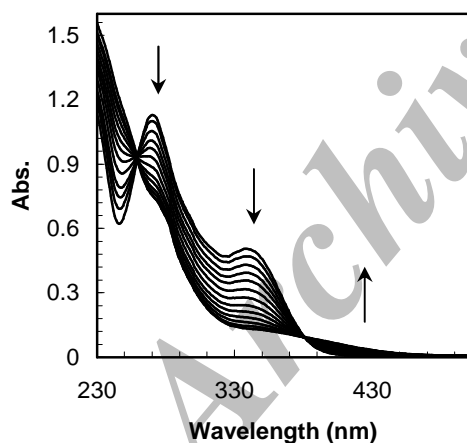
VO(IV) salt react with Schiff base ligands in 1:2 molar ratio in alcoholic medium to afford greenish-grey complexes.

Table 2. IR Spectral Data (cm⁻¹) of the Complexes

Compounds	ν_{O-H}	ν_{C-H}	$\nu_{C=N}$	$\nu_{C=C}$	ν_{M-N}	$\nu_{V=O}$	$\nu_{C=N}$
[VO(L ¹) ₂]	3425	2920	1606	1542	426	977	
[VO(L ²) ₂]		2997	1612	1542	440	972	
[VO(L ³) ₂]	3440	2854	1604	1502	426	974	
[VO(L ⁴) ₂]	3444	2965	1608	1504	432	978	
[VO(L ⁵) ₂]		2998	1612	1542	420	975	
[VO(L ⁶) ₂]		2889	1604	1539	435	983	
[VO(L ⁷) ₂]		3012	1608	1542	452	975	
[VO(L ⁸) ₂]	3444	3042	1604	1539	462	983	
[VO(L ⁹) ₂]	3444	2296	1608	1542	416	976	2229
[VO(L ¹⁰) ₂]		2986	1604	1585	466	983	2221
[VO(L ¹¹) ₂]	3445	2885	1608	1558	432	985	
[VO(L ¹²) ₂]	3483	2885	1604	1581	424	983	
[VO(L ¹³) ₂]	3444	2980	1612	1546	420	991	

Table 3. UV-Vis^a, Mass Spectra and Elemental Analysis Data of the Complexes

	λ_{max} (nm)	Mass spectra (m/z)	Elemental analysis (% , Found)		
			C	H	N
[VO(L ¹) ₂].H ₂ O	264,330(sh)	459, 263, 196	65.41(65.81)	4.64(4.25)	5.87(6.01)
[VO(L ²) ₂]	270,350,407(sh)	519, 293, 226, 66	64.74(64.64)	4.66(4.72)	5.39(5.29)
[VO(L ³) ₂].0.25H ₂ O	267,338(sh)	491, 213, 197, 66	62.97(62.55)	4.17(3.95)	5.65(5.89)
[VO(L ⁴) ₂].H ₂ O	266,349,410(sh)	491, 279, 213, 66	61.30(61.32)	4.35(4.39)	5.50(5.44)
[VO(L ⁵) ₂]	268,336(sh)	527, 298, 231, 66	59.11(57.52)	3.43(3.34)	5.30(4.99)
[VO(L ⁶) ₂]	266,340(sh)	527, 231, 66	59.11(59.51)	3.43(3.33)	5.30(5.07)
[VO(L ⁷) ₂]	266,336(sh)	614, 340, 276	50.60(50.29)	2.94(3.25)	4.54(4.73)
[VO(L ⁸) ₂].0.1H ₂ O	266,337(sh)	614, 340, 276	50.45(50.82)	2.96(2.82)	4.53(4.17)
[VO(L ⁹) ₂].0.75H ₂ O	244,273(sh)	508, 288, 221, 66	64.31(64.39)	3.76(3.43)	10.71(10.69)
[VO(L ¹⁰) ₂]	272,331(sh)	509, 221, 66	66.02(66.15)	3.56(3.51)	11.00(11.42)
[VO(L ¹¹) ₂].0.3H ₂ O	278,355(sh)	549, 308, 242, 66	56.29(56.03)	3.38(3.19)	10.10(10.22)
[VO(L ¹²) ₂].0.25H ₂ O	270,345(sh)	549, 308, 242, 66	56.38(56.33)	3.37(3.18)	10.12(10.22)
[VO(L ¹³) ₂].0.5H ₂ O	274,352	487,277,211	67.74(67.81)	5.08(5.25)	5.64(6.01)

^aSolvent is MeOH.**Fig. 1.** The variation of the electronic spectra of H₂L¹¹ titrated with VO(SO₄).nH₂O at 25 °C in 96% methanol.

