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New tetradentate Schiff bases of 2,2-dimethyl-1,3-diaminopropane and acetylacetone derivatives and their vanadyl complexes

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Two new symmetrical tetradentate Schiff base ligands have been synthesized.
- Their oxovanadium(IV) complexes have been synthesized and characterized.
- From TG curves, the order of thermal stability for the complexes is VOL¹ > VOL².
- The electrochemical properties of the vanadyl complexes were investigated in DMF.



The new tetradentate Schiff bases and their vanadyl complexes were synthesized and spectrally charac-

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ABSTRACT

A series of new VO(IV) complexes with two new tetradentate Schiff base of 4,4'-(2,2-dimethylpropane -1,3-diyl)-bis(azan-1-yl-1-yldene)dipent-2-en-2-ol) $[H_2L^1]$ and 3,3'-(2,2-dimethylpropane-1,3-diyl)azan-1-yl-1-ylidene)-bis(1-phenylbut-1-en-1-ol) $[H_2L^2]$ (which have been derived from 2,2-dimethyl-1,3-diaminopropan, and diketones of acetylacetone and benzoylacetone) were synthesized and characterized by ¹H NMR, ¹³C NMR, FT–IR, mass and UV–Vis spectrophotometry. The electrochemical properties of the vanadyl complexes were investigated by means of cyclic voltammetry. The oxidation potentials are increased by increasing the electron-withdrawing properties of functional groups of the Schiff base ligands according to the trend of Me < Ph. The thermogravimetry (TG) and differential thermoanalysis (DTA) of the VO(IV) complexes were carried out in the range of 20–700 °C. The complexes were decomposed in two stages. Also, decomposition of the synthesized complexes is related to the Schiff base characteristics. The thermal decomposition of the studied reactions was first order. The kinetic parameters for the decomposition steps in vanadyl complexes thermograms have been calculated.

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1. Introduction

Schiff bases are one of the most versatile classes of ligands for the study of the coordination chemistry of transition metals [1]. Their ease of synthesis (by the condensation of an aldehyde/ketone with an amine), multidenticity (from mono to hexadentate), combination of donor atoms (coordination usually through the imine nitrogen and other atoms like oxygen, sulfur or nitrogen) and stability have made them the preferred ligand systems in catalysis, biological modeling, the design of molecular ferromagnets, liquid crystals [2–4], medical imaging [5] and optical materials [6]. Schiff

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base ligands are able to coordinate many different metals [7–10], and to stabilize them in various oxidation states.

The interest in vanadium coordination chemistry promoted by the presence of this element in biological systems [11], and by catalytic [12], and medicinal [13] properties of its compounds. The potential catalytic abilities of vanadium compounds have led to an increasing interest in vanadium coordination chemistry in recent years [8]. Homogeneous catalysts of oxovanadium(IV) complexes have been shown to induce organic reactions such as the oxidation of sulfides and sulfones [14,15], the epoxidation of alkenes [12,16,17], the hydroxylation of hydrocarbons [18], and the oxidation of alcohols to aldehydes and ketones [19,20]. These studies are indicative that oxovanadium(IV) complexes are potential catalysts to influence the yield and selectivity in chemical transformation. Furthermore, complexes of Schiff bases showed promising applications in biological activity and biological modeling applications [21–23]. Besides the insulin-like activity of oxovanadium(IV) and oxovanadium(V) compounds [24,25], its presence in vanadium dependent haloperoxidases has particulary stimulated the search for structural and functional models [26].

In the present study, we report acetylacetone derivative Schiff base ligands. The structures of these compounds were studied by ¹H NMR, ¹³C NMR, IR, UV–Vis and mass spectra. Then their vanadyl complexes were prepared and the spectral and thermal properties of these complexes were studied in details. Also the kinetic parameters for decomposition steps in thermograms of these complexes were calculated. The electronic influence of acetylacetone derivatives on electrochemical properties of vanadyl(IV) Schiff base complexes were studied.

