

Electrochemistry, Thermal analysis, and Theoretical Study of Vanadyl Schiff Base Complexes

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ABSTRACT

The VO(IV) complexes of tridentate ONO Schiff base ligands derived from 2-aminobenzoic acid and salicylaldehyde derivatives were synthesized and characterized by IR, UV-Vis and elemental analysis. Electrochemical properties of the vanadyl complexes were investigated by cyclic voltammetry. A good linear correlation was observed between the oxidation potentials and the electron-withdrawing character of the substituents on the Schiff bases, showed the following trend: Me O < H < Br < NO₂. The thermogravimetry (TG) and differential hemiparalysis (DTA) of the synthesized complexes were carried out in the range of 20–700 °C. All of the complexes decomposed in three steps. The thermal decomposition pathways were closely related to the nature of the Schiff base ligands and preceded via first-order kinetics. The structures of compounds were determined by ab initio calculations. The optimized molecular geometry was calculated at the B3LYP/6-31G(d) level. The results suggested that, in the complexes, V(IV) ion was in square-pyramid or TBP (trigonal bipyramidal) NO₄ coordination geometry. Also, the bond lengths and angles were studied and compared.

Keywords: Hemiparalysis, Molecular Geometry, Trigonal Bipyramidal, Thermogravimetry

I. INTRODUCTION

Metal Schiff base complexes have been investigated because of their interesting and important property such as their ability to reversibly bind oxygen [1]. The applications of these compounds in many areas were increased because of the high stable potential of Schiff base complexes in different oxidation states. They were used as catalysts for oxygenation and oxidation reactions of organic compounds and also electrochemical reduction reactions [2-7]. Vanadyl Schiff bases played a unique role [8] and had been investigated as model compounds to clarify several biochemical processes [9,10]. Also the tridentate vanadyl Schiff base complexes acted as protein tyrosine phosphates inhibitors [11] and showed photo-induced DNA cleavage are also reported and discussed. The structures of compounds are determined by ab initio calculations. The optimized

molecular geometry is calculated at the B3LYP/6-31G(d) level.

Thermogravimetry and hemiparalysis techniques are valuable for studying the thermal properties of compounds [13-17]. The electrochemical methods can 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 metal Schiff base complexes may prove to be critical in the design of new catalysts. Having continued our studies on vanadyl Schiff base complexes [18-21], herein 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).

II. EXPERIMENTAL

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 done on a CHN-O-Heraeus elemental analyzer. Infrared spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4,000-400 cm^{-1} . UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190-900 nm. 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 $^{\circ}\text{C min}^{-1}$. Cyclic voltammograms were performed using an autolab modelar electrochemical system (ECO Chemie, Utrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie) in conjunction with a threeelectrode 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 electrode (Metrohm glassy carbon, 0.0314 cm^2) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in dimethylformamide (DMF) solution with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

Synthesis of Schiff Base Ligands The L1 Schiff base ligand was synthesized according to the literature [23]. The other tridentate Schiff base ligands, L 2 -L 4, were prepared according to the following procedure. The appropriate amounts of salicylaldehyde and its derivatives were added to a methanolic solution of 2-aminobenzoic acid (1:1 mol ratio). The solution was refluxed for 3 h. The precipitate was filtered, washed

with methanol and recrystallized by dichloromethane/methanol mixed solvent through the partial evaporation of dichloromethane. L 1 : Yield: 81%, m.p.: 212 $^{\circ}\text{C}$. IR (KBr pellets, cm^{-1}): 2500-3100 (νOH), 1685 ($\nu\text{C=O}$) and 1617 ($\nu\text{C=N}$). λ_{max} (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) (ethanol): 255 (25000), 339 (9800). L 2 : Yield: 82%, m.p.: 190 $^{\circ}\text{C}$. IR (KBr pellets, cm^{-1}): 2500-3100 (νOH), 1700 ($\nu\text{C=O}$) and 1635 ($\nu\text{C=N}$). $^1\text{H NMR}$ (DMSO, δH): 12.41 (s, 1H, OH), 10.23 (s, 1H, phenolic, OH), 8.88 (s, 1H, imine), 6.48-7.84 (m, aromatic protons), 3.16-3.73 (m, methoxy), ppm, λ_{max} (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) (Ethanol): 253 (12700), 348 (4900), 430 (1000). L 3 : Yield: 80%, m.p.: 205 $^{\circ}\text{C}$. IR (KBr pellets, cm^{-1}): 2500-3100 (νOH), 1700 ($\nu\text{C=O}$) and 1636 ($\nu\text{C=N}$). λ_{max} (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) (ethanol): 257 (10000), 341 (2900), 420 (1100). L 4 : Yield: 76%, m.p.: 273 $^{\circ}\text{C}$. IR (KBr pellets, cm^{-1}): 2500-3100 (νOH), 1705 ($\nu\text{C=O}$), 1636 ($\nu\text{C=N}$) and 1328 (νNO_2). $^1\text{H NMR}$ (DMSO, δH): 12.01 (s, 1H, OH), 10.27 (s, 1H, phenolic, OH), 9.08 (s, 1H, imine), 6.45-8.75 (m, aromatic protons), ppm, λ_{max} (nm) (ϵ , $1 \text{ mol}^{-1} \text{ cm}^{-1}$) (ethanol): 277 (8800), 375 (900).

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