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

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ABSTRACT

The new tetradentate unsymmetrical N_2O_2 Schiff base ligands and VO(IV) complexes were synthesised and characterized by using IR, UV–Vis and elemental analysis. 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 MeO < H < Br < NO_2. 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 synthesised complexes is related to the Schiff base characteristics. The thermal decomposition of the studied reactions was first order.

1. Introduction

The high stability potential of Schiff base complexes with different oxidation states extended the application of these compounds in a wide range. The complexes studied were known as catalysts in organic redox and electrochemical reduction reactions [1–4]. Knowledge of electronic and steric effects to control the redox chemistry of these compounds may prove to be critical in designing new catalysts. The vanadyl Schiff base complexes play an important rule in this area [5]. Vanadium complexes are very interesting model compounds to clarify several biochemical processes [6,7].

Thermogravimetry (TG) and differential thermoanalysis (DTA) are valuable technics for studying the thermal behaviour of chemical compounds [8–12]. Also the electrochemical methods can be envisioned to provide valuable information on the catalytic processes since catalytic conversions are frequently accompanied with the changes in the structure of complexes and metal oxidation states. The present study describes the electronic influence of salophen derivatives on thermal and electrochemical properties of vanadyl(IV) Schiff base complexes (Fig. 1). The electrochemical properties of the vanadyl complexes were studied by cyclic voltammetry in DMF solvent. Kinetics and thermodynamic parameters were calculated using Coats and Redfern [13] method.

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 analyses were determined by CHN–O–Heraeus elemental analyzer. Infrared spectra were recorded by FT-IR JASCO-680 spectrophotometer in the 4000–400 cm^{-1}. UV–Vis spectra were recorded by means of JASCO V-570 spectrophotometer in the range of 190–900 nm. The ^1H NMR spectra were recorded in DMSO-d_6 solvent by DPX-400 MHz FT-NMR. 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}.

Cyclic voltammograms were performed by using an autolab modelar electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie) in conjunction with a three-electrode system and a PC for data 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 (metrom glassy carbon, 0.0314 cm^2) were used for the electrochemical studies. Voltammetric measurements were performed at room temperature in DMF solution with

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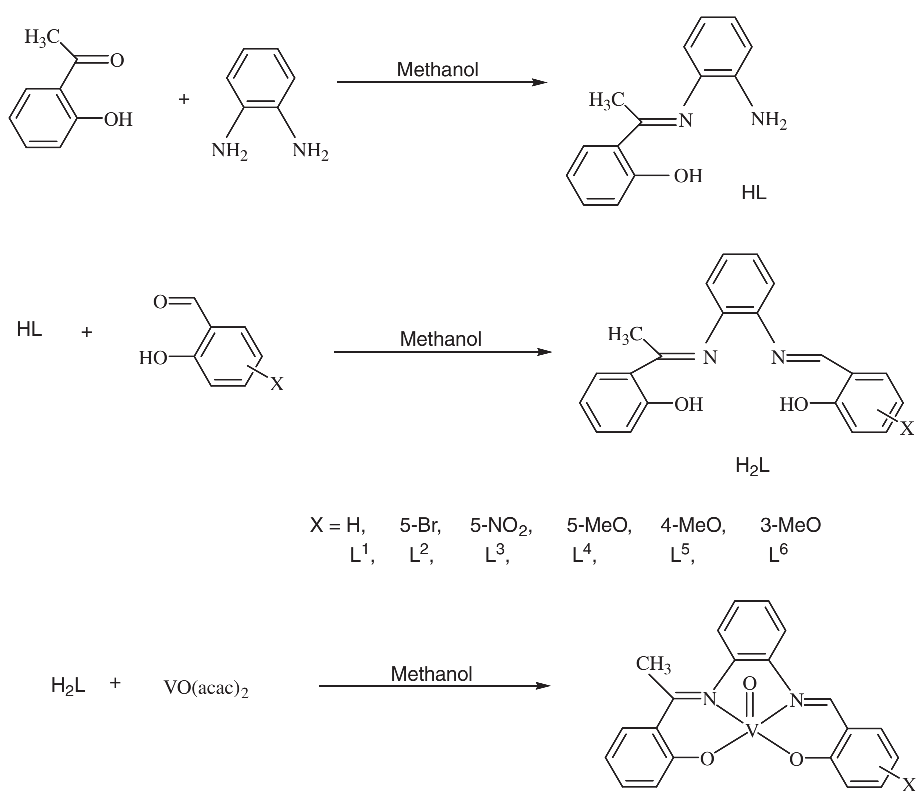

Fig. 1. The structure of Schiff bases and their complexes.

