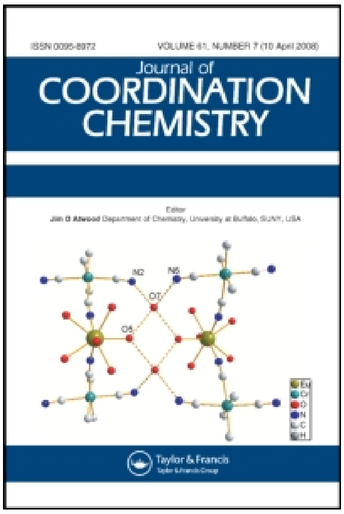

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Synthesis, characterization and studies of mechanochemical, electrochemical, and thermal behavior of electronegative oxovanadium(IV) Schiff-base complexes

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Synthesis, characterization and studies of mechanochemical, electrochemical, and thermal behavior of electronegative oxovanadium(IV) Schiff-base complexes

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This article describes the synthesis and characterization of electronegative oxovanadium(IV) complexes containing tetradentate Schiff-base ligands derived from condensation of 1,3-propanediamine and 1,8-naphthylamine with 5-bromo-3-nitro-2-hydroxybenzaldehyde. New VOL^1: [VO(5-Br-3-NO_2salnaph)] and VOL^2: [VO(5-Br-3-NO_2salpn)] complexes were obtained in orange polymeric form with (V=O) stretching bands at 884 and 876 cm^{-1}, respectively. The orange VOL^1 and VOL^2 complexes turn dark brown and green, respectively, when ground thoroughly in mortars. X-ray powder diffraction patterns of the ground VOL^1 complex (VOL^{1g}) scarcely show diffraction peaks. The data suggest that the linear chain polymeric structure in VOL^1 is destroyed on grinding to yield fragments of the polymeric chains. The color of VOL^2 changed from orange to dark green (VOL^{2g}), and the intensity of the V=O stretching bands of the polymeric form decreased with a complementary increase of those of the monomeric forms on grinding. The ground product of VOL^2 showed the V=O stretching band at 984 cm^{-1}, in addition to the original 860 cm^{-1} absorption. The dark green VOL^{2g} complex and dark brown VOL^{1g} complex turned to orange complexes after being suspended in absolute ethanol (99.8%, UV–IR spectroscopic grade), as a mechanochemical behavior. The redox processes of $VOL^{1,2}$ were reversible in DMF solution. The redox potentials of $VOL^{1,2}$ were determined to be 920 and 950 mV, respectively.

Keywords: Mechanochemical; Thermal; Oxovanadium(IV) complexes; Electrochemical

1. Introduction

Tetradentate Schiff-base complexes of oxovanadium(IV) have green monomeric structures with square-pyramidal coordination or orange linear chain structures ($\cdots V{=}O \cdots V{=}O \cdots V{=}O \cdots$) with distorted octahedral coordination in the solid state [1–3]. The green monomeric structure is observed for complexes like [VO (salen)] (salen: *N*,*N*′-salicylideneethylenediamine) and the orange polymeric linear chain structure is observed for complexes like [VO(5-NO_2-salen)] (5-NO_2-salenH_2: *N*,*N*′-di-5-nitrosalicylideneethylenediamine) with electron-withdrawing nitro substituents at the

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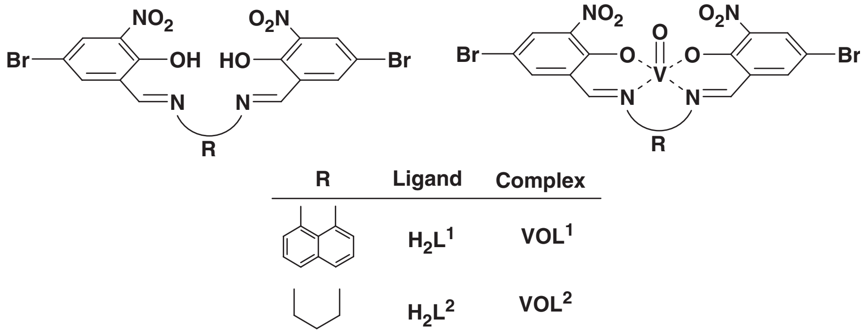

Scheme 1. Vanadyl Schiff base complexes.