The ligands and the complexes are stable at room temperature and are nonhygroscopic. The synthesized ligands and their complexes were characterized by elemental analysis, mass and spectral techniques. Furthermore, the thermodynamics and the antioxidant properties of the complexes were studied. The

optimum geometry of one of the newly synthesized complexes was 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 [21]. In addition the spectra of the ligands show -C=N band in the region 1608-1620 cm⁻¹, which is shifted to lower frequencies in the spectra of all the complexes (1606-1612 cm⁻¹) indicating the involvement of the -C=N nitrogen in the coordination to the metal ion [22,23]. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at 400-450 cm⁻¹ and 450-500 cm⁻¹ which could be attributed to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively [24,25]. Thus the oxovanadium(IV) complexes have the general structure which were shown in Scheme 2.

Elemental analysis. The stoichiometry of the ligands and the 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 the VO(IV)

complexes show good agreement with the proposed structures of the complexes (Table 3).

Mass spectra. The mass spectra of the vanadium(IV) chelates show intense peaks including $[\text{VOL}_2]$ and $[\text{VOL}_2+\text{H}]^+$ 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 $[\text{VOL}]^+$ and L^+ fragments (Table 3).

UV-Vis analysis. The ligands show two absorption bands at UV-Vis region. A $n-\pi^*$ transition band at 326-410 nm and a $\pi-\pi^*$ transition band at 240-300 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.

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 3). The electronic spectra of the formed complexes at the end of the titration process were the same as the electronic spectra of the separately synthesized complexes as is seen in Fig. 2.

Thermal analysis. The thermal dehydration and the decomposition of three ligands, HL^1 , HL^2 , HL^{10} and their complexes, $\text{VO}(\text{L}^1)_2$, $\text{VO}(\text{L}^2)_2$, $\text{VO}(\text{L}^{10})_2$, under investigation were studied to evaluate their thermal stability and thermal decomposition pathways, as can be seen from the TG/DTG curves presented in Fig. 3.

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 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 [26,27] in the temperature range 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.

From the thermogravimetric curve of HL^1 one can see that

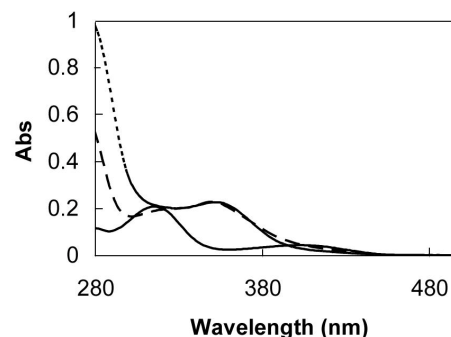


Fig. 2. UV-Vis spectra of HL^{13} (—), $\text{VO}(\text{L}^{13})_2$ separately synthesized (---) and the product at the end of titration (.....).

the weight loss of the ligand takes place in single-step in the temperature range 180-300 °C without residue in the sample holder at 300 °C (Fig. 3, curve a).

The thermal decomposition of HL^2 occurs in three steps. The first mass loss (observed 46.6%), can be seen between 300-400 °C (calcd. weight loss for 1 mol of $\text{C}_7\text{H}_8\text{O}$ 47.5%) corresponding to the elimination of 1 mol $\text{C}_7\text{H}_8\text{O}$ group. The decomposition continues with the gradual weight loss up to 450 °C. This weight loss in the temperature range 400-450 °C (observed 10%), assuming weight removal of the OH group (calcd. 7.5%). The third step of the thermal decomposition, which occurs in the range 450-600 °C, was assigned to the loss of the C_6H_6 group (observed 33.3%) (calcd. 34.4%) The final residue with attaining a constant weight (observed 10.6%) roughly corresponds to NC group (calcd. 11.4%) (Fig. 3, curve b).

For HL^{10} , a mass loss occurred within the temperature range 118-280 °C corresponding to the loss of the hydrated water molecule (observed 4.8%) (calcd. 7.4%) since the elemental analysis does not suggested water of hydration. The HL^{10} shows good stability and the decomposition temperature start above 320 °C. In the temperature range 320-396 °C a mass loss (observed 23%) occurred corresponding to the loss of CN and OH groups (calcd. 18.3%). At the temperature range 396-600 °C a mass loss (observed 23%) (calcd. 18.3% assuming weight loss for 1 mol of C_6H_6 group), occurred due to the elimination of a C_6H_6 group. The final residue with attaining a constant weight (observed 43%) roughly