2. Experimental

2.1. Reagents and instruments

All of the chemicals and solvents used for synthesis were of commercially available reagent grade and used without purification. They included 2,2-dimethyl-1,3-diaminopropan, acetylacetone, benzoylacetone, vanadyl acetylacetonate. Organic solvents used included methanol, *n*-hexane, *n*-heptane and ethylacetate. All reagents and solvents were commercially obtained from Merck, Aldrich or Fluka.

Infrared spectra were recorded as KBr pellets using Shimadzu FTIR-8300 spectrophotometer. ¹H and ¹³C NMR spectra were obtained in CDCl₃ solutions with a Bruker Avance DPX-500 spectrometer. All of the scanning UV–Vis spectra were recorded on a Per-kin–Elmer Lambda 25 spectrophotometer. Thermogravimetry (TG) and differential thermoanalysis (DTA) were carried out by using a PL-1500. The measurements were performed in air atmosphere. The heating rate was held at 10 °C min⁻¹. A Metrohm 797 VA system was employed to evaluate electrochemical measurements. Voltammetric measurements were performed at room temperature (25 °C) in DMF solution with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. An Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a *Pt* wire as counter electrode and a glassy carbon electrode as working electrole (metrohm glassy carbon, 0.0314 cm²) were used for the electrochemical studies.

2.2. Synthesis of the ligands

2.2.1. The preparation of 4,4'-(2,2-dimethylpropane-1,3-diyl)-bis(azan-1-yl-1-yldene)dipent-2-en-2-ol), $[H_2L^1]$

To a stirred methanolic solution (30 ml) of acetylacetone (1 ml, 10 mmol) 2,2-dimethyl-1,3-diaminopropan (0.50 g, 5 mmol) was added. The bright yellow solution was stirred and heated to reflux for 12 h. A white precipitate was obtained that was filtered off,

recrystallized with ethylacetate and *n*-hexane. Yield (80%), m.p.: 68 °C; ¹HNMR (δ , ppm, 500 MHz, CDCl₃): 1.09 (s, 6H, CH₃), 1.92 (s, 6H, CH₃), 2.03 (s, 6H, CH₃), 3.15 (d, *J* = 5, 4H, CH₂), 5.00 (s, 2H, HC=C), 11.20 (b, 2H, NH); ¹³CNMR (δ , ppm, 125 MHz, CDCl₃): 19.39, 24.00, 29.09, 36.18, 50.77, 95.91, 195.38; FT–IR (KBr, cm⁻¹): 3400 (ν _{N-H}), 3000, 2900 (ν _{C-H}), 1620 (ν _{C=O}), 1470, 1430 (ν _{C=C}); ESI–MS (m/z(%)): 266 [M⁺], 251, 182, 154, 124, 112, 98, 70, 55; UV–Vis: (λ _{max}, nm, MeOH): 262, 311, 318.

2.2.2. Preparation of $3,3'-(2,2-dimethylpropane-1,3-diyl)azan-1-yl-1-ylidene)-bis(1-phenylbut-1-en-1-ol), <math>[H_2L^2]$

To a stirred *n*-heptane solution (30 ml) of benzoylacetone, (1.62 g, 10 mmol) 2,2-dimethyl-1,3-diaminopropan (0.50 g, 5 mmol) was added. The bright yellow solution was stirred and heated to reflux for 10 h. A white precipitate was obtained that was filtered off, recrystallized with heated methanol. Yield (80%), m.p.: 110 °C; ¹HNMR (δ , ppm, 500 MHz, CDCl₃): 1.24 (s, 6H, CH₃), 2.11 (s, 6H, CH₃), 3.34 (d, *J* = 5, 4H, CH₂), 5.70 (s, 2H, HC=C), 7.42–7.90 (m, 10H, Ar), 11.91 (b, 2H, NH); ¹³CNMR (δ , ppm, 125 MHz, CDCl₃): 19.98, 24.27, 36.30, 51.11, 93.02, 127.33–140.71, 188.48; FT–IR (KBr, cm⁻¹): 3400 (v_{N-H}), 3100, 3000 (v_{C-H}), 1610 (v_{C=O}), 1470, 1440 (v_{C=C}); ESI–MS (m/z(%)): 390 [M⁺], 285, 216, 174, 158, 105; UV–Vis: (λ_{max} , nm, MeOH): 246, 346.

