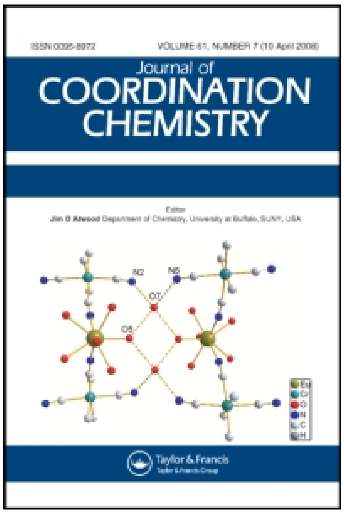

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Synthesis, characterization, electrochemical and solvatochromic investigations of novel monomeric and polymeric vanadyl Schiff-base complexes

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Synthesis, characterization, electrochemical and solvatochromic investigations of novel monomeric and polymeric vanadyl Schiff-base complexes

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This article describes the synthesis and characterization of oxovanadium(IV) complexes containing tetradentate Schiff-base ligands derived from condensation of ethylenediamine, meso-1,2-diphenyl-1,2-ethylenediamine, 1,2-orthophenylenediamine and 1,2-cyclohexanediamine with 5-bromo-3-nitro-2-hydroxybenzaldehyde. The novel VOL^1:[VO(5-Br-3-NO$_2$salen)], VOL^2:[VO(5-Br-3-NO$_2$saloph)] and VOL^3:[VO(5-Br-3-NO$_2$salchxn)] complexes were obtained in orange polymeric form with (V=O) stretching bands at 878, 884 and 884 cm^{-1}, respectively, but the VOL^4 complex was obtained as a green monomer with (V=O) stretching band at 978 cm^{-1}. The redox process in acetonitrile was reversible for VOL^4 and E° was determined to be approximately 950 mV but for VOL$^{1-3}$ this process was irreversible or quasi-reversible. The VOL^4 complex is considerably soluble in a wide variety of solvents and shows solvatochromic behavior. The $^2B_2 \rightarrow {}^2E(I)$ transition wavenumber shows a linear correlation to the D.N. of the solvent.

Keywords: Monomeric form; Polymeric form; Oxovanadium(IV) complexes; Solvatochromism

1. Introduction

There is considerable interest in catalytic reactivity, solvatochromism effect and mechanochemical reactions of oxovanadium(IV) complexes. [1]. Tetradentate Schiff-base complexes can form a green monomeric structure with square-pyramidal coordination or an orange polymeric linear chain structure ($V{=}O \cdots V{=}O \cdots$) [2]. The green monomeric structure is observed for complexes like [VO (salen)] (salen: *N*,*N*′-salicylideneethylenediamine) but 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 5-position of the salicylaldehyde moieties [3]. 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 [4–7]. Electrochemical investigations of Vanadyl Schiff-base complexes have been the subject of several studies [8].

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Electronic studies of Vanadyl complexes with one 3d electron have also been reported [9, 10]. In earlier work we synthesized some similar Schiff-base complexes of oxovanadium(IV) [11, 12] and studied the reactivity of these complexes as catalysts for the aerobic oxidation of olefins [13, 14]. In this article we report the synthesis, characterization, electrochemical and solvatochromic studies of polymeric and monomeric oxovanadium(IV) Schiff-base complexes derived from ethylenediamine, meso-1,2-diphenyl-1,2-ethylenediamine, 1,2-orthophenylenediamine and 1,2-cyclohexanediamine as the diamine and 5-bromo-3-nitro-2-hydroxybenzaldehyde as the aldehyde (figure 1).

2. Experimental

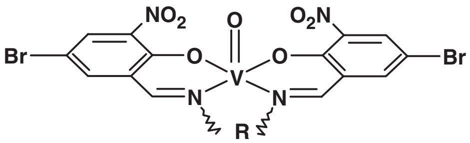
2.1. *Physical measurements*

IR spectra were recorded as KBr pellets using a Unicam Mattson 1000 FT-IR, ^{1}HNMR 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 757 VA 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 tetrabutylammoniumhexafluorophosphate as supporting electrolyte and 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. 1,2-Cyclohexanediamine and ethylenediamine were distilled prior to use and 5-bromo-3-nitro-2-hydroxybenzaldehyde [15] and meso-1,2-diphenyl-1,2-ethylenediamine [16] were prepared according to the literature procedures.