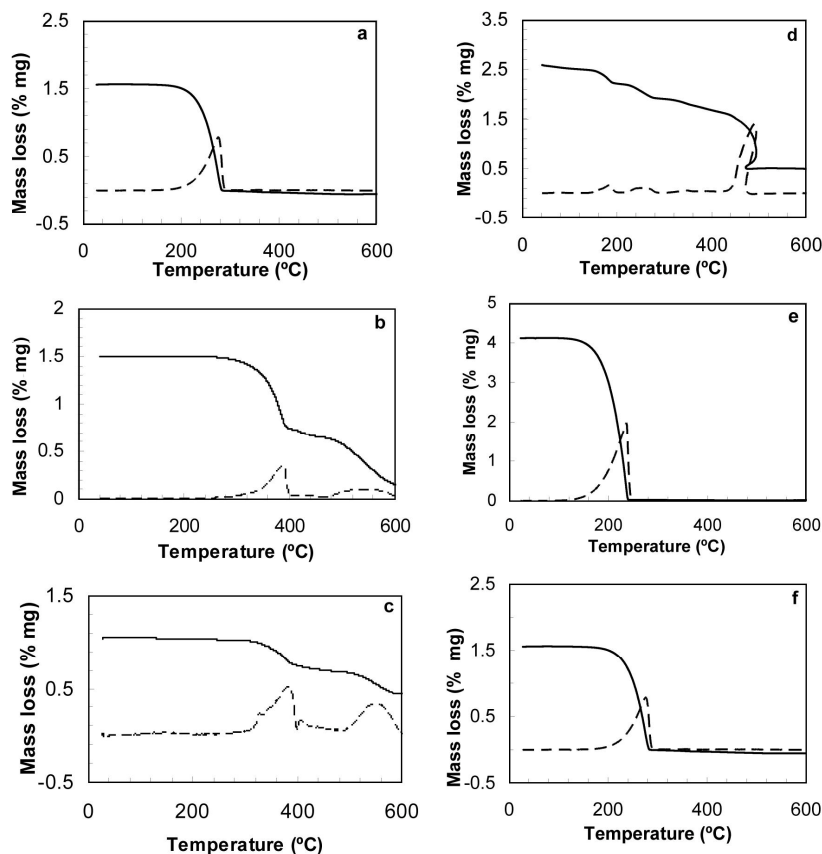


Fig. 3. TG (solid) and DTG (dash) curves: (a) HL^1 ; (b) HL^2 ; (c) HL^{10} ; (d) $[VO(L^1)_2]$; (e) $[VO(L^2)_2]$ and (f) $[VO(L^{10})_2]$.

corresponds to C_7H_7N (calcd. 43.7%) (Fig. 3, curve c).

The complex $VO(L^1)_2$ decomposes in three steps. The first step occurs between 151-207 °C (observed 12%) due to the hydrated water molecule in the structure. According to this the real mass loss is about 207 °C. The second thermal event was observed in the range of 207-300 °C is probably a partial decomposition of the ligand (observed 16%). The third mass loss between 300-500 °C was assigned to the loss of the rest of the ligand with the residue about 4% in the sample holder (Fig. 3, curve d).

The weight loss of $VO(L^2)_2$ and $VO(L^{10})_2$ takes place in a single-step. The decomposition temperatures of $VO(L^2)_2$ and $VO(L^{10})_2$ observed in the range of 140-245 °C and 194-290 °C, respectively without residue in the sample holder at 600 °C (Fig. 3, curves e,f).

According to the results discussed above, the order for

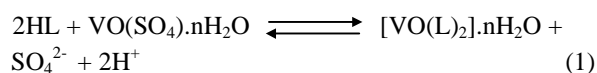
thermal stability found for the ligands is: $HL^{10} > HL^2 > HL^1$ and for the complexes is: $VO(L^1)_2 > VO(L^{10})_2 > VO(L^2)_2$. The number of decomposition steps of the ligand depends on the substituent group leading to differences in thermal process for the complexes, the number of steps and, in particular, the initial temperature of decomposition of these complexes depend on the equatorial ligand.

Thermodynamic Interpretations

With the goal of the study of the steric and the electronic parameters of the ligands on the formation constants and the thermodynamic free energy, the interaction of the ligands as donors and VO(IV) as acceptor were carried out.

The formation constants, K_f , were calculated using SQUAD computer program [28,29], 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 4.)

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 $\text{OH} > \text{OCH}_3 > \text{H} > \text{Br} \geq \text{Cl} > \text{CN}$. In fact, for the selected Schiff bases, Hammett type relationships were found between the $\log K_f$ values and σ_p , the *para*-substituent constant [30-32]. Such correlations are shown in Fig. 4.

