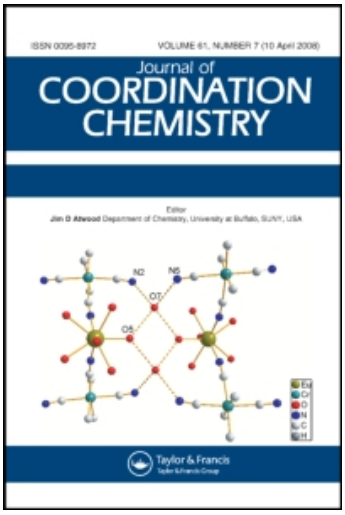


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# Unsymmetrical mononuclear and insoluble polynuclear oxo-vanadium(IV) Schiff-base complexes

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# Unsymmetrical mononuclear and insoluble polynuclear oxo-vanadium(IV) Schiff-base complexes

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Unsymmetrical and symmetrical mononuclear and insoluble polynuclear oxo-vanadium(IV) Schiff-base complexes were prepared and characterized. The complexes [VO(5-*x*-6-*y*-Sal)(5-*x*′-6-*y*′-Sal)en)] (where *x*, *x*′ = H, Br and *y*, *y*′ = H, OMe) were obtained in monomeric form while for *x* or *x*′ = $NO_2$ polymers were produced. In the case of [VO(5-*x*-6-*y*-Sal)(5-*x*′-6-*y*′-Sal)pn)] with a six-member N–N chelating ring, oxo-vanadium(IV) complexes were polynuclear. The tetradentate $N_2O_2$-Schiff-base ligands are coordinated in the equatorial plane of oxo-vanadium(IV). Electrochemical and spectroscopic data (UV–Vis and IR) suggest importance of coordination geometry and the substiuents on phenyl rings and the bridge group. Electron density of the vanadium center decreases by the electron-withdrawing groups on the ligand while electron density on vanadium increases via $\sigma$-donation of phenolic oxygen.

*Keywords*: Polynuclear oxo-vanadium(IV); Unsymmetrical tetradentate $N_2O_2$ ligands; Electrochemistry of oxo-vanadium(IV)



## 1. Introduction

Oxo-vanadium(V) complexes induce oxidation of alkenes, aryl alcohols, alcohols and sulfides [1–7]. A number of investigations have focused on recycling heterogeneous catalysts of transition-metal complexes [8–10], because heterogeneous catalysts can provide high yield and selectivity [11–15].

Most oxo-vanadium(IV) complexes with a tetradentate Schiff-base ligand like Salen have green monomeric structures with square-pyramidal coordination geometry. However, orange polynuclear linear chain structures have been observed for the six-member N–N chelating ring for vanadyl Schiff-base complexes [16, 17], especially for Schiff-base ligands with electron-withdrawing substituents [4, 18]. Accordingly, the numbers of active centers of vanadium are larger than those of usual polymer-supported complexes. The tetradentate Salen or Salpn ligands coordinate in the equatorial plane of oxo-vanadium(IV) as monomer units.

In order to incorporate transition-metal complexes into heterogeneous supports for recycling catalysts and easy separation of the product from the catalyst, we prepared insoluble polynuclear vanadium complexes of a functionalized Salen

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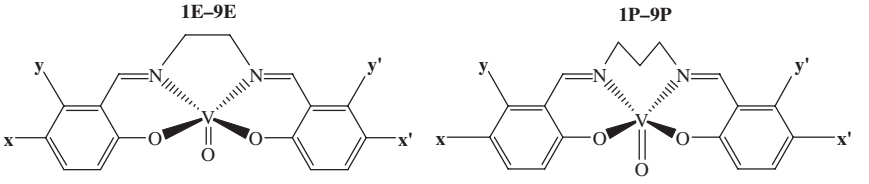