VOL^1; R: ethylenediamine (en)

VOL^2; R: 1,2- orthophenylenediamine (phen)

VOL^3; R: 1,2-cyclohexanediamine (chxn)

VOL^4; R: meso-1,2-diphenyl-1,2-ethylenediamine (stein)

Figure 1. Schiff-base Vanadyl complexes VOL^x ($x = 1$–4).

2.3. *Synthesis of Schiff-base ligands*

The Schiff-base ligands were quantitatively prepared by reaction of meso-1,2-diphenyl-1,2-ethylenediamine, ethylenediamine, 1,2-orthophenylenediamine and 1,2-cyclohexanediamine with two equivalents of 5-bromo-3-nitro-salicylaldehyde in ethanol.

2.3.1. Synthesis of H_2L^1: (5-bromo-3-nitro salen). To a vigorously stirred ethanolic solution (40 mL) of 5-bromo-3-nitro-salicylaldehyde (0.492 g, 2 mmol) was added dropwise a solution of ethylenediamine (1 mmol) in 40 mL of ethanol. After the addition was complete, the mixture was stirred and refluxed for 45 minutes. The mixture was then cooled and the yellow precipitate was collected by filtration, washed with ethanol and dried in a desiccator. Yield of [5-bromo-3-nitro salen]: 0.423 g (82%). Anal. Calcd for $C_{16}H_{12}Br_2N_4O_6$: C, 37.24; H, 2.32; N, 10.85. Found: C, 36.98; H, 2.45; N, 10.53. m.p.: 140°C. IR (KBr, cm^{-1}): 1653 [υ(C=N)], 3442 [υ(O–H)]. ^{1}HNMR (500 MHz, $CDCl_3$): 13.3 (s, 2H, OH), 8.5 (s, 2H, Ar–CH=N), 6.8–7.8 (m, 4H, Ar), 4.2 (s, 4H, Alkane).

2.3.2. Synthesis of H_2L^2: (5-bromo-3-nitro saloph). This ligand was prepared following the same procedure as described for H_2L^1 except orthophenylenediamine was used instead of ethylenediamine. Yield of [5-bromo-3-nitrosaloph]: 0.501 g (89%). Anal. Calcd for $C_{20}H_{12}Br_2N_4O_6$: C, 42.55; H, 2.13; N, 9.93. Found: C, 42.68; H, 2.32; N, 9.73. m.p.: 220°C. IR (KBr, cm^{-1}): 1607 [υ(C=N)], 3440 [υ(O–H)]. ^{1}HNMR (500 MHz, $CDCl_3$): 12.3 (s, 2H, OH), 8.9 (s, 2H, Ar–CH=N), 6.6–7.8 (m, 8H, Ar).

2.3.3. Synthesis of H_2L^3: (5-bromo-3-nitrosalchxn). This ligand was prepared following the same procedure as described for H_2L^1 except 1,2-cyclohexanediamine was used instead of ethylenediamine, and after the addition of 1,2-cyclohexanediamine, and refluxing for 1.5 h, the mixture was cooled to about 5°C and the red precipitate was collected by filtration, washed with ethanol and dried in a desiccator. Yield of [5-bromo-3-nitro salchxn]: 0.41 g (72%). Anal. Calcd for $C_{20}H_{18}Br_2N_4O_6$: C, 42.1; H, 3.16; N, 9.82. Found: C, 41.98; H, 3.01; N, 9.63. m.p.: 147°C. IR (KBr, cm^{-1}): 1646 [υ(C=N)], 3440 [υ(O–H)]. ^{1}HNMR (500 MHz, $CDCl_3$): 12.8 (s, 2H, OH), 8.6 (s, 2H, Ar–CH=N), 7–7.8 (m, 4H, Ar), 4.2 (m, 2H, Alkane), 3.5 (m, 8, Alkane).