To study the effect of the position of the substituents on the formation of the complexes, the substituted Schiff bases in the position-3 by hydroxy, chloro, bromo, nitro and cyano were selected. The results show that for substituents in position-3, $\log K_f$ has decreased, which indicates that this position has more steric effect than position-4. (See Table 4).

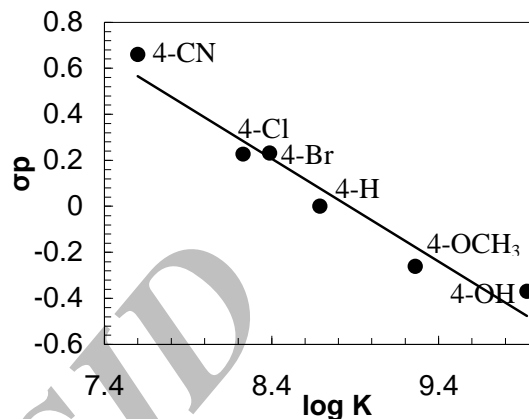


Fig. 4. Linear correlation between the *para* substituent constants, σ_p , and $\log K_f$ for the complexes, $\text{VO}(\text{L}^1)_2$, $\text{VO}(\text{L}^2)_2$, $\text{VO}(\text{L}^4)_2$, $\text{VO}(\text{L}^6)_2$, $\text{VO}(\text{L}^8)_2$ and $\text{VO}(\text{L}^{10})_2$ in methanol at 25 °C according to Scheme 2.

Solvent Effect

For studying the effects of solvent on the formation constant, we carried out the interaction of the metal ion with ligands in MeOH and CH_3CN solvents. The results show that the formation constants were solvent dependent and the trend

Table 4. The Formation Constants, $\log K_f$, for the VO(IV) Schiff Base Complexes at 25 °C in Methanol

ligand	$\log K_f$	ΔG° (kJ mol ⁻¹)	σ_p
HL ¹	8.69 ± 0.55	-49.58 ± 1.11	0
HL ²	9.26 ± 0.06	-52.81 ± 0.76	-0.268
HL ³	9.64 ± 0.24	-54.98 ± 0.19	
HL ⁴	9.93 ± 0.66	-56.63 ± 0.07	-0.370
HL ⁵	8.09 ± 0.09	-46.14 ± 0.09	
HL ⁶	8.23 ± 0.32	-46.93 ± 0.32	0.227
HL ⁷	8.22 ± 0.10	-46.88 ± 0.19	
HL ⁸	8.39 ± 0.23	-47.85 ± 0.37	0.232
HL ⁹	7.02 ± 0.15	-40.03 ± 0.44	
HL ¹⁰	7.60 ± 0.49	-43.34 ± 0.19	0.660
HL ¹¹	6.68 ± 0.10	-38.09 ± 0.12	
HL ¹³	8.46 ± 0.41	-48.25 ± 0.74	

Table 5. The Formation Constants, $\log K_f$, for the VO(IV) Complexes at 25 °C in Two Solvents

	HL ²	HL ³	HL ⁴	HL ⁸
CH ₃ CN	10.28 ± 0.16	9.86 ± 0.10	10.06 ± 0.63	8.98 ± 0.13
96% methanol	9.26 ± 0.06	8.98 ± 0.10	9.07 ± 0.69	8.39 ± 0.23

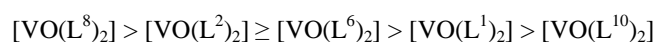
is related to the donor number of the solvents. The Gutmann donor number for CH₃CN is 14.1 and for MeOH is 30 [33]. The formation constants in MeOH with higher donor number are less than those in CH₃CN, therefore the formation constant decreases with increasing in donor number of the solvent (Table 5). These results show that the acceptor is better solvated in MeOH than in CH₃CN. According to Eq. (1), MeOH with higher donor number solvates VO(IV) center stronger than CH₃CN, so the metal ion tendency for the interaction with the donors decreases and the formation constants become lower in this solvent (See Table 5).

Trolox Equivalent Antioxidant Assay

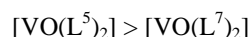
The Trolox Equivalent Antioxidant Capacity (TEAC) value is defined as the millimolar concentration of a Trolox solution having an antioxidant capacity equivalent to a 1 mM solution of the substance under investigation. Higher TEAC values indicate higher antioxidant activity; values ≥ 1 are highly desirable.