| No. | Complex Name[a] | Bridge | x | x′ | y | y″ |
|---|---|---|---|---|---|---|
| **1E** | VO[$(Sal)_2$en] | en | H | H | H | H |
| **2E** | VO[(Sal)(5-Br-Sal)en] | en | H | Br | H | H |
| **3E** | VO[$(5\text{-}NO_2\text{-}Sal)_2$en] | en | $NO_2$ | $NO_2$ | H | H |
| **4E** | VO[(Sal)(5-$NO_2$-Sal)en] | en | H | $NO_2$ | H | H |
| **5E** | VO[(5-Br-Sal)(5-$NO_2$-Sal)en] | en | Br | $NO_2$ | H | H |
| **6E** | VO[$(5\text{-Br-Sal})_2$en] | en | Br | Br | H | H |
| **7E** | VO[(5-Br-Sal)(5-Br-6-MeO-Sal)en] | en | Br | Br | H | MeO |
| **8E** | VO[$(5\text{-Br-6-MeO-Sal})_2$en] | en | Br | Br | MeO | MeO |
| **9E** | VO[(5-$NO_2$-Sal)(5-Br-6-MeO-Sal)en] | en | $NO_2$ | Br | H | MeO |
| **1P** | VO[$(Sal)_2$Pn] | Pn | H | H | H | H |
| **2P** | VO[(Sal)(5-Br-Sal)Pn] | Pn | H | Br | H | H |
| **3P** | VO[$(5\text{-}NO_2\text{-}Sal)_2$Pn] | Pn | $NO_2$ | $NO_2$ | H | H |
| **4P** | VO[(Sal)(5-$NO_2$-Sal)Pn] | Pn | H | $NO_2$ | H | H |
| **5P** | VO[(5-Br-Sal)(5-$NO_2$-Sal)Pn] | Pn | Br | $NO_2$ | H | H |
| **6P** | VO[$(5\text{-Br-Sal})_2$Pn] | Pn | Br | Br | H | H |
| **7P** | VO[(5-Br-Sal)(5-Br-6-MeO-Sal)Pn] | Pn | Br | Br | H | MeO |
| **8P** | VO[$(5\text{-Br-6-MeO-Sal})_2$Pn] | Pn | Br | Br | MeO | MeO |
| **9P** | VO[(5-$NO_2$-Sal)(5-Br-6-MeO-Sal)Pn] | Pn | $NO_2$ | Br | H | MeO |

Figure 1. Oxo-vanadium(IV) Salen **1E–9E** and oxo-vanadium(IV) SalPn **1P–9P** complexes. Complexes **2E**, **4E**, **5E**, **7E**, **8E**, **9E**, **2P**, **4P**, **5P**, **7P**, **8P**, **9P** are new.



(salicylideneethylenediimine) or Salpn (salicylidenepropenediimine) monomer to develop heterogeneous catalysts with high efficiency of recycling and catalysis in oxidation of organic substrates.

Two types of tetradentate Schiff-base ligands consisting of the aldehyde of 5-*x*-6-*y*-2-hydroxybenzaldehyde and 1,2-diaminoethane (Salen) or 1,3-diaminopropane (Salpn) and their oxo-vanadium(IV) complexes were prepared and characterized with the intention to obtain new stable polynuclear oxo-vanadium(IV) complexes (figure 1).

## 2. Experimental

### 2.1. *Reagents*

2-Hydroxybenzaldehyde, 5-nitro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde and vanadyl acetylacetonate were used as received from commercial suppliers (Merck, Aldrich). 1,3-Diaminopropane(pn) and 1,2-diaminoethane were purified by distillation under vacuum. $CHCl_3$, $CH_2Cl_2$, $CH_3CN$, methanol and ethanol were distilled and dried before use by standard methods. DMF, DMSO,

tetrabutylammonium hexafluorophosphate (TBAHP) and THF were purchased from Merck, Aldrich and Fluka and used without purification. Other chemicals were used as received from commercial suppliers. 5-Bromo-6-methoxy salicylaldehyde was synthesized (section 2.3.1).

### 2.2. *Physical measurements*

Infrared spectra were recorded using a Perkin-Elmer 781 IR spectrophotometer. Electronic absorption spectra were recorded on a Jasco V-530 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were obtained on Bruker FT-NMR AC-250 (250 MHz) spectrophotometers using TMS as internal standard and $CDCl_3$ and DMSO-$d_6$ as solvents. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN–O-Rapid (Elemental-Analyses system, GmbH-West Germany) and vanadium percent was measured by a Shimadzu atomic absorption B-300. Melting points were determined on a B-540 Buchi melting point apparatus. Cyclic voltammograms (CVs) were obtained using an electrochemical system (Palm Sens, The Netherlands) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl)/3M KCl reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode were employed for the electrochemical studies. Voltammometric measurements were performed at room temperature in DMF with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.