2.3.4. Synthesis of H_2L^4: (5-bromo-3-nitro-sal-meso-stien). This ligand was prepared following the same procedure as described for H_2L^1 except meso-1,2-diphenyl-1,2-ethylenediamine was used instead of ethylenediamine. Yield of light orange precipitate of [5-bromo-3-nitro-sal-meso-stien]: 0.487 g (73%). Anal. Calcd for $C_{28}H_{20}Br_2N_4O_6$: C, 50.33; H, 3.01; N, 8.38. Found: C, 50.61; H, 3.17; N, 8.57. m.p.: 213°C. IR (KBr, cm^{-1}): 1638 [υ(C=N)], 3437 [υ(O–H)]. ^{1}HNMR (500 MHz, $(CD_3)_2SO$): 14.2 (s, 2H, OH), 8.4 (s, 2H, Ar–CH=N), 6.9–8 (m, 14H, Ar), 4.9 (s, 2H, Alkane).

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

All of the complexes were prepared by the reaction of Schiff-base ligands with an equivalent amount of vanadyl acetylacetonate [$VO(acac)_2$] in methanol.

2.4.1. Synthesis of [VO(5-Br-3-NO$_2$salen)]. To a hot methanolic solution (70 mL) of VO(acac)$_2$ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosalen (0.515 g, 1 mmol) and pyridine (1.5 mL), and the mixture was vigorously stirred for 90 min 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$_2$salen)]: 0.529 g (87%). Anal. Calcd for $C_{16}H_{10}Br_2N_4O_7V.1.5H_2O$: C, 31.60; H, 2.14; N, 9.21. Found: C, 31.85; H, 2.34; N, 9.05. m.p. (dec.): 345°C. IR (KBr, cm^{-1}): 876 [υ(V=O)], 1646 [υ(C=N)]. Uv–Vis spectrum [DMSO (nm), ε(L mol^{-} cm^{-1})]: 13,698 (123), 17,985 (343) shoulder, 24,509 (5968) (figure 2a).

2.4.2. Synthesis of the [VO(5-Br-3-NO$_2$saloph)]. To a hot methanolic solution (70 mL) of VO(acac)$_2$ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosaloph (0.564 g, 1 mmol) and pyridine (1.5 mL), and the mixture was vigorously stirred for 150 min under reflux. The resulting light brown polymeric precipitate was collected by filtration, washed with ethanol and ether and dried in air. Yield of [VO(5-Br-3-NO$_2$saloph)]: 0.511g (79%). Anal. Calcd for $C_{20}H_{10}Br_2N_4O_7V.\ H_2O$: C, 37.09; H, 1.85; N, 8.65. Found: C, 37.25; H, 1.96; N, 8.53. m.p. (dec): 384°C. IR (KBr, cm^{-1}): 884 [υ(V=O)], 1623 [υ(C=N)]. UV-vis spectrum [DMSO (nm), ε(L mol^{-1} cm^{-1})]: 13,755 (155), 17,331 (508) shoulder, 22,026 (6344) (figure 2b).

2.4.3. Synthesis of [VO(5-Br-3-NO$_2$ salchxn)]. To a hot methanolic solution (70 mL) of VO(acac)$_2$ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosaloph (0.57 g, 1 mmol) and pyridine (1.5 mL), and the mixture was vigorously stirred for 90 min 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$_2$salchxn)]: 0.48 g (%84). Anal. Calcd for $C_{20}H_{16}Br_2N_4O_7V.\ 2H_2O$: C, 35.77; H, 2.98; N, 8.35. Found: C, 35.65; H, 2.91; N, 8.13. m.p. (dec): 355°C. IR (KBr, cm^{-1}): 884 [υ(V=O)], 1638 [υ(C=N)]. UV-vis spectrum [DMSO (nm), ε(L mol^{-1} cm^{-1})]: 14,044 (182), 24,096 (6508) (figure 2c).

2.4.4. Synthesis of [VO(5-Br-3-NO$_2$sal-meso-stein)]. To a hot methanolic solution (70 mL) of VO(acac)$_2$ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosalen (0.668 g, 1 mmol) and pyridine (1.5 mL). The mixture was vigorously stirred for 180 min under reflux. The resulting green monomeric precipitate was collected by filtration, washed with ethanol and ether and dried in air. Yield of [VO(5-Br-3-NO$_2$sal-meso-stein)]: 0.534 g (72%). Anal. Calcd for $C_{28}H_{18}Br_2N_4O_7V.\ 0.5H_2O$: C, 45.31; H, 2.56; N, 7.54. Found: C, 45.71; H, 2.66; N, 7.31. m.p. (dec): 297°C. IR (KBr, cm^{-1}): 976 [υ(V=O)], 1630 [υ(C=N)]. UV-vis spectrum [DMSO (nm), ε(L mol^{-1} cm^{-1})]: 13,262 (130), 17,730 (243) shoulder, 24,330 (5555) (figure 2d).