The total antioxidant capacities of the tested substances are shown in Table 6. According to these results, the investigated complexes did not show any significant antioxidant capacity.

According to these results, [VO(L⁸)₂] has the highest TEAC among all the other complexes. The complexes TEAC trend is as follow:



and



Computational Studies

Methodology. Molecular structural calculations were performed using GAUSSIAN03 [34] program at B3LYP/6-

Table 6. The Antioxidant Assay Results for the Compounds at 30 °C^a

Complexes	TEAC ^b
[VO(L ¹) ₂]	0.35 ± 0.08
[VO(L ²) ₂]	0.42 ± 0.19
[VO(L ⁵) ₂]	0.19 ± 0.05
[VO(L ⁶) ₂]	0.36 ± 0.11
[VO(L ⁷) ₂]	0.05 ± 0.02
[VO(L ⁸) ₂]	0.48 ± 0.02
[VO(L ¹⁰) ₂]	0.07 ± 0.04

^at = 6 min. ^bTEAC = Trolox equivalent antioxidant capacity.

311g//HF/6-311g level of theory. Geometry optimizations were carried out in the gas phase of the bis(salicylideneaniline)oxovanadium(IV) complex without imposing geometrical restrictions on the *cis* and *trans* conformers. Both conformers were optimized at HF/6-311g level of theory following the optimization by the MM+ molecular mechanic force field to assign force field parameters on the basis of bonding characteristics using standard package. In two cases, the local minimum energy of the optimized structures was computed at B3LYP using 6-311g basis set for studying the HOMO, LUMO, and the gap. The electronic properties of model compound, dipole moment and atomic charges, were also computed at the same level of theory.

Structural properties. The optimized structures of the *cis* and the *trans* conformers of the bis(salicylideneaniline)oxovanadium(IV), [VO(L¹)₂], (Scheme 2) are shown in Fig. 5. It can be seen that the *cis* conformer involves the H₂O molecule coordinated *cis* to V=O; the *trans* conformer has the H₂O molecule coordinated *trans* to V=O. Table 7 shows the

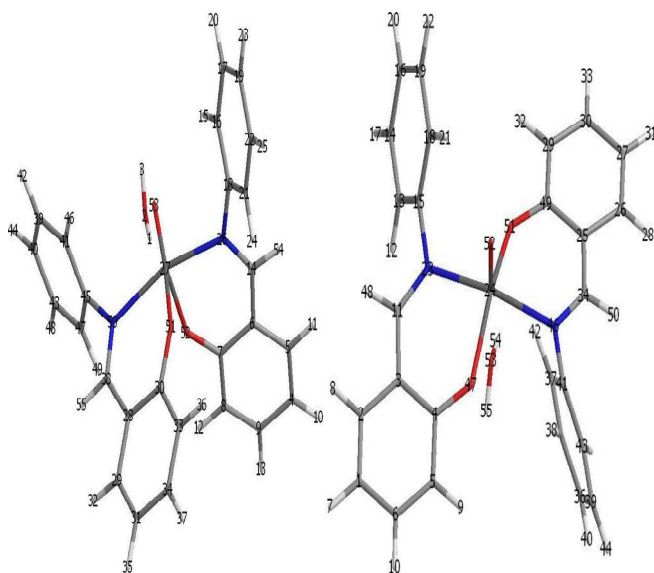


Fig. 5. The optimized structure for the *trans* (right) and *cis* (left) conformers of the salicylideneaniline complex, $[\text{VO}(\text{L}^1)_2]$. [Oxygen, red; nitrogen, blue; carbon, dark gray; hydrogen, light gray].

geometrical parameters, bond lengths and bond angles, computed at B3LYP/6-311g level of theory for the most stable conformer of the complex, *i.e.* *trans* conformer. The functional groups taking place in the different position leads the bond distances to be different in both conformers.

The distance between vanadium and oxygen of the water (V-O53) in *trans* conformer is longer than the V-O bond length, 2.362 Å versus 1.791 Å, as estimated for a V-O bond of unit valency [35]. This indicates that the water content is not coordinated to Vanadium oxide, V=O. On the other side, the bond length (1.571 Å) in V-O52 is in accord with theoretical study (1.59 Å) [36] and X-ray method (1.598 Å) [37]. Since the bond length reported here is less than a single bond; therefore, the double bond property is expected for V-O52 as also have been observed experimentally.

Electronic properties. It is reasonable to expect that the electronic properties of the *cis* and *trans* conformers to be quite different. The basic parameters of conformers calculated at B3LYP/6-311g level of theory are shown in Table 8.