0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

2.2. Synthesis

The tetradentate Schiff base ligands, L^1–L^4, the new L^5 and L^6 were prepared according to the literature [14]. The vanadyl complexes were synthesised by refluxing a methanolic solution of the tetradentate Schiff base ligands and vanadylacetylacetonate. The reaction was continued for 2 h until a green precipitate was obtained. It was filtered, washed with methanol and dried in vacuum.

H_2L^5 yield (80%): ($C_{21}H_{18}N_2O_2$), FT-IR (KBr cm^{-1}) ν_{max} 1635 (C=N), 1504 (C=C), 1222 (C–O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) ($CHCl_3$): 313 (3400), 278 (7400). ^1H NMR (DMSO-d_6, 400 MHz) $\delta = 2.50$ (s, 3H, CH_3), $\delta = 3.80$ (s, 3H, O–CH_3), $\delta = 6.20$–7.80 (m, 11H), $\delta = 9.00$ (s, 1H, HC=N), $\delta = 12.90$ (s, 1H, OH), $\delta = 14.30$ (s, 1H, OH).

H_2L^6 yield (85%): ($C_{21}H_{18}N_2O_2$), FT-IR (KBr cm^{-1}) ν_{max} 1643 (C=N), 1461 (C=C), 1257 (C–O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) ($CHCl_3$): 343 (14 000), 265 (42 000). ^1H NMR (DMSO-d_6, 400 MHz) $\delta = 2.50$ (s, 3H, CH_3), $\delta = 3.60$ (s, 3H, O–CH_3), $\delta = 6.10$–7.50 (m, 11H), $\delta = 9.80$ (s, 1H, HC=N), $\delta = 15.40$ (s, 2H, OH).

VOL^1 yield (80%): Anal. Calc. for $C_{21}H_{16}N_2O_3V$: C, 63.79; H, 4.05; N, 7.08. Found: C, 63.95; H, 4.09; N, 7.12%. FT-IR (KBr cm^{-1}) ν_{max} 1610 (C=N), 976 (V=O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 393 (24 500), 320 (27 000), 244 (58 000).

VOL^2 yield (80%): Anal. Calc. for $C_{21}H_{15}BrN_2O_3V$: C, 52.95; H, 3.16; N, 5.90. Found: C, 53.57; H, 3.21; N, 5.98%. FT-IR (KBr cm^{-1}) ν_{max} 1600 (C=N), 981 (V=O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 389 (11 500), 320 (13 000), 277 (19 000), 249 (32 000).

VOL^3 yield (85%): Anal. Calc. for $C_{21}H_{15}N_3O_5V$: C, 57.27; H, 3.40; N, 9.54. Found: C, 57.89; H, 3.47; N, 9.83%. FT-IR (KBr cm^{-1}) ν_{max} 1609 (C=N), 1324 (NO_2), 991 (V=O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 372 (40 000), 311 (48 000).

VOL^4 yield (85%): Anal. Calc. for $C_{22}H_{18}N_2O_4V$: C, 62.11; H, 4.23; N, 6.58. Found: C, 62.68; H, 4.32; N, 6.87%. FT-IR (KBr cm^{-1}) ν_{max} 1614 (C=N), 1273 (C–O), 980 (V=O). UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 469(sh) (19 000), 397 (29 000), 322 (45 000), 247 (84 000).

VOL^5 yield (80%): Anal. Calc. for for $C_{22}H_{18}N_2O_4V$: C, 62.11; H, 4.23; N, 6.58. Found: C, 62.46; H, 3.25; N, 6.65%. FT-IR (KBr cm^{-1}) ν_{max} 1614 (C=N), 1242 (C–O), 978 (V=O) . UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 387 (26 000), 325 (21 000), 243 (37 000).

VOL^6 yield (75%): Anal. Calc. for for $C_{22}H_{18}N_2O_4V$: C, 62.11; H, 4.23; N, 6.58. Found: C, 62.93; H, 4.28; N, 6.77%. FT-IR (KBr cm^{-1}) ν_{max} 1605 (C=N), 1249 (C–O), 986 (V=O) . UV–Vis, λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (ethanol): 401 (4200), 342 (65 000), 310 (56 000), 241 (93 000).

3. Results and discussion

3.1. IR characteristics

The IR spectra of the free Schiff base ligands and the complexes show several bands in the 400–4000 cm^{-1} region. The OH stretching frequency of the ligands is observed in the region of 2500–3100 cm^{-1} due to the internal hydrogen bonding vibration (O–H···N). This band disappeared in the spectra of the complexes [11,12,15].

The free ligands have a characteristic C=N bond in 1611–1643 cm^{-1} region. For the Schiff base complexes C=N was observed in 1600–1614 cm^{-1}. The C=N stretching band of the schiff base complexes is generally shifted to a lower frequency, indicating a decrease in the C=N bond order due to the coordinate bond