3. Results and discussions

3.1. *Characterization of vanadyl complexes*

The desired oxovanadium(IV) complexes were obtained by reaction of tetradentate ligands with VO(acac)$_2$ [17] in reasonable yields. The IR spectra VOL$^{1-3}$ show VO

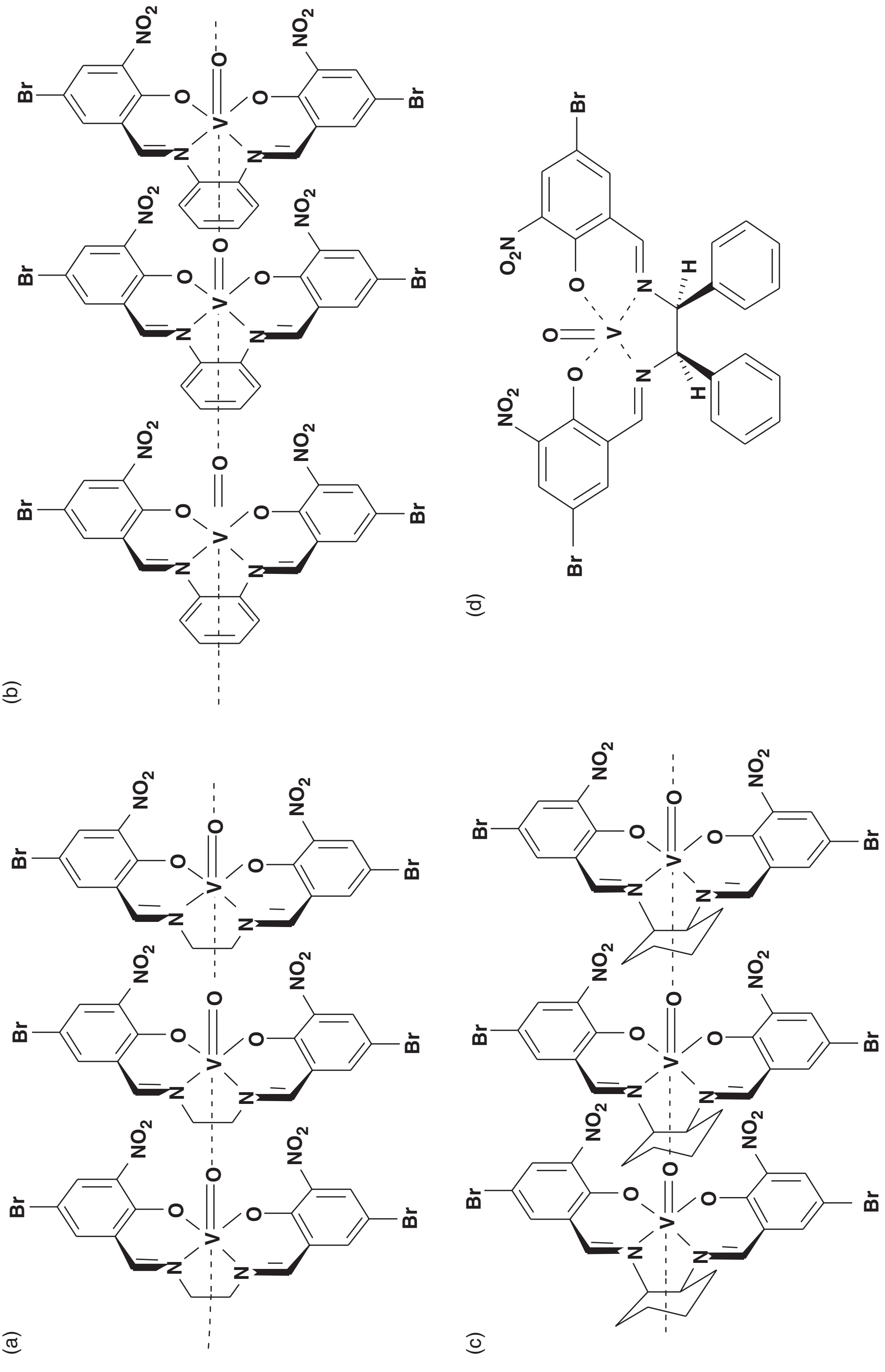


Figure 2. Polymeric VOL$^{1-3}$ (a, b, c) and monomeric VOL^{4} (d).