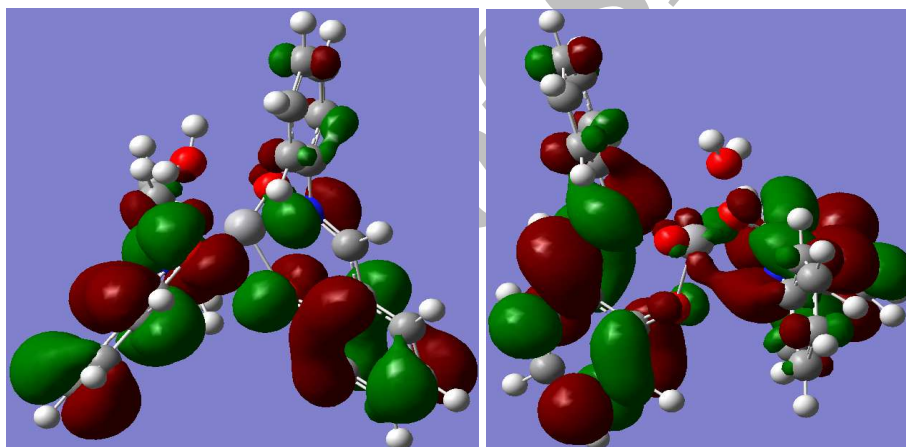
The lowest molecular energy corresponds to the molecular geometry in vacuo that shows the *trans* conformer is more stable than *cis* conformer by 10.503 kJ mol⁻¹. The molecular

Table 7. Structural Parameters for the Ground State of the *trans* Conformer of Salicylideneaniline Calculated at B3LYP/6-311g Level of Theory. Labels for Atoms can be Found in Fig. 5

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
V-O53	2.362	H54-O53-H55	115.896	O52-V-O53-H54	32.234
V-O47	1.943	O52-V-O47	105.298	O52-V-O53-H55	147.722
V-O51	1.943	O52-V-N23	96.185	O47-V-O53-H54	171.663
V-O52	1.571	O52-V-O51	105.296	O47-V-O53-H55	-8.294
V-N23	2.175	O52-V-N46	96.188	O51-V-O53-H54	-8.337
V-N46	2.175	O52-V-O53	180.000	O51-V-O53-H55	171.707
C4-O47	1.316	V-O51-C49	135.734	O52-V-O51-C49	80.666
C49-O51	1.316	V-O23-C15	117.998	O52-V-N46-C34	-95.859
O53-H54	0.943	V-O47-C4	135.733	O52-V-N46-C41	79.948
O53-H55	0.943	V-O53-H55	122.041	O52-V-N24-C41	79.948
C41-N46	1.436	V-O53-H54	122.063	O52-V-N23-C11	-95.838
C34-N46	1.284	V-N23-C11	124.039	O52-V-N23-C15	79.959
C15-N23	1.436	V-N46-C41	117.996	O51-V-O47-C4	-99.374
C11-N23	1.284	V-N46-C34	124.041	N23-V-O53-H55	-95.340

Table 8. The Computed Electronic Properties for the *cis* and the *trans* Conformers of the Complex

	<i>Cis</i>	<i>Trans</i>
E_{HF} (a.u.)	-2358.577	-2358.581
μ (Debye)	3.265	4.720
point group	C1	C1
HOMO (a.u.)	-0.080	-0.072
LUMO (a.u.)	-0.062	-0.063
HOMO-LUMO gap (eV)	0.488	0.254

**Fig. 6.** HOMO (left) and LUMO (right) orbitals of the *cis* conformer *in vacuo*.

energies mainly reflect the differences in bond distances and angles and to a much less extent the changes in torsional angles between the two conformers.

The *trans* conformer increases the HOMO and decreases the LUMO level, which shrinks the HOMO-LUMO gap (compared to *cis* conformer) by 0.234 eV.

As shown in Figs. 6 and 7, in the *cis* conformer the HOMO and LUMO are localized over the rings. While in the *trans* conformer, the HOMO is localized over the center of the molecule, involving V-O channels, and LUMO that is distributed over the complex is delocalized. Therefore, a *trans* conformer is expected to reduce the HOMO-LUMO gap of the complex. As a result, the electric dipole moment in the *cis* conformer is less than *trans* that in part explains the instability

of the conformer.

The atomic charges calculated by *ab initio* method at B3LYP/6-311g level of theory for two conformers are shown in Table 9. The trend of reinforcing by the enhancement of the charge over the vanadium in *trans* relative to the *cis* conformer suggests that this conformer might offer a valid effect on the structural properties of the complex although the charge on the center of the complex (V) for two conformers is not appreciably different.