### 2.3. *Preparation of the ligands and oxo-vanadium Schiff-base complexes*

The symmetrical ligands $H_2$[(Sal)$_2$en] (**1E**), $H_2$[(5-$NO_2$-Sal)$_2$en] (**3E**), $H_2$[(5-Br-Sal)$_2$en] (**6E**) and $H_2$[(Sal)$_2$pn] (**1P**), $H_2$[(5-$NO_2$-Sal)$_2$pn] (**3P**) and $H_2$[(5-Br-Sal)$_2$pn] (**6P**) were obtained by conventional one-step Schiff-base condensation of appropriate diamine with 2-hydroxybenzaldehyde, 5-nitro-2-hydroxybenzaldehyde or 5-bromo-2-hydroxybenzaldehyde, respectively, in 1 : 2 molar ratio, according to the similar procedures as those employed for $H_2$[(5-Br-6-MeO-Sal)$_2$en] and characterized by comparing to literature [4–8, 19–22]. Complexes were prepared by previously described methods [5, 7, 19].

**2.3.1. Preparation procedure and spectroscopic data of 5-bromo-6-methoxy-salicylaldehyde.** A solution of $Br_2$ (3.94 g, 25 mmol) in $CH_2Cl_2$ (45 mL) was slowly added to 6-methoxysalicylaldehyde (2 g, 14.7 mmol) in dry $CH_2Cl_2$ (45 mL). After stirring at 0°C for 1 h, a saturated aqueous solution of $Na_2S_2O_5$ was added. After separation, water was added to the organic phase. The organic phases were dried over $MgSO_4$ and 5-bromo-6-methoxysalicylaldehyde (3.16 g, 90%) was obtained as a yellow solid. Elemental analysis for $C_8H_7BrO_3$, M.W. 231.04; Calcd (%): C, 41.59; H, 3.05. Found: C, 41.71; H, 3.17. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 3.85 (s, 3H; $CH_3$), 6.61–7.37(d, 2H, ArH), 9.97(s, 1H; C*H*O), 11.48(s, 1H; OH); (KBr): $\nu$ ($cm^{-1}$) = 2887, 1654, 1609.

**2.3.2. Synthesis of *N,N′*-propylene *bis*(salicylideneiminato) type ligands.** *Synthesis of $H_2$[(Sal)(5-Br-Sal)pn]*: to a vigorously stirred and cool dilute solution (−5°C)

of 10 mmol 1,3-diaminopropane in 40 mL of anhydrous ethanol, a cooled solution of 8 mmol 2-hydroxybenzaldehyde in 40 mL anhydrous ethanol was added dropwise. After the addition was complete, the mixture was stirred for 15 min and then refluxed for 15 min. The resulting solution was evaporated in a vacuum to remove the solvent and excess diamine and was used as precursor for next step without further purification. To a stirred solution of this precursor in 30 mL anhydrous ethanol, a solution of 8 mmol 5-bromo-2-hydroxybenzaldehyde in 30 mL anhydrous ethanol was added and the solution refluxed for 60 min. The mixture was concentrated by solvent evaporation in a vacuum giving yellow $H_2$[(Sal)(5-Br-Sal)pn]. The product was filtered and recrystallized from ethanol until pure product was obtained. Yield 75%, based on 2-hydroxybenzaldehyde. M.p. 111–114°C. Elemental analysis for $C_{17}H_{17}BrN_2O_2$; M.W.: 361.23; Calcd (%): C, 56.52; H, 4.74; N, 7.75. Found: C, 56.63; H, 4.86; N, 8.03. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.13 (qn, 2H, C-$CH_2$-C), 3.75 (t, 4H, N–$CH_2$–C–$CH_2$–N), 6.77–7.41 (m, 7H, ArH), 8.30 (s, 1H, –HC=N), 8.38 (s, 1H, –HC=N), 13.37 (s, 1H, OH), 13.43 (s, 1H, OH); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 31.2, 56.7(2), 108.9, 117.1, 120.9(2), 123.2(2), 130.4(2), 137.0(2), 156.2, 160.1, 163.3, 165.2; IR (KBr): $\nu$ ($cm^{-1}$) = 1629. Other ligands were prepared by use of appropriate 5-*x*-6-*y*-2-hydroxybenzaldehyde (where *x*= H, Br, $NO_2$ and *y*= H, OMe) with similar procedures as employed for $H_2$[(Sal)(5-Br-Sal)pn].