stretching vibrations at 884–876 cm^{-1}, which is indicative of polymeric complexes [4, 5]. IR spectrum of VOL^4 shows this vibration band at 976 cm^{-1}, indicative of monomeric square-pyramidal [2]. The monomeric form of this complex was interesting for us because of the presence of the electronegative groups on the ligand system. The origin of this monomeric form is not clear but we are trying to obtain suitable crystals for X-ray crystallography. The C=N stretching vibrations of the ligands are centered around 1607−1653 cm^{-1} which shift approximately 10 cm^{-1} to lower wave numbers upon coordination to VO. Electronic spectra of the complexes show d-d bands around 12,000–25,000 cm^{-1} in DMSO which are similar to those in the spectra of VOL^x in polar solvents [9]. Elemental analyses are in agreement with the structure of the complexes.

3.2. *Electrochemical studies*

Electrochemical studies were carried out in anhydrous acetonitrile and DMF solutions by cyclic voltammetery. 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 tetrabutylammoniumhexafluorophosphate as supporting electrolyte and 10^{-3} M complexes. Figures 3–6, respectively, show the cyclic voltammetry curve of 10^{-3} M of VOL^{1-4} complexes in DMF and acetonitrile solution at variable scan rates (100, 200 and 300 $mV\,s^{-1}$).

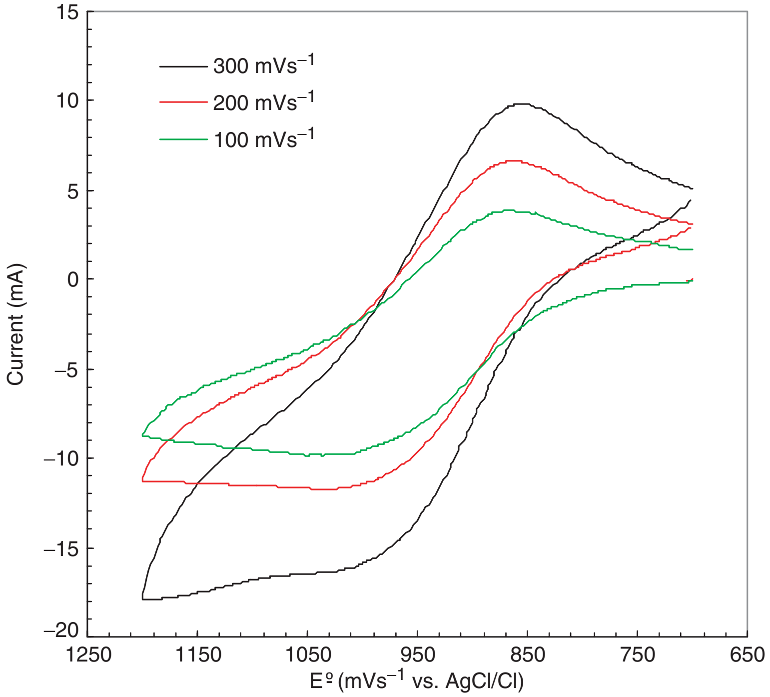


Figure 3. CV curve of 10^{3-} M VOL^4 in Acetonitrile solution containing 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. Scan rates were 100, 200, and 300 ($mV\,s^{-1}$).