Stability of the bis(salicylideneaniline)oxovanadium (IV) derivatives. The aim of this study was two-fold. First, synthesize the stable complexes of the salicylideneaniline and characterize them by the experimental results. Second, to investigate the conformer structures of a representative

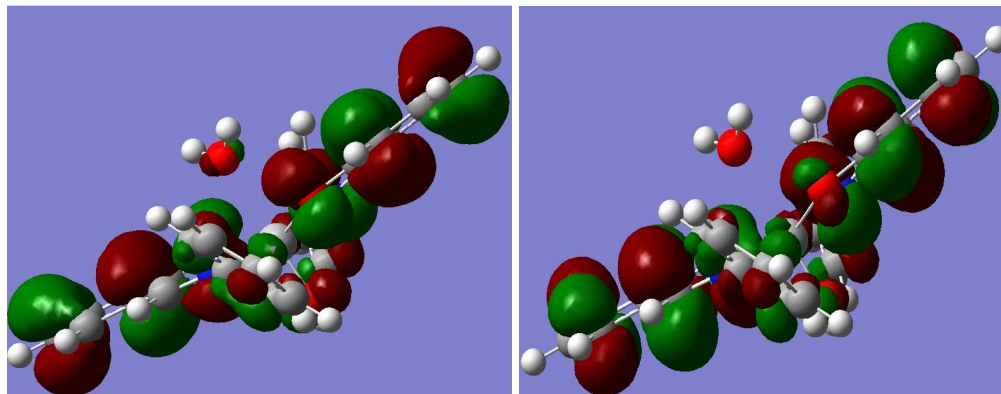


Fig. 7. The same as Fig. 6 but for the *trans* conformer.

Table 9. The Computed Mulliken Atomic Charges of the Complex for the *cis* and the *trans* Conformers. See Fig. 5 for Atomic Labels

No.	<i>Trans</i> conformer		<i>Cis</i> conformer	
	Symbol	Atomic charge	Symbol	Atomic charge
1	C	-0.1806	C	-0.2122
2	C	-0.1437	C	-0.0923
3	C	-0.1196	H	0.1476
4	C	0.3990	H	0.1523
5	C	-0.2163	H	0.1601
6	C	-0.0960	H	0.1479
7	H	0.1475	C	0.0847
8	H	0.1531	H	0.1996
9	H	0.1683	C	-0.1023
10	H	0.1474	C	-0.1851
11	C	0.0669	C	0.0671
12	H	0.1592	C	-0.1256
13	C	-0.0986	H	0.1576
14	C	-0.1738	C	-0.0852
15	C	0.1236	C	-0.1773
16	C	-0.1272	H	0.1553
17	H	0.1479	H	0.1782
18	C	-0.0687	H	0.1551
19	C	-0.1851	N	-0.6466
20	H	0.1502	V	1.6555
21	H	0.2019	C	-0.1059
22	H	0.1530	C	-0.1465
23	N	-0.6632	C	0.3884

Table 9. Continued

24	V	1.6689	C	-0.1808
25	C	-0.1195	H	0.1511
26	C	-0.1437	C	-0.2100
27	C	-0.1807	C	-0.0979
28	H	0.1531	H	0.1453
29	C	-0.2164	H	0.1473
30	C	-0.0961	H	0.1441
31	H	0.1476	C	0.0721
32	H	0.1683	C	-0.1794
33	H	0.1474	C	-0.1250
34	C	0.0669	C	-0.0483
35	C	-0.1852	H	0.1475
36	C	-0.1273	C	-0.1742
37	C	-0.0687	H	0.1496
38	H	0.1531	C	0.0728
39	C	-0.1738	H	0.1529
40	H	0.1502	C	-0.0704
41	C	0.1237	H	0.1497
42	H	0.2019	H	0.1756
43	C	-0.0985	N	-0.6374
44	H	0.1479	O	-0.7451
45	H	0.1592	O	-0.7122
46	N	-0.6630	O	-0.4994
47	O	-0.7214	H	0.1800
48	H	0.1825	H	0.1790
49	C	0.3990	C	-0.2122
50	H	0.1825	C	-0.0923
51	O	-0.7215	H	0.1476
52	O	-0.4946	H	0.1523
53	O	-0.8064	H	0.1601

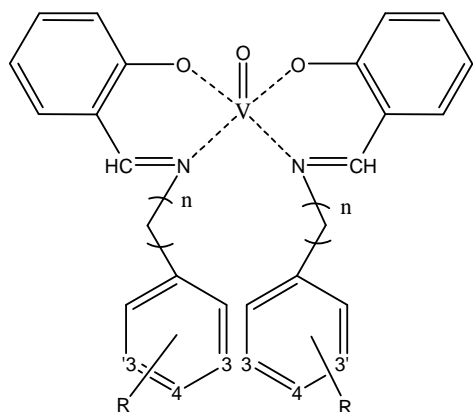
complex by structural optimization using the energy minimization in the gas phase.