2.3. Preparation of vanadyl complexes

The complexes were prepared by a general procedure: the ligand, H_2L^1 (0.053 g, 0.2 mmol) or H_2L^2 (0.078 g, 0.2 mmol) was dissolved in 20 ml of methanol. A methanolic solution of vanadyl acetylacetonate (0.05 g, 0.2 mmol) was added to above solution and the reaction mixture was refluxed for 4 h. The colored solution was concentrated to yield green powders. The products washed with water and dried in vacuum. General structure of oxovanadium(IV) complexes has been shown in Fig. 1.

VOL¹: yield: 60%, m.p.: >250 °C; FT–IR (KBr, cm⁻¹): 2925 (v_{C-H}), 1555 ($v_{C=N}$), 1420 ($v_{C=C}$), 1359 (v_{C-O}), 998 (v_{V-O}); ESI–MS (m/ z(%)): 331 [M⁺]; UV–Vis: (λ_{max} , nm, MeOH): 273, 305, 400.

VOL²: yield: 50%, m.p.: >250 °C; FT–IR (KBr, cm⁻¹): 3056, 2962 (ν_{C-H}), 1597 ($\nu_{C=N}$), 1450 ($\nu_{C=C}$), 1294 (ν_{C-O}), 988 (ν_{V-O}); ESI–MS (m/z(%)): 455 [M⁺]; UV–Vis: (λ_{max} , nm, MeOH): 242, 342, 420.

3. Results and discussion

3.1. ¹H NMR spectra

The ¹H NMR spectra of ligands were recorded in CDCl₃. The ¹H NMR spectra of the ligands show a broad resonance at δ 11.20, 11.91 ppm due to the hydrogen-bonded N—H moiety, indicating that the ligands are in the keto–amine tautomers. Further, the



Fig. 1. General structure of oxovanadium(IV) complexes.



Scheme 1. Tetradentate Schiff base tautomers.



Scheme 2. Mass fragmentation pattern of H₂L¹ compound.

spectrum shows the phenyl multiple at δ 7.42–7.90 ppm for H₂L² ligand. The resonances about δ 5.00 and 5.70 ppm are consistent with a vinyl center. The signals observed at δ 3.15 and 3.34 ppm are assigned to $-CH_2$ protons of diamine, that coupling with the -NH. The signals due to the methyl protons of the diketones are observed at δ 1.92, 2.03, 2.11 ppm. The sharp singlet signals observed at δ 1.09 and 1.24 ppm are assigned to methyl protons of the propyl bridge.

Tetradentate Schiff base ligands, have been studied extensively for more than 50 years [27,28]. Theoretically, this type of ligands can exist in the three tautomeric forms shown in Scheme 1. Typical R-groups have been —Me, —Ph. The most common backbones (BB) have been straight alkyl chains containing 2–12 CH₂ groups, short branched alkyl chains [27–29].

3.2. ESI-Mass spectral studies of Schiff bases and their complexes

The fragmentation mode of H_2L^1 occurs through three main pathways in Scheme 2. The spectrum showed a molecular ion peak at m/z 266 which is equivalent to its molecular weight. In case of H_2L^2 , the molecular ion peak at m/z 390 is ascribed to $C_{25}H_{30}N_2O_2$. In the spectrum of VOL¹ complex, the molecular ion peak M⁺, which is equivalent to its molecular weight is observed at m/z 331. In the spectrum of VOL² complex, the molecular ion peak M⁺, which is equivalent to its molecular weight is observed at m/z 455.