*$H_2$[(Sal)(5-$NO_2$-Sal)pn]*: Yield 68%; brown powder; m.p. 145–146°C; elemental analysis for $C_{17}H_{17}N_3O_4$; M.W.: 327.33; Calcd (%): C, 62.38; H, 5.23; N, 12.84. Found: C, 62.27; H, 5.01; N, 12.61. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.17(m, 2H, C–C**H$_2$**–C), 2.83 (t, 2H, N–C**H$_2$**–C), 3.70 (t, 2H, C–C**H$_2$**–N), 6.68–7.68 (m, 7H, Ar**H**), 8.27 (s, 1H, –**H**C=N), 8.38 (s, 1H, –**H**C=N); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 32.1, 56.4(2), 115.9, 116.1, 120.8, 124.6(3), 128.0, 131.3(2), 141.0, 159.1, 162.5(2), 168.4; IR (KBr): $\nu$ ($cm^{-1}$) = 1624, 1629.

*$H_2$[(5-Br-Sal)(5-$NO_2$-Sal)pn]*: Yield 61%; yellow-green crystal; M.p. 219–221°C; elemental analysis for $C_{17}H_{16}BrN_3O_4$; M.W.: 406.23; Calcd (%): C, 50.26; H, 3.97; N, 10.34. Found: C, 50.12; H, 3.88; N, 10.50. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.21 (m, 2H, C–C**H$_2$**–C), 3.37 (t, 2H, N–C**H$_2$**–C), 3.38 (t, 2H, C–C**H$_2$**–N), 6.68-8.26 (m, 6H, Ar**H**), 8.32 (s, 1H, –**H**C=N), 8.47 (s, 1H, –**H**C=N), 13.25 (s, 1H, O**H**), 14.48 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 32.8, 57.3(2), 115.8(2), 117.9, 125.2(2), 126.5, 128.1, 132.3, 135.1, 141.0, 159.6, 164.1(2), 168.3; IR (KBr): $\nu$ ($cm^{-1}$) = 1646, 1630.

*$H_2$[(5-Br-Sal)(5-Br-6-MeO-Sal)pn]*: Yield 40%; yellow crystal; m.p. 129–131°C; elemental analysis for $C_{18}H_{18}Br_2N_2O_3$; M.W.: 470.16; Calcd (%): C, 45.98; H, 3.86; N, 5.96. Found: C, 46.28; H, 3.99; N, 5.75. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.17 (m, 2H, C–C**H$_2$**–C), 3.69 (t, 2H, N–C**H$_2$**–C), 3.75 (t, 2H, C–C**H$_2$**–N), 3.87 (s, 3H, O–C**H$_3$**), 6.82–7.45 (m, 5H, Ar**H**), 8.26 (s, 1H, –**H**C=N), 8.63 (s, 1H, –**H**C=N), 13.35 (s, 1H, O**H**), 15.18 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 31.5, 56.8(2), 64.2, 101.2, 108.6, 110.8, 119.0, 120.0, 133.4(2), 135.0(2), 160.2(2), 164.3(2), 169.1; IR (KBr): $\nu$ ($cm^{-1}$) = 1647, 1629.

*$H_2$[(5-$NO_2$-Sal)(5-Br-6-MeO-Sal)pn]*: Yield 45%, brown powder; m.p. 177–179°C; elemental analysis for $C_{18}H_{18}BrN_3O_5$; M.W.: 436.26; Calcd (%): C, 49.56; H, 4.16; N, 9.63. Found: C, 49.73; H, 4.35; N, 9.41. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.20 (m, 2H, C–C**H$_2$**–C), 3.82 (t, 2H, C–C**H$_2$**–N), 3.89 (t, 2H, N–C**H$_2$**–C), 4.00 (s, 3H,

O–C**H$_3$**), 6.98–8.25 (m, 5H, Ar**H**), 8.46 (s, 1H, –**H**C=N), 8.63 (s, 1H, –**H**C=N), 14.47 (s, 1H, O**H**), 15.27 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 31.5, 56.9(2), 64.3, 101.3, 108.6, 111.1, 116.2, 123.4(2), 133.1, 135.9, 140.1, 161.4(2), 163.5(2), 168.8; IR (KBr): $\nu$ ($cm^{-1}$) = 1652, 1626.