The substitution of R with different groups provides different complexes. It is interesting to understand the role of R group (Scheme 3) as it produces preferentially certain complexes.

The optimized structures of the VO(IV) complex have been taken to describe molecular energies of the bis(salicylidene-3-chloroaniline)oxovanadium(IV) and bis

(salicylidene-4-chloroaniline)oxovanadium(IV). For this purpose we should have certain structural implications of increasing stability. The analysis of the molecular electronic structures of complexes revealed that occupying positions 3-3, 3-3', 3'-3', and 4-4 of the VO(IV) complex by chloride group lead to complexes with different stabilities. The computations indicate that 4-4 position (4-Cl) provides the most stable accommodation. See Fig. 8 for detail.

The most striking outcome of the present *ab initio* studies



Scheme 3. Occupying positions by R (Cl) group in the complex to be studied

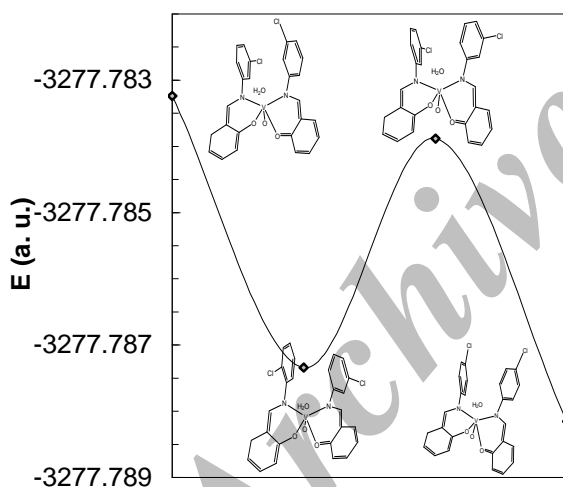


Fig. 8. The energy profile for the conformations of the bis(salicylidene-3-chloroaniline)oxovanadium(IV) and bis(salicylidene-4-chloroaniline)oxovanadium(IV) complexes as calculated at the B3LYP/6-311g level of theory.

is the observation that the structure with 4-4 positions occupied is consistent with the experimental formation constant of the salicylidene-chloroaniline. Therefore, the

bis(salicylidene-4-chloroaniline)oxovanadium(IV) is the most stable structure between chloride substituent complexes considered (Fig. 8) in gas phase and in methanol media. These results shed some additional light on the nature of the stability of the conformers and the most stable conformer of the derivatives of bis(salicylideneaniline)oxovanadium(IV) complex.

CONCLUSIONS

The structural, geometrical, thermal, thermodynamics and antioxidant properties of the oxovanadium(IV) complexes have been investigated. The structural and electronic properties of the *cis* and the *trans* conformers of the bis(salicylideneaniline)oxovanadium(IV) have been investigated by means of *ab initio* computational techniques. These calculations have shown that the *trans* conformer has a profound effect on the properties of the complex, $[\text{VO}(\text{L}^1)_2]$. The structural properties of *cis* and *trans* are similar and the geometrical differences are mainly limited to the position of the functional groups in the rest of complexes. The '*trans*' conformer is the most stable complex in gas phase. It is argued that substitution in 4-4 positions increases the stability. This explains the experimental formation constants values. Interestingly, according to the electronic structure, occupying the 4-4 positions with Cl promotes the complex by a reduction in HOMO-LUMO gap which leads to an increase in the formation of *trans* conformer. This finding is further supported by the fact that the experimental formation constant of the bis(salicylidene-4-chloroaniline)oxovanadium(IV) complex determined is larger than bis(salicylidene-3-chloroaniline)oxovanadium(IV). According to the thermodynamic studies, the formation constants of the complexes depend upon the steric and the electronic characteristic of the ligands. Moreover, the molecular electronic structure of each complex plays an important role on its thermodynamics and the thermal properties. It is evident that there is a close relationship between these various properties. According to the antioxidant capacities of the tested substances, the investigated complexes did not show any significant antioxidant capacity.

ACKNOWLEDGMENTS

We are grateful to Shiraz University Research Council for their financial support.

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