3.3. Infrared spectral studies of Schiff bases and their complexes

The IR spectra of the free Schiff base ligands and the complexes show several bands in the 400-4000 cm⁻¹ region. It would be difficult to elucidate the correct tautomer from the IR spectra of H₂L¹ and H_2L^2 . The hydrogen-bonded N–H bands are extremely weak and broad, spanning from about 2700 to 3700 cm⁻¹ with the center somewhere 3400 cm⁻¹. The carbonyl stretch shows a strong band about 1610 cm⁻¹. The C–N stretching mode shows up clearly as a strong band about 1300 cm⁻¹. The comparison of the spectra of the complexes with the ligands provides evidence for the coordination mode of ligand in catalysts. Absence of N-H band in the spectra of complexes indicates the breaking of hydrogen bonding followed by coordination of nitrogen to the metal ion after deprotonation [30]. A sharp band appearing at 1540–1619 cm^{-1} due to $\nu_{(C=N)}$ (azomethine) [30,31]. This indicates the involvement of azomethine nitrogen in coordination. Vanadyl complexes have the band which appeared at 988–998 cm⁻¹ is assigned to $v_{(V=O)}$ [32,33]. The band is observed as a new peak for the complexes and is not observed in the spectra of free ligands. Tetradentate Schiff base oxovanadium(IV) complexes with $\nu_{(V=0)}$ around 970 cm^{-1} are in a monomeric form. Thus, both of VOL^1 and VOL^2 are assigned to have monomeric structure [34]. The IR spectra of H_2L^1 and VOL^1 are shown in Figs. 2 and 3.



Fig. 3. IR spectrum of VOL¹ compound.

3.4. Electronic spectra

In solution, the electronic spectra of the Schiff base ligands consist of a relatively intense band in the 250–300 nm region, involving intraligand $\pi \to \pi^*$ transition [35]. The complexes show an intense CT transition in 400–420 nm regions. Also, the d–d transition in this type of complexes appears in the range above of 500 nm. However, this band does not appear due to the low intensity of the d–d transitions [36]. The electronic spectra of the H_2L^2 and VOL^2 are shown in Fig. 4.

3.5. The electrochemical study of vanadyl complexes

The cyclic voltammetry of VOL complexes were carried out in DMF solution at room temperature. An oxidation peak is observed at about Ca. -0.754 V. VOL¹ is oxidized to [VOL¹(solvent)]⁺ in a quasireversible (peak-to-peak separation >100 mV) one electron



Fig. 4. Electronic spectra of the H_2L^2 and VOL^2 .

 Table 1

 Electrochemical data for the oxidation of oxovanadium(IV) complexes in DMF.

Complex	E_p^a (V)	E_p^c (V)	$E_{1/2}(V)$	$\Delta E_{\rm p}\left(V\right)$
VOL ¹ VOL ²	$-0.754 \\ -0.503$	$-0.900 \\ -0.996$	$-0.827 \\ -0.749$	0.146 0.493

step [25]. The electron is removed from the nonbonding orbitals and the V(V) complex is formed. Upon reversal of the scan direction, the V(V) complex is reduced to V(IV) at lower potentials. Multiple scans which resulted in nearly superposable cyclic voltammograms show that the five coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. The oxidation potentials for complexes are shown in Table 1. The formal potentials $(E_{1/2} (IV/V))$ of the V(IV/V) redox couple were calculated as the average of the cathodic E_{pc} and anodic E_{pa} potentials peak of this process. The cathodic peak current of the complexes were increased and the peak shifted to more negative potentials direction with increasing the scan rates. To studying the effect of functional groups of the Schiff base ligands on the oxidation potentials of [VOL], two vanadyl Schiff base complexes were studied by the cyclic voltammetry method. The results show that the anodic peak potential E_{pa} varies as can be expected from the electronic effects of the substituents on Schiff base complexes. Thus, E_{pa} becomes more positive according to the sequence Me < Ph, which reflect the variation of the electrode potential as a function of the electron-withdrawing ability of the substituent.