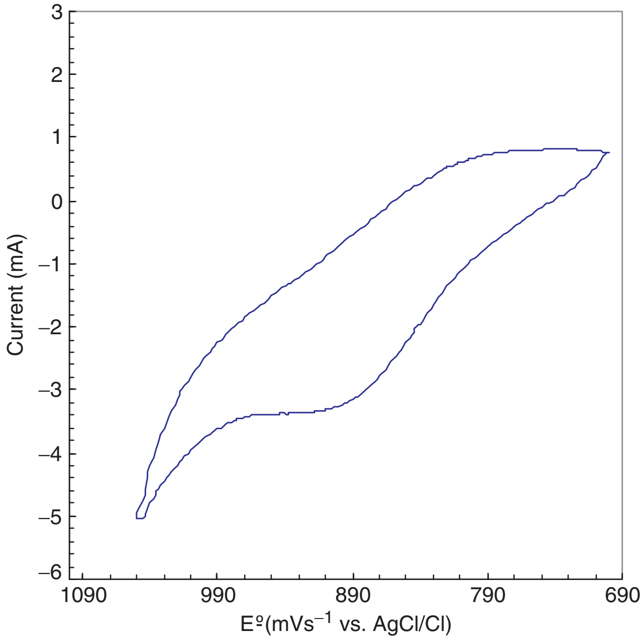


Figure 4. CV curve of 10^{3-} M VOL^3 in DMF solution containing 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. Scan rates was 100 (mV s^{-1}).

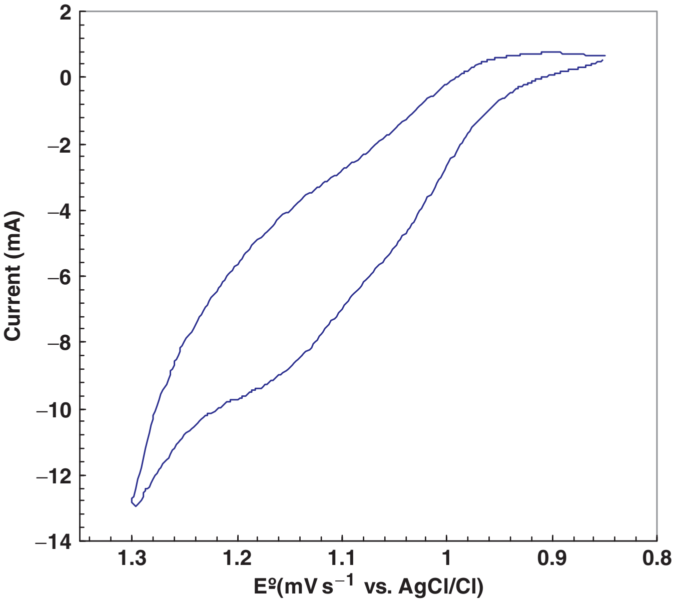


Figure 5. CV curve of 10^{3-} M VOL^2 in DMF solution containing 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. Scan rates was 100 (mV s^{-1}).

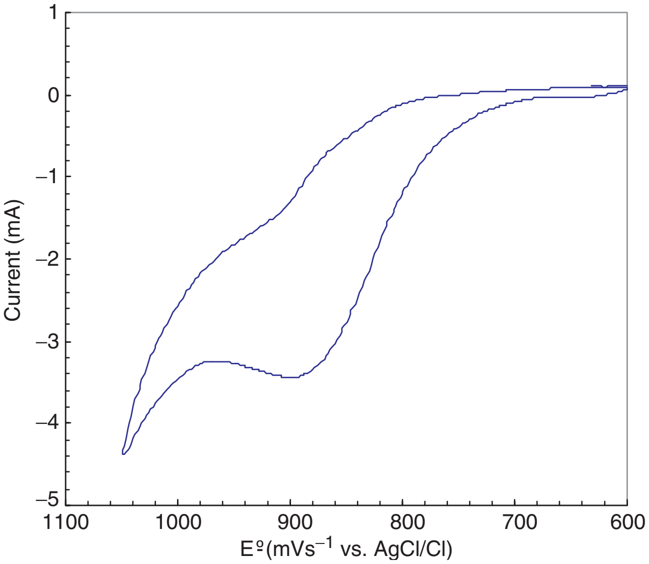


Figure 6. CV curve of 10^{3-} M VOL^1 in DMF solution containing 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. Scan rates was 100 ($mV\,s^{-1}$).

The redox process in acetonitrile was reversible for VOL^4, however, the cathodic peak current of the complex was increased and the peak potentials shifted to more negative potentials with increase of scan rate. The redox potential of VOL^4 was determined to be approximately 950 mV. The redox processes for $VOL^{1,2}$ in DMF solution were irreversible with an anodic current, while the CV curve of VOL^3 showed quasi-reversible redox behavior.