*Synthesis of* $H_2$[(5-*Br*-6-*MeO*-*Sal*)$_2$*pn*]: to a stirred solution of 10 mmol of 1,3-diaminopropane in 40 mL of anhydrous ethanol was added a cooled solution of 18 mmol 5-bromo-6-methoxy-2-hydroxybenzaldehyde in 70 mL anhydrous ethanol. After addition was complete, the mixture was stirred for 15 min and then refluxed for 90 min. The resulting solution was evaporated in a vacuum to remove the solvent and the excess diamine. The product was dissolved in 25 mL anhydrous ethanol and concentrated by solvent evaporation in a vacuum until yellow-orange $H_2$[(5-Br-6-MeO-Sal)$_2$pn] precipitated. The product was filtered and recrystallized from ethanol until pure product was obtained. Yield 85%; m.p. 144–146°C; elemental analysis for $C_{19}H_{20}Br_2N_2O_4$; M.W.: 500.18; Calcd (%): C, 45.62; H, 4.03; N, 5.60. Found: C, 45.78; H, 4.21; N, 5.55. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 2.20 (qn, 2H, C–C**H$_2$**–C), 3.81 (t, 4H, N–C**H$_2$**–$CH_2$–C**H$_2$**–N), 3.92 (s, 6H, O–C**H$_3$**), 7.25–7.72 (m, 4H, Ar**H**), 8.63 (s, 2H, –**H**C=N), 15.27 (s, 2H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 31.4, 56.4(2), 64.1(2), 100.9(2), 108.4(2), 111.0(2), 133.5(2), 160.8(2), 163.0(2), 169.1(2); IR (KBr): $\nu$ ($cm^{-1}$) = 1648.

$H_2$[(*Sal*)(5-*Br*-*Sal*)*en*]: Yield 69%; yellow crystal; m.p. 177–179°C; elemental analysis for $C_{16}H_{15}BrN_2O_2$; M.W.: 347.21; Calcd (%): C, 55.35; H, 4.35; N, 8.07. Found: C, 55.74; H, 4.33; N, 7.85. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 3.97 (s, 4H, N–C**H$_2$**–C**H$_2$**–N), 6.83–7.40 (m, 7H, Ar**H**), 8.28 (s, 1H, –**H**C=N), 8.36 (s, 1H, –**H**C=N), 13.13 (s, 1H, O**H**), 13.20 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 56.1, 59.6, 100.3, 116.1(2), 119.0, 120.0, 126.1(2), 133.6(2), 135.2, 160.0(2), 165.3(2); IR (KBr): $\nu$ ($cm^{-1}$) = 1631.

$H_2$[(*Sal*)(5-*NO$_2$*-*Sal*)*en*]: Yield 62%; yellow solid; m.p. 284–286°C; elemental analysis for $C_{16}H_{15}N_3O_4$; M.W.: 313.31; Calcd (%): C, 61.34; H, 4.83; N, 13.41. Found: C, 61.22; H, 4.69; N, 13.32. IR (KBr): $\nu$ ($cm^{-1}$) = 1646, 1630.

$H_2$[(5-*Br*-*Sal*)(5-*NO$_2$*-*Sal*)*en*]: Yield 53%; yellow solid; m.p. 202–204°C; elemental analysis for $C_{16}H_{14}BrN_3O_4$; M.W.: 391.02; Calcd (%): C, 49.00; H, 3.60; N, 10.71. Found: C, 48.83; H, 3.48; N, 10.57. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 4.00 (s, 4H, N–C**H$_2$**–C**H$_2$**–N), 6.83–8.24 (m, 6H, Ar**H**), 8.31 (s, 1H, –**H**C=N), 8.47 (s, 1H, –**H**C=N), 13.00 (s, 1H, O**H**), 4.34 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 56.0(2), 116.1, 117.0, 119.1, 125.8(2), 126.9(2), 133.4, 135.5, 140.8, 159.1, 162.3,165.3, 169.3; IR (KBr): $\nu$ ($cm^{-1}$) = 1632.

$H_2$[(5-*Br*-*Sal*)(5-*Br*-6-*MeO*-*Sal*)*en*]: Yield 47%; yellow semisolid; elemental analysis for $C_{17}H_{16}Br_2N_2O_3$; M.W.: 456.13; Calcd (%): C, 44.76; H, 3.54; N, 6.14. Found: C, 45.00; H, 3.67; N, 5.92. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 3.76 (s, 4H, N–C**H$_2$**–C**H$_2$**–N), 3.92 (s, 3H, OC**H$_3$**), 6.81–7.66 (m, 5H, Ar**H**), 8.26 (s, 1H, –**H**C=N), 8.62 (s, 1H, –**H**C=N), 10.27 (s, 1H, O**H**), 12.62 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 55.7, 56.0, 59.6, 102.5, 111.4, 114.5, 119.2, 119.9, 124.1, 133.8, 135.2, 137.5, 160.0(2), 162.3(2), 193.9; IR (KBr): $\nu$ ($cm^{-1}$) = 1629.