3.6. Thermal analysis

The thermal decomposition of the studied complexes presented pathways which depend on the nature of the ligands. The TG and DTA figures of another compound have the same trend. The absence of weight loss up to 80 °C indicates that the crystalline solids have no water molecule. Also, in the studied complexes, the TG showed no weight loss up to 150 °C indicating the absence of water molecule coordinated to complexes [30,31]. The complexes were decomposed in two steps. The DTA curve of VOL¹ shows endothermic peak in the temperature range 200-275 °C which is due to weight loss of 70.86 % (calculated weight loss for 1 mol of organic part of the complex: 69.55%) corresponding to the elimination of organic part. The second step of the thermal decomposition, which occurs in the range 300-390 °C, is also endothermic, was assigned to the loss of oxygen atom (observed 4.59 %) (calculated 4.84 %) and VO_3 formed. Finally, the metal oxide corresponds to V_2O_5 formed above 660 °C with exothermic peak. The DTA curve of VOL² shows endothermic peak in the temperature range 210– 290 °C which is due to weight loss of 31.04 % corresponding to the elimination of partial organic part. The second step of the thermal decomposition, which occurs in the range 385-475 °C, is also endothermic, was assigned to the loss of residue of organic part (observed 50.95 %). Finally, the metal oxide corresponds to V_2O_5 formed above 660 °C with exothermic peak. The temperature range and the percent of loss weight calculated and found for two steps are presented in Table 2.

Table 2

Thermal and kinetics parameters for vanadyl complexes.

3.7. Kinetic studies

All the well-defined stages were selected to study the decomposition kinetics of the complexes. Various methods exist for studying the thermal decomposition of complexes. In this work, Broido's method was utilized [37]. Broido has suggested a simple and sensitive graphical method for the treatment of TGA data. According to this method, the weight at any time, $t(W_t)$ is related to the fraction of initial molecules not yet decomposed (y) by the equation:

$$v = \frac{N}{N_0} = \frac{(W_t - W_\infty)}{(W_0 - W_\infty)}$$
(1)

where W_0 is the initial weight of the materials and W_{∞} is the weight of residue at the end of decomposition.

If the pyrolysis is carried out isothermically, the velocity of the reaction is given by:

$$\frac{dy}{dt} = ky^n \tag{2}$$

where n is the reaction order. The velocity constant k changes with absolute temperature according to the equation of Arrhenius.

$$k = A \cdot e^{-E/RT} \tag{3}$$

and if *T* is linear function of time *t*, therefore:

$$T = T_0 + u \cdot t \tag{4}$$

u is the heating rate. The first derivative of this equation is:

$$dT = u \cdot dt \tag{5}$$

This rearranges to:

$$\frac{dy}{y^n} = -\left(\frac{A}{u}\right) \cdot e^{-\frac{E}{RT}} dt \tag{6}$$

The thermogravimetric analysis curve for this reaction represents the last equation integrated from a temperature T_0 , where y = 1, to a temperature for another value of y.

$$\int_{y}^{1} \frac{dy}{y^{n}} = -\frac{A}{u} \int_{T_{0}}^{T} e^{-\frac{E}{RT}} dT = \frac{A}{u} \int_{T}^{T_{0}} e^{-\frac{E}{RT}} dT$$
(7)

The main consideration of this method is that the reaction is of the first order. With this supposition, the left side of the reaction can be resolved.

$$\int_{y}^{1} \frac{dy}{y^{n}} = \int_{y}^{1} \frac{dy}{y} = -\ln y = \ln\left(\frac{1}{y}\right)$$
(8)

There are various methods for resolving the right side of the equation. Broido's method is based on approximations done by other authors. We have utilized the approximations introduced by Wendland [38].

$$e^{-\frac{E}{RT}} \approx \left(\frac{T_m}{T}\right)^2 e^{-\frac{E}{RT_m}} \tag{9}$$

 T_m is the temperature at which the maximum reaction velocity occurs. Introducing this approximation has