5-position of the salicylaldehyde [4]. IR spectra of vanadyl Schiff-base complexes show two kinds of V=O stretching bands around 960–990 cm^{-1} for the monomeric forms and 850–880 cm^{-1} for the polymeric forms [5–8]. Electrochemical investigations of vanadyl Schiff-base complexes have been reported several times [9]. Also, electronic studies of vanadyl complexes with one 3d electron have been reported [10, 11]. There is considerable interest in catalytic reactivity, solvatochromism, and mechanochemical reactions of oxovanadium(IV) complexes [12]. In earlier work, we have synthesized some similar Schiff-base complexes of oxovanadium(IV) [13, 14] and have studied the reactivity of these complexes as catalysts for the aerobic oxidation of olefins [15–17]. Currently, we report the solvatochromism behavior of new electronegative vanadyl Schiff-base complexes [18]. In this article we report the synthesis, characterization, electrochemical, thermal, and mechanochemical behavior of new polymeric oxovanadium(IV) Schiff-base complexes derived from 1,3-propanediamine and 1,8-naphthylamine as the diamine and 5-bromo-3-nitro-2-hydroxybenzaldehyde as the aldehyde (scheme 1).

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as KBr pellets using a Unicam Matson 1000 FT-IR, ^1H NMR spectra by a Bruker FT NMR 500 (500 MHz) spectrophotometer ($CDCl_3$ and $(CD_3)_2SO$) and electronic spectra on a CARY 100 Bio UV–Vis spectrophotometer. Elemental analyses (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN–O–Rapid (Elementar-Analysesysteme, GmbH).

Cyclic voltammetry was performed using a 757VA Computrace Metrohm. The working, auxiliary, and reference electrodes were glassy carbon, platinum wire, and AgCl/Ag, respectively. Electrochemical measurements were performed at room temperature under argon with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte with 10^{-3} M complexes.

2.2. *Materials*

The solvents were of spectroscopic grade and used without purification, except in the case of pyridine, which was distilled immediately before use. 1,3-Propanediamine was distilled prior to use and 5-bromo-3-nitro-2-hydroxybenzaldehyde was prepared according to the literature procedures [19].

2.3. *Synthesis of Schiff-base ligands*

The Schiff-base ligands were quantitatively prepared by reaction of 1,8-naphthylamine, 1,3-propanediamine, with 2 equivamounts of 5-bromo-3-nitro-salicylaldehyde in absolute ethanol.

2.3.1. Synthesis of H_2L^1: (5-bromo-3-nitro salnaph). To a stirred ethanolic solution (30 mL) of 5-bromo-3-nitro-salicylaldehyde (0.492 g, 2 mmol) a solution of 1,8-naphthylamine (1 mmol) in 30 mL of absolute ethanol was added dropwise. After the addition was complete, the mixture was stirred and refluxed for 1 h. The mixture was then cooled and the red precipitate of the ligand was collected by filtration, washed with ethanol and dried in a desiccator. Yield of [5-bromo-3-nitro salnaph]: 0.276 g (45%). Anal. Calcd for $C_{24}H_{14}N_4O_6Br_2$: C, 46.90; H, 2.28; N, 9.12. Found: C, 46.62; H, 2.08; N, 9.07. m.p.: 153°C. IR (KBr, cm^{-1}): 1608 [υ(C=N)], 3390 [υ(O–H)]. ^1H NMR (500 MHz, $CDCl_3$): 14.1 (s, 2H, OH), 9.4 (s, 2H, Ar–CH=N), 6.8-8.0 (m, 10H, Ar).

2.3.2. Synthesis of H_2L^2: (5-bromo-3-nitro salpn). This ligand was prepared following the same procedure as described for H_2L^1 except 1,3-propanediamine was used instead of 1,8-naphthylamine. Yield of [5-bromo-3-nitro salpn]: 0.397 g (75%). Anal. Calcd for $C_{17}H_{14}Br_2N_4O_6$: C, 38.49; H, 2.64; N, 10.56. Found: C, 38.55; H, 2.32; N, 10.23. IR (KBr, cm^{-1}): 1636 [υ(C=N)], 3443 [υ(O–H)]. ^1H NMR (500 MHz, $CDCl_3$): 13.6 (s, 2H, OH), 8.6 (s, 2H, Ar–CH=N), 6.8–7.8 (s, 4H, Ar), 4.1 (t, 4H, α-CH_2), 2.1 (q, 2H, β-CH_2).

2.4. *Preparation of the vanadyl Schiff-base complexes*

All complexes were prepared by reaction of Schiff bases with equiamounts of vanadyl acetylacetonate [$VO(acac)_2$] in absolute methanol.

2.4.1. Synthesis of the [VO(5-Br-3-NO_2salnaph)]$\cdot 2H_2O$. To a hot methanolic solution (70 mL) of $VO(acac)_2$ (0.265 g, 1 mmol), 5-bromo-3-nitrosalnaph (0.614 g, 1 mmol) and pyridine (1.5 mL) was added, and the mixture was vigorously stirred for 2 h under reflux. The resulting orange polymeric precipitate was collected by filtration, washed with ethanol and ether, and dried in air. Yield of [VO(5-Br-3-NO_2salnaph)]: 0.300 g (42%). Anal. Calcd for $C_{24}H_{12}Br_2N_4O_7V \cdot 2H_2O$: C, 40.27; H, 2.23; N, 7.83. Found: C, 40.5; H, 2.38; N, 8.01. IR (KBr, cm^{-1}): 884 [υ(V=O)], 1601 [υ(C=N)]. UV–Vis spectrum [DMSO (nm), ε(l $mol^{-1}cm^{-1}$)]: 763 (123), 561 (343) [figure 1(a)].

2.4.2. Synthesis of the [VO(5-Br-3-NO_2salpn)]$\cdot H_2O$. To a hot methanolic solution (70 mL) of $VO(acac)_2$ (0.265 g, 1 mmol), 5-bromo-3-nitrosalpn (0.530 g, 1 mmol) and pyridine (1.5 mL) was added, and the mixture was vigorously stirred for 2 h under reflux. The resulting light brown polymeric precipitate was collected by filtration,

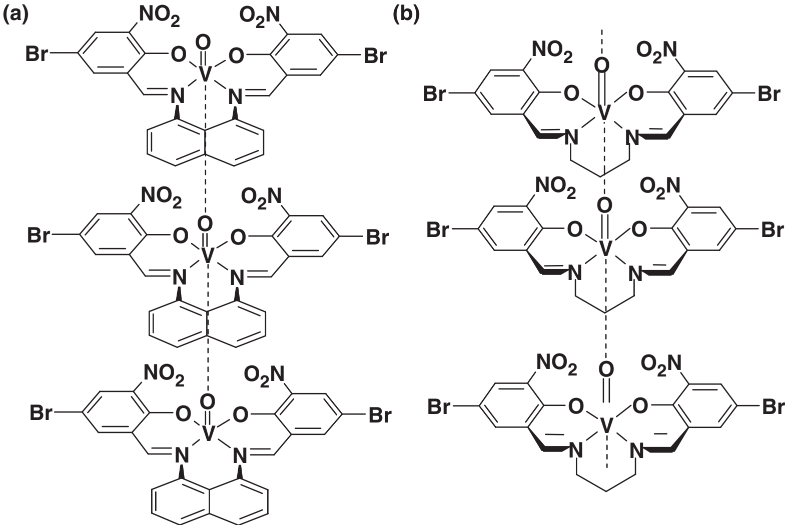

Figure 1. Polymeric form of VOL^1 (a) and VOL^2 (b).

washed with ethanol and ether, and dried in air. Yield of [VO(5-Br-3-NO_2salpn)]: 0.511 g (79%). Anal. Calcd for $C_{17}H_{12}Br_2N_4O_7V{\cdot}H_2O$: C, 33.28; H, 2.28; N, 9.13. Found: C, 33.51; H, 2.45; N, 9.42. IR (KBr, cm^{-1}): 876 [υ(V=O)], 1615 [υ(C=N)]. UV–Vis spectrum [DMSO (nm), ε(l $mol^{-1}cm^{-1}$)]: 729 (155), 556 (508) shoulder, 411 (6344) [figure 1(b)].

3. Results and discussions

3.1. *Characterization of vanadyl complexes*

Oxovanadium(IV) complexes were obtained by reaction of tetradentate ligands with $VO(acac)_2$ [20]. The yields of the complexes were reasonable. The IR spectrum of $VOL^{1,2}$ show V=O stretching at 884–876 cm^{-1}, indicative of polymeric form of the complexes [5, 6]. The C=N stretching vibrations of the ligands are at 1608–1636 cm^{-1} and shift approximately $10 \pm 5\,cm^{-1}$ to lower wave numbers upon coordination to V=O. Electronic spectra of the complexes show d–d bands around 763–411 nm in DMSO, similar to those of VOL^x in polar solvents [10]. Elemental analyses are in agreement with the structure of the complexes.

3.2. *Electrochemical studies*

Electrochemical studies were carried out in anhydrous DMF by cyclic voltammetry. The working, auxiliary, and reference electrodes were glassy carbon, platinum wire, and AgCl/Ag, respectively. Electrochemical measurements were performed at room temperature under argon with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte with 10^{-3} M complexes. Figures 2(a) and 2(b) respectively show the cyclic voltammetry curves of 10^{-3} M of VOL^1 and VOL^2 in DMF at variable

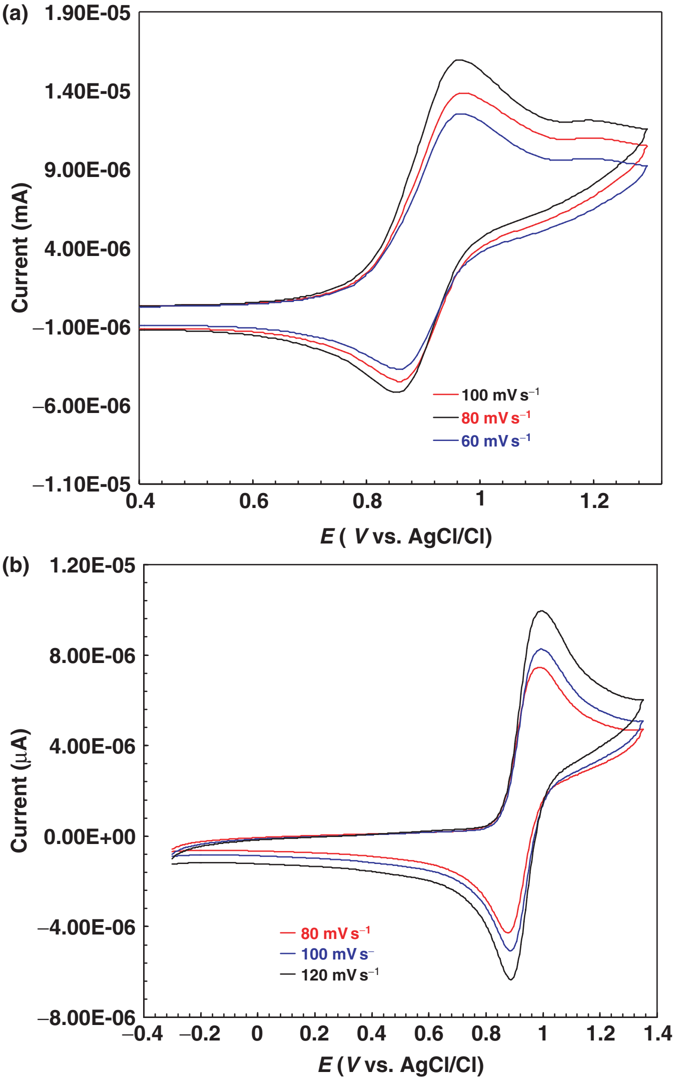

Figure 2. CV curve of 10^{-3} M of VOL^1 (a) and VOL^2 (b) complexes in DMF solution at variable scan rates (80, 100, and 120 mVs^{-1}).

scan rates (60, 80, and 100 and 80, 100, and 120 mVs^{-1}, respectively). The redox processes were reversible for VOL^{1,2}, however, the cathodic peak current of VOL^1 was increased and the peak potentials shifted to slightly negative potentials with increase of scan rate. The redox potentials of VOL^{1,2} were determined to be approximately 920 and 950 mV, respectively.

3.3. *Mechanochemical behavior of VOL^{1,2}*

The orange polymeric oxovanadium(IV) Schiff-base complex VOL^1 {[VO(5-Br-3-NO_2salnaph)]$\cdot 2H_2O$} turned to dark brown VOL^{1g} when ground thoroughly in a mortar in air. The dark brown complex VOL^{1g} turned orange VOL^{1gs} after being suspended in absolute ethanol (99.8%, UV–IR spectroscopic grade). IR spectra of tetradentate Schiff-base complexes of oxovanadium(IV) generally show V=O stretching around 970–990 cm^{-1} for monomeric form and 840–903 cm^{-1} for a linear chain polymeric form. IR spectra of VOL^1, VOL^{1g}, and VOL^{1gs} [figures S1(a), S1(b) and S1(c) in Supplementary Material online] show a strong V=O stretching band at 884 cm^{-1} for VOL^1 in KBr. When VOL^1 was ground in a mortar, the color changed from orange to dark brown and the intensity of the V=O stretching band of the polymeric form (884 cm^{-1}) decreased significantly and all bands broadened. Weak and broad new bands appeared about 980–995 cm^{-1} in the spectrum of VOL^{1g}. Grinding of VOL^1 causes a significant decrease in the intensity of the V=O stretching bands, which did not occur by simply pressing the samples. The mechanochemical behavior in VOL^1 complex is different from the mechanochemical conversion from a polymeric to a monomeric form observed for some oxovanadium(IV) Schiff-base complexes [21, 22]. In those cases, the color changed from orange to green, and the intensity of the V=O stretching bands of the linear chain polymeric forms decreased with an increase of those of the monomeric forms on grinding. However, a decrease in intensity of the V=O stretching band at 876 cm^{-1} was observed in the spectrum of VOL^{1g}.

The X-ray powder diffraction patterns (XRD) of VOL^1, VOL^{1g} and VOL^{1gs} are also shown in figures S2(a), S2(b) and S2(c). The XRD pattern of VOL^1 shows several diffraction peaks in the range of 2θ (Cu-Kα) = 10–30°, while the ground product (VOL^{1g}) is amorphous, indicating that crystalline VOL^1 turned to an amorphous product VOL^{1g} on grinding. The diffraction pattern of VOL^{1gs} shows several diffraction peaks, which clearly defines the recombination of the fragments to form a new crystalline form. The XRD pattern of VOL^{1gs} is not exactly the same as that of VOL^1, indicating that VOL^{1gs} and VOL^1 do not have the same crystalline structures.

Thermogravimetry (TG) measurements revealed that VOL^1 and VOL^{1gs} have two and one H_2O molecules of crystallization per vanadium atom, respectively. The first mass loss of the VOL^1 complex [figure S3(a)] occurred up to about 125°C and was attributed to the release of two H_2O molecules of crystallization per vanadium (TG = 4.8%; Calcd = 5.0%). The first mass loss of VOL^{1gs} complex [figure S3(b)] occurred up to about 125°C and was attributed to the release of one H_2O molecules of crystallization per vanadium atom (TG = 2.6%; Calcd = 2.5%). The decrease of the crystal water from two H_2O for VOL^1 to one H_2O for VOL^{1gs} indicates removal of weakly bound crystal water on grinding of VOL^1. The thermal decomposition of VOL^1 and VOL^{1gs} complexes which occur in the range 310–450°C resulted in the formation of the V_2O_5 (TG = 11.9%; Calcd = 12.7%) and V_2O_5 (TG = 12.3%; Calcd = 13%), respectively. The orange polymeric oxovanadium(IV) Schiff-base complex VOL^2 {[VO(5-Br-3-NO_2salpn)] · H_2O} turned to a dark green VOL^{2g} when it was ground thoroughly in a mortar in the air. The dark green complex VOL^{2g} turned to primary orange complex VOL^{2gs} after being suspended in absolute ethanol (99.8%, UV–IR spectroscopic grade).

The mechanochemical behavior in this study seems to be same as to the mechanochemical conversion reaction from a polymeric to a monomeric form as observed for [VO{sal-(*R*,*R*)-stien}] and [VO(5-Brsalen)] [21, 22]. In those cases, the color changed from orange to green, and the intensity of the V=O stretching bands of the polymeric forms decreased with a complementary increase of the monomeric forms on grinding. In this work, the orange VOL^2 complex with a polymeric structure turned to a dark green powder VOL^{2g} on grinding, and showed the V=O stretching band at 984 cm^{-1}, in addition to the original 876 cm^{-1} absorption [figure S4(a)]. Although a new band which could be assignable to V=O stretching band of a monomeric form appeared at 984 cm^{-1} in the spectrum of VOL^{2g}, the intensity was weak. To study the solvent-dependent conversion of monomeric/polymeric forms of the Schiff-base complexes, VOL^{2g} was added to spectroscopic grade ethanol. VOL^{2g} was slightly soluble in absolute ethanol and there was an almost immediate color change from dark green to orange and orange VOL^{2gs} precipitated, suggesting that the monomeric form was converted to polymeric VOL^{2gs}. The IR spectrum of VOL^{2gs} showed a strong V=O stretching band at 876 cm^{-1} and the band at 984 cm^{-1} completely vanished. The IR observations supported the idea that a polymeric form was regenerated.

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