$H_2$[(5-*NO$_2$*-*Sal*)(5-*Br*-6-*MeO*-*Sal*)*en*]: Yield 58%; yellow solid; m.p. 283–284°C; elemental analysis for $C_{17}H_{16}BrN_3O_5$; M.W.: 422.23; Calcd (%): C, 48.36;

H, 3.82; N, 9.95. Found: C, 48.51; H, 3.99; N, 10.09. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 3.77 (t, 2H, N–C**H$_2$**–C**H$_2$**–N), 3.98 (t, 2H, N–C**H$_2$**–C**H$_2$**–N), 4.05 (s, 3H, OC**H$_3$**), 6.35–7.32 (m, 5H, Ar**H**), 8.24 (s, 1H, –**H**C=N), 8.45 (s, 1H, –**H**C=N), 14.17 (s, 1H, O**H**), 15.22 (s, 1H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 56.2(2), 59.9, 101.8, 110.9, 113.7, 118.1, 124.8(2), 126.9, 135.5, 140.9, 159.3, 161.5, 165.3, 167.4, 189.1; IR (KBr): $\nu$ ($cm^{-1}$) = 1646, 1619.

*Synthesis of H$_2$[(5-Br-6-MeO-Sal)$_2$en]*: this ligand was prepared by use of appropriate 1,2-diamino ethane according to the similar procedures as those employed for $H_2$[(5-Br-6-MeO-Sal)$_2$pn]. Yield 95%, based on 5-bromo-6-methoxy-2-hydroxybenzaldehyde; yellow crystal; m.p. 291–293°C; elemental analysis for $C_{18}H_{18}Br_2N_2O_4$; M.W.: 486.15; Calcd (%): C, 44.47; H, 3.73; N, 5.76. Found: C, 44.74; H, 3.95; N, 5.60. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 3.78 (s, 4H, N–C**H$_2$**–C**H$_2$**–N), 4.02 (s, 6H, OC**H$_3$**), 7.25–7.72 (m, 4H, Ar**H**), 8.59 (s, 2H, –**H**C=N), 14.98 (s, 2H, O**H**); $^{13}$C NMR (250 MHz, $CDCl_3$): $\delta$ (ppm) = 56.1(2), 59.9(2), 102.4(2), 110.8(2), 114.1(2), 137.6(2), 159.5(2), 161.6(2), 192.8(2); IR (KBr): $\nu$ ($cm^{-1}$) = 1618.



**2.3.3. Preparation of the oxo-vanadium Schiff-base complexes.** *Synthesis of VO[(Sal)(5-Br-Sal)pn]*, (**2P**): to a stirred and hot solution of 2 mmol $H_2$[(5-Br-Sal)(Sal)pn] in 25 mL ethanol was added a hot solution of 2 mmol (530 mg) VO(acac) in 15 mL methanol. The reaction mixture was then refluxed for 60 min. The colored solution was concentrated and cooled to yield orange-red powder. The product was filtered, recrystallized from ethanol and dried in 50°C until pure product was obtained. Yield 92%.

The oxo-vanadium Schiff-base complexes **1P**, **3P**–**9P** and **1E**–**9E** were prepared by use of appropriate Schiff-base ligand according to the same procedures as employed for **2P**. Yields were in the range 85–95%.

## 3. Results and discussion

Oxo-vanadium(IV) and oxo-vanadium(V) complexes with tetradentate Schiff-base ligands are usually so stable that they can easily be isolated as single crystals and they exhibit a reversible vanadium(IV/V) redox response with electrodes in various electrolyte solutions. In particular, the structures of the complexes with Schiff-base ligands derived from salicylaldehyde have been widely characterized [23]. The most typical example is [*N*,*N*′-ethylene-*bis*(salicylideneiminato)]oxovanadium(IV) ([VO(Sal)$_2$en)], **1E**) which is five-coordinate with a square-pyramidal geometry and is stable in air in solid state and solution [24].

### 3.1. *Synthesis and spectroscopic study of oxo-vanadium complexes*

Some new oxo-vanadium(IV) Schiff-base complexes with ethylene (en) (**1E–9E**) and 1,3-propylene (pn) bridge (**1P–9P**) were synthesized. The Schiff-base ligands and corresponding oxo-vanadium(IV) complexes **2E**, **4E**, **5E**, **7E**, **8E**, **9E**, **2P**, **4P**, **5P**, **7P**, **8P** and **9P** are new. The complexes were used for the electrochemical, microanalyses (A.A.)