Compounds	ΔT^{a} (°C)	Reduce mass ^b (%)	E_a (kJmol ⁻¹)	$A(s^{-1})$	ΔS (Jmol ⁻¹ K ⁻¹)	ΔH (kJmol ⁻¹)	ΔG (kJmol ⁻¹)
VOL ¹	200-275	69.55(70.86)	323.78	1.82×10^9	-73.0	319.22	359.06
VOL ²	300-390 210-290	4.84(4.59) 30.12(31.04)	34.47 77.51	1.05×10^{-3} 3.20×10^{-3}	-327 -297	28.95 72.83	245.76 240.04
	385-475	49.91(50.95)	122.48	8.90×10^{-2}	-273	116.26	320.47

^a The temperature range of decomposition pathways.

^b Percent of weight lose calculated (found).

$$\ln\frac{1}{y} = \frac{A}{u} \int \left(\frac{T_m}{T}\right)^2 e^{-\frac{E}{RT}} dT$$
(10)

changing variable has

$$x = \frac{1}{T} \Rightarrow dx = \frac{1}{T^2} dT \Rightarrow dT = -\left(\frac{1}{x^2}\right) dx \tag{11}$$

$$\ln\frac{1}{y} = \frac{A}{u}T_m^2 \int x^2 e^{-\frac{E}{h}x} \left(-\frac{1}{x^2}\right) dx \tag{12}$$

$$\ln\frac{1}{y} = \frac{A.R.T_m^2}{E.u} \cdot e^{-\frac{E}{R}X}$$
(13)

$$\ln\frac{1}{y} = \frac{A.R.T_m^2}{E.u} \cdot e^{-\frac{E(1)}{R(T)}}$$
(14)

This equation can be represented by:

$$\ln(\ln 1/y) = -\frac{E}{R}\left(\frac{1}{T}\right) + const.$$
(15)

Eq. (15) is a straight line. The gradient of the graph lnln(1/y) vs. (1/T) is the activation energy $E_a^{\#}$ and the intercept is frequency factor *A*.

$$-E_a^{\#} = slope \times 2.303 \times R \tag{16}$$

where $E_a^{\#}$ is activation energy and *R* is the gas constant. Application of this method used to determine the kinetic parameters for complexes.

The entropy of activation $\Delta S^{\#}$ was calculated using the equation

$$A = \frac{kTm}{h} e^{\frac{hS^{\#}}{R}}$$
(17)

where k, h and T_m are the Boltzmann's constant, the Planck's constant and the peak temperature, respectively. The enthalpy and free energy of activation were calculated using equations:

$$\Delta H^{\#} = E_a^{\#} - RT \tag{18}$$

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{19}$$

The activation energy $E_a^{\#}$ in the different stages is in the range of 34–323 kJmol⁻¹. The respective values of the pre-exponential factor A vary from 1.05×10^{-4} to 1.82×10^9 s⁻¹. The corresponding values of the entropy of activation, $\Delta S^{\#}$, were in the range of -73 to $-327 \text{ Jmol}^{-1}\text{K}^{-1}$. The $\Delta S^{\#}$ values for complexes were found to be negative. This indicates that the activated complex is more ordered than the reactants and/or the reactions are slow [39]. The enthalpy of activation, $\Delta H^{\#}$, values were in the range of 28–319 kJmol⁻¹. The positive values of $\Delta H^{\#}$ means that the decomposition processes are endothermic. The corresponding values of the free energy of activation, $\Delta G^{\#}$, were in the range of 240–359 kJmol⁻¹.

4. Conclusions

In this work, two new symmetrical tetradentate Schiff base ligands containing the N₂O₂ donor group have been synthesized and spectrally characterized. Then, their oxovanadium(IV) complexes have been synthesized and characterized by several spectroscopic methods. According to the results discussed from TG curves, the order of thermal stability for the complexes is $VOL^1 > -$ VOL². The number of decomposition steps of the ligands depends on the substituent group leading to differences in thermal process for the complexes. The electrochemical properties of the vanadyl complexes were investigated in DMF show the anodic peak potential becomes more positive according to the sequence Me < Ph.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.07.062.

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