3.3. *Spectral studies and solvatochromic behavior of vanadyl Schiff-base complexes*

Electronic spectra of the complexes show d–d bands around 13,000–25,000 cm^{-1} (table 1). For most VO^{2+} complexes, three bands have been reported and assigned according to the Ballhausen–Gray (BG) scheme [18] as shown in table 2. The first transition in the electronic spectra according to the Ballhausen and Gray (BG) molecular orbital scheme [18] is $^2B_2 \rightarrow {}^2E(I)$. The b_2 level is presumed to be an almost pure vanadium $3d_{xy}$ orbital, while the $e\pi^*$ orbital is made up of a linear combination of vanadium $3d_{xz}$ and $3d_{yz}$ orbitals with $2P_x$ and $2P_y$ orbitals of oxygen. Thus the energy level should be sensitive to any perturbation that changes the axial compression in the VO bond [19]. This band normally appears broad and in some cases it is hardly distinct from the tail of the second band. Indeed, a strong axial perturbation would be expected to reduce the vanadium–oxygen interaction, resulting in the lowering of the $e\pi^*$ level with respect to b_2. The electronic data in table 3 show that the first band shifts to lower energies on going from solvents with low donor numbers to higher donor numbers. The complex VOL^4 is soluble in a wide variety of solvents and in almost all of them were found reversible color change and therefore chromotropism phenomena. This allowed us to study the solvatochromic behavior of this complex. In solvents

Table 1. Absorption spectra of Vanadyl Schiff-base complexes VOL^x ($x = 1$–4).

Complexes	Solvents	Wavenumber, cm^{-1} ($\varepsilon_{\max}$, 1 mol^{-1} cm^{-1})
VO(5-bromo-3-nitrosal-meso-stein)	DMSO	13,262 (130), 17,730 (243)[b], 24,330 (5555)
	DMA	13,440 (160), 18,281 (312)[b], 23,255 (5793)
	THF	~14,005 (192), 17,361 (285), 24,696 (~5792)
	Acetone	14,204 (184)[a], 17,421 (276), 24,509 (5566)
	Acetonitrile	14,198 (160)[b], 17,421 (285), 24,630 (5793)
	DMF	13,661 (124), 17,700 (213), 24,630 (~5793)
	Dichloromethane	16,592 (363), 24,154 (5746)
	Py	13,495 (206), 17,921 (317), 24,390 (5714)
	Nitrobenzene	~17,006 (476), 23,364 (~5710)
VO(5-bromo-3-nitro-salen)	DMSO	13,698 (123), 17,985 (343)[a], 24,509 (5968)
VO(5-bromo-3-nitro-saloph)	DMSO	13,755 (155), 17,331 (508), 22,026 (6344)
VO(5-bromo-3-nitro-salchxn)	DMSO	14,044 (182), 24,096 (6508)

[a] Shoulder, [b] Inflection.

Table 2. Band assignments for VO^{2+} complexes according to the BG scheme.

Band no.	M.O. assignment	Transition in C$_{4v}$ field	Transition in d-orbitals
I	$^2B_2 \to {}^2E(I)$	$b_2 \to e\pi^*$	$x_y \to xz, yz$
II	$^2B_2 \to {}^2B_1$	$b_2 \to b_1^*$	$x_y \to x^2 - y^2$
II	$^2B_2 \to {}^2A_1$	$b_2 \to 1a_1^*$	$xz \to z^2$

Table 3. Wavenumber of first transition of VOL^4 in different solvents.

Solvent	Solution color	D.N.	Wavenumber (cm^{-1})
Pyridine (Py)	Dark orange	33.1	13,495
Dimethylsulfoxide (DMSO)	Orange	29.8	13,262
N,*N*-Dimethylacetamide (DMA)	Light orange	27.8	13,440
N,*N*-Dimethylformamide (DMF)	Orange	26.6	13,661
Tetrahydrofuran (THF)	Dark green	20.0	14,005
Acetone	Green	17.0	14,204

with lower D.N. often the first band is covered by the second band. As can be seen from table 3, on going from solvents with lower D.N. to solvents with higher D.N., the first band, I, shifts to lower wavenumbers. This suggests coordinating ability of the solvent, which results in the shift of the band to lower wavenumbers.