Table 1. Electronic, spectral and physical data of oxo-vanadium(IV) complexes **1E**–**9E** and **1P**–**9P**.

| No. | Complex name | $E_{pa}$ (mV)[a] | $\lambda_{max}(\varepsilon)$ nm | $\lambda_{CT}$ $(\varepsilon)$[b] | $\nu_{C=N}$ ($cm^{-1}$)[c] | %V (Calcd) | $\nu_{V=O}$ ($cm^{-1}$) | Color |
|---|---|---|---|---|---|---|---|---|
| **1E** | VO[$(Sal)_2$en] | 290 | 581 (94) | 361 (44540) | 1600 | 15.26 (15.29) | 985 | Deep green |
| **2E** | VO[(Sal)(5-Br-Sal)en] | 373 | 544 (66) | 372 (24060) | 1598, 1600w | 12.20 (12.36) | 961 | Deep green |
| **3E** | VO[$(5\text{-}NO_2\text{-}Sal)_2$en] | 562 | 546 (67) | 366 (14790) | 1612 | 11.83 (12.04) | 876 | Deep brown |
| **4E** | VO[(Sal)(5-$NO_2$-Sal)en] | 576 | 551 (33) | 357 (9680) | 1612, 1601w | 13.33 (13.47) | 872 | Brown |
| **5E** | VO[(5-Br-Sal)(5-$NO_2$-Sal)en] | 565 | 550 (225) | 363 (20050) | 1607, 1600 | 11.08 (11.14) | 867 | Brown |
| **6E** | VO[$(5\text{-Br-Sal})_2$en] | 397 | 564 (350) | 367 (8590) | 1598 | 10.22 (10.37) | 945 | Deep green |
| **7E** | VO[(5-Br-Sal)(5-Br-6-MeO-Sal)en] | 385 | 576 (98) | 370 (4100) | 1592, 1600 | 9.80 (9.78) | 970 | Deep green |
| **8E** | VO[$(5\text{-Br-6-MeO-Sal})_2$en] | 437 | 614 (235) | 412 (12960) | 1593 | 9.18 (9.24) | 985 | Deep green |
| **9E** | VO[$(5\text{-}NO_2\text{-Sal})$(5-Br-6-MeO-Sal)en] | 575 | 548 (192) | 363 (21870) | 1596, 1608w | 10.15 (10.46) | 876 | Brown |
| **1P** | VO[$(Sal)_2$pn] | 407 | 513 (800) | 388 (29000) | 160 | 14.39 (14.67) | 855 | Orange |
| **2P** | VO[(Sal)(5-Br-Sal)pn] | 483 | 544 (66) | 372 (2400) | 1630, 1607w | 11.69 (11.95) | 865 | Orange-red |
| **3P** | VO[$(5\text{-}NO_2\text{-Sal})_2$pn] | 709 | 545 (550) | 368 (15728) | 1588 | 11.47 (11.65) | 866 | Orange-brown |
| **4P** | VO[(Sal)(5-$NO_2$-Sal)pn] | 569 | 416sh (3700) | 361 (5390) | 1634, 1596w | 12.80 (12.99) | 857 | Orange-brown |
| **5P** | VO[(5-Br-Sal)(5-$NO_2$-Sal)pn] | 707 | 544 (4) | 366 (2020) | 1634, 1615w | 10.66 (10.81) | 863 | Orange |
| **6P** | VO[$(5\text{-Br-Sal})_2$pn] | 601 | 588 (67) | 371 (4526) | 1619 | N/A | 879 | Cream |
| **7P** | VO[(5-Br-Sal)(5-Br-6-MeO-Sal)pn] | 470 | 539 (170) | 370 (12580) | 1608, 1614w | 9.38 (9.52) | 858 | Orange-brown |
| **8P** | VO[$(5\text{-Br-6-MeO-Sal})_2$pn] | N/A | 592 (39) | 413 (45130) | 1601 | N/A | 879 | Cream |
| **9P** | VO[$(5\text{-}NO_2\text{-Sal})$(5-Br-6-MeO-Sal)pn] | 734 | 545 (11) | 366 (5300) | 1600, 1591w | 9.94 (10.16) | 861 | Brown |

[a]$E_{pa}$ means anodic peak potential. Potentials are (*vs.*) SCE, R.T., DMF as solvent and TBAHP as supporting electrolyte in 0.0001 molar concentration complex for V(IV)/VV) couples and scan rate 50 $mVs^{-1}$. CV s of **1E**, **6E**, **7E** and **1P** shows reversible behavior with $\Delta E_P$ in range 74–85 mV.
[b]CT is charge transfer peak in UV–Vis spectra that obtained from 0.0001 M of oxo-vanadium complex in DMF.
[c]w means weak.

and UV–Vis absorption. Some of the results are summarized in table 1. The vanadium measurements by atomic absorption spectroscopy show 1:1 molar ratio of Schiff-base ligand to vanadium.

V=O stretching frequencies in the solid state are given in table 1. Oxo-vanadium complexes as monomeric (green) and polymeric (orange-brown) have $\nu$(V=O) values about $970 \pm 30$ and $850 \pm 30\,cm^{-1}$, respectively, with coordination numbers five and six, a criterion for discriminating the coordination number of oxo-vanadium complexes [4, 25, 26]. The green complexes **1E**, **2E**, **6E**, **7E**, **8E** whose $\nu$(V=O) values are around 945–985 $cm^{-1}$, are monomeric penta-coordinate with square-pyramidal geometries and the orange-brown complexes **3E**, **4E**, **5E**, **9E**, **1P**–**9P** whose $\nu$(V=O) values are around 855–879 $cm^{-1}$, are polymeric hexa-coordinate with octahedral geometries [27, 28].

Six coordinate polymeric complexes are promoted by increasing of the chelate ring from five to six in **1P**–**9P** and/or increasing of electron withdrawing of the ligand. Electron withdrawing of nitro on the phenyl ring affects $\sigma$ accepting properties of C=N. Evidence for this is increasing stretching frequency upon coordination, while in other cases decreasing of C=N stretch has been seen. Thus, transfer of electron-withdrawing properties of ligand to vanadium occurs through $\sigma$ not $\pi$ interaction. Electron donating of ligands to vanadium occur through phenol's oxygen by both $\sigma$ and $\pi$ donating interaction.

UV–Vis data (table 1) of vanadyl complexes show both d–d and charge transfer. Charge transfers are seen about 361–413 nm with high extinction coefficient ($\varepsilon = 7000$-25000). Usually d–d transitions are seen with very low extinction coefficient ($\varepsilon = 10$-300) around 420–750 nm for green complexes and around 513 and 690 nm for brown and orange ones.

Six-coordinate polymeric vanadium(IV) complexes with $d^1$ electronic configuration have first-order Jahn–Teller effect (FOJT) [39] that causes tetragonal distortion to a structure with $C_{4v}$ symmetry. The strong color of the complex indicates low-energy CT bands that originate from the filled high-energy ligand $\pi$ orbitals to the metal $t_{2g}$ and/or $e_g$ orbitals. The ligand $\pi$ level consists of $t_{2u}$, $t_{1u}$ and $t_{1g}$ orbitals, and the possible low-energy ligand-to-metal charge transfer (LMCT) transitions induce vibrations of the $T_{1u}$ and $T_{2u}$. The $T_{1u}$ normal mode vibration not only causes deformation to the $C_{4v}$ symmetry, but also places vanadium off the equatorial plane. Because vanadium(IV) in the VO(Salpn) or VO(Salen) species are located slightly above the ONNO pseudo-plane of the ligand, second-order Jahn–Teller effect (SOJT) is proposed [29].

Increasing electron withdrawing of the ligand decreases the LMCT energy from 361 to 413 nm (table 1); $\lambda_{max}$ of d–d transitions increases by the decreasing electron-withdrawing substituents on the ligands from 5-$NO_2$ to 6-MeO, 5-Br. These results are in agreement with those expected on the basis of $\pi$ donation of oxygen of phenoxy to the $t_{2g}$ orbital of vanadium in $O_h$ ligand field. On the basis of CFT, $\Delta$ decreases with electron-donating substituents on the ligand.

### 3.2. *Electrochemical study*

Electrochemical behaviors of oxo-vanadium Schiff-base complexes were studied by voltammometry in DMF solution with TBAHP at RT in the potential range 0.0 to 1.0 V *versus* Ag/AgCl (table 1). Variation of the anodic peak potentials of CV's ($E_{pa}$) for the

