



Synthesis, spectroscopy, electrochemistry and thermal study of vanadyl tridentate Schiff base complexes

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ABSTRACT

The VO(IV) complexes of tridentate ONO Schiff ligands were synthesised and characterized by IR, UV–vis and elemental analysis. The electrochemical properties of the vanadyl complexes were investigated by cyclic voltammetry. A good correlation was observed between the oxidation potentials and the electron withdrawing character of the substituents on the Schiff base ligands, showing the following trend: MeO < H < Br < NO₂ and H < Cl. The thermogravimetry (TG) and differential thermoanalysis (DTA) of the VO(IV) complexes were carried out in the range of 20–700 °C. The VOL¹(OH₂) decomposed in two steps whereas the remaining six complexes decomposed in three steps. The thermal decomposition of these complexes is closely related to the nature of the Schiff base ligands and proceeds via first order kinetics.

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1. Introduction

Schiff bases are a good series of ligands capable of binding metal ions leading to metal complexes with interesting properties. The high stable potential of Schiff base complexes in different oxidation states increased the application of these compounds in a wide range. Some of these types of ligands and their metal complexes have been investigated because of their interesting and important properties such as their ability to reversibly bind oxygen [1] and their use in catalyses for oxygenation and oxidation reactions of organic compounds and electrochemical reduction reactions [2–6]. The vanadyl Schiff base complexes play an important role in this area [7] and have been investigated as model compounds to clarify several biochemical processes [8,9]. In this area tridentate vanadyl Schiff base complexes act as protein tyrosine phosphates inhibitors [10] and show photo-induced DNA cleavage activities [11].

Thermogravimetry (TG) and differential thermoanalysis (DTA) are valuable techniques for studying the thermal properties of compounds [12–16]. The electrochemical methods would be envisioned to provide highly valuable information on the catalytic processes since catalytic conversions are frequently accompanied by the change in the oxidation state of the central metal and the structure of the complex. Knowledge of electronic and steric effects to control the redox chemistry of these metal complexes may prove to be critical in the design of new catalysts. Having continued our

studies on vanadyl Schiff base complexes [17,18], here in we report the electronic influence of salicylaldehyde derivatives of ONO tridentate Schiff bases on thermal and electrochemical properties of vanadyl(IV) Schiff base complexes (Fig. 1). The thermal decomposition kinetic parameters, calculated using Coats and Redfern method [19], are also reported and discussed.

2. Experimental

2.1. Chemicals and apparatus

All of the chemicals and solvents used for synthesis and electrochemistry were of commercially available reagent grade and used without purification. The elemental analysis was determined on a CHN-O-Heraeus elemental analyzer. Infrared spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4000–400 cm⁻¹. UV–vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. The ¹H NMR spectra were recorded in DMSO-d₆ on DPX-400 MHz FT-NMR. Thermogravimetry (TG) and differential thermoanalysis (DTA) were carried out on a PL-1500. The measurements were performed in air atmosphere. The heating rate was kept at 10 °C min⁻¹.

Cyclic voltammograms were performed using an autolab modeler electrochemical system (ECO Chemie, Utrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working

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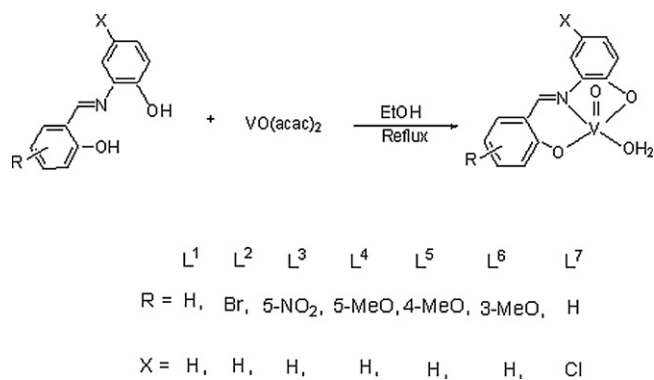


Fig. 1. The structure of Schiff bases and their complexes.

Table 1
Elemental analysis data for the complexes.

Compounds	Calculated/found (%)		
	C	H	N
VOL ¹	52.72 (53.48)	3.74 (4.07)	4.73 (5.25)
VOL ²	41.62 (41.23)	2.68 (2.89)	3.74 (4.23)
VOL ³	45.76 (45.29)	2.93 (3.12)	8.21 (8.65)
VOL ⁴	51.55 (51.83)	4.02 (4.18)	9.62 (10.15)
VOL ⁵	51.55 (52.15)	4.02 (4.27)	9.62 (10.24)
VOL ⁶	51.55 (52.31)	4.02 (4.25)	9.62 (9.98)
VOL ⁷	47.21 (47.96)	3.05 (3.26)	4.23 (4.74)

electrode (metrom glassy carbon, 0.0314 cm²) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in acetonitrile solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

2.2. Synthesis

The tridentate Schiff base ligands, L¹–L⁷, were prepared according to the literature [20]. The vanadyl complexes were synthesised by refluxing methanolic solutions of the tridentate Schiff base ligands and vanadylacetylacetonate. The reaction was continued for 2 h. The resulting green precipitate was filtered off, washed with methanol and dried in vacuum.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis (Table 1) is in good agreement with those calculated for the proposed formula.

3.2. IR characteristics

The IR spectra of the free Schiff base ligands and the complexes exhibit several bands in the 400–4000 cm⁻¹ region (Table 2). The OH stretching frequency of the ligands was approved in the 2500–3500 cm⁻¹ region due to the internal hydrogen bonding vibration (O–H...N). This band was disappeared in the spectra of the complexes [15,16,21].

The characteristic C=N bond appears in 1611–1643 cm⁻¹ and 1597–1607 cm⁻¹ region for ligands and complexes respectively. The C=N stretching in the complexes is generally shifted to a lower frequency, indicating a decrease in the C=N bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair [15,16].

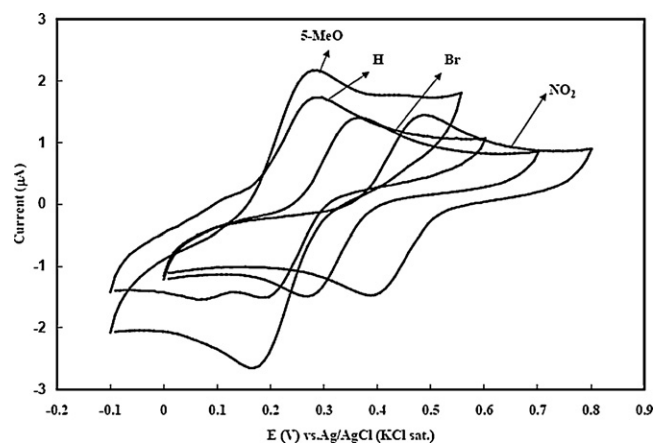


Fig. 2. Cyclic voltammograms of VOL in acetonitrile at room temperature. Scan rate: 100 mV/s.

The band at 963–989 cm⁻¹ is assigned to $\nu(\text{V}=\text{O})$. This band is observed as a new peak for the complexes and is not observed in the spectrum of free ligands [22].

3.3. Electronic spectra

The spectral data of the free ligands and their complexes are collected in Table 3.

The electronic spectra of the Schiff base ligands in solution consists of relatively intense bands in the 250–400 nm region, involving $\pi \rightarrow \pi^*$ transitions [20]. The bands at higher energies correspond to $\pi \rightarrow \pi^*$ transitions of aromatic rings, while the band at lower energies is attributed to the $\pi \rightarrow \pi^*$ transition of azomethine group. Some of the vanadyl complexes exhibit an intense CT transition in 400–470 nm regions, which overlaps with the azomethine transition.

3.4. The electrochemical study of vanadyl complexes

The cyclic voltammetry of VOL(OH₂) complexes were carried out in acetonitrile solution at room temperature. A typical cyclic voltammogram of VOL¹(OH₂) complex in the potential range from 0.0 to 1.0 V (vs. Ag/AgCl) is shown in Fig. 2 (H). An oxidation peak is observed at about Ca. 0.287 V. VOL¹(OH₂) is oxidized to the mono cation [VOL¹(OH₂)]⁺ in a fully reversible one electron step [18]. 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 resulted in nearly superposable cyclic voltammograms, thereby showing that the five coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. These results revealed that the redox process of all vanadyl Schiff base complexes under study is the one-electron transfer reaction. The oxidation potentials for the different complexes are set out in Table 4. The formal potentials ($E_{1/2}(\text{IV} \leftrightarrow \text{V})$) for the V(IV/V) redox couple were calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials of this process.

In order to investigate the effect of functional groups of the Schiff base ligands on the oxidation potential of [VOL(OH₂)], a series of the vanadyl Schiff base complexes were studied by the cyclic voltammetry method. The results show that the anodic peak potential (E_{pa}) varies as it can be expected from the electronic effects of the substituents at position 5. Thus, E_{pa} becomes more positive showing the following trend; MeO < H < Br < NO₂ and H < Cl. Similar results have been reported previously for analogous vanadyl(IV), copper(II), nickel(II) and cobalt(III) systems, and have been

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