As shown in figure 7, this low-energy shift of the (I) band, for DMSO and DMF, reaches a maximum. For the VOL^4 complex, there is a linear correlation between the D.N. of the solvents and the wavenumber of this transition, evidence for a solvatochromic shift (figure 8). This solvatochromic shift refers to a strong dependence of absorption and emission spectra with the solvent D.N.

In DMSO, DMF and Py (coordinating solvents), the solution color is orange, but in CH_2Cl_2 and CH_3CN it is light green and in THF deep green. The second band (II): ($^2B_2 \to {}^2B_1$ transition) shifts to higher wavenumbers on changing the solvent from CH_2Cl_2 to DMF and DMSO. Band III has been chosen to represent, alternatively, a d–d band [20], a spin forbidden ligand band [21] and a charge transfer band [8]. But

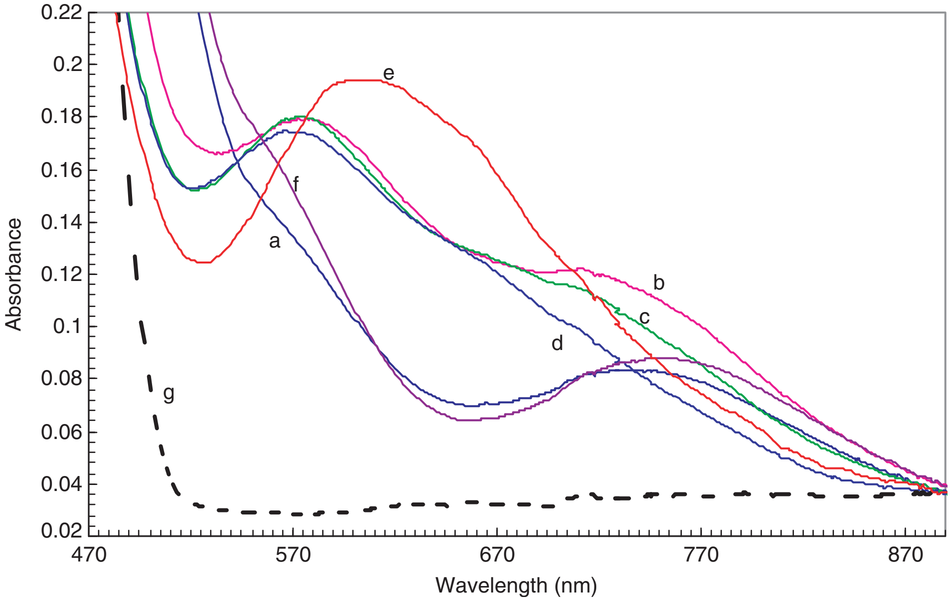


Figure 7. Electronic spectra of VOL^4 in (a) DMF, (b) THF, (c) Acetone, (d) Acetonitrile, (e) CH_2Cl_2, (f) DMSO and (g) Ligand H_2L^4 in acetone at room temperature.

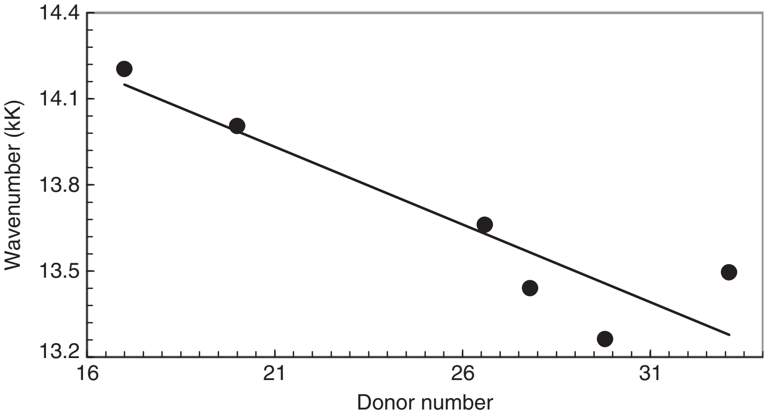


Figure 8. Correlation between wavenumber of first transition of VOL^4 and donor number.

with increasing D.N. of the solvents, this band shifts to lower wavenumbers and in DMF and DMSO it covers, to some extent, the (II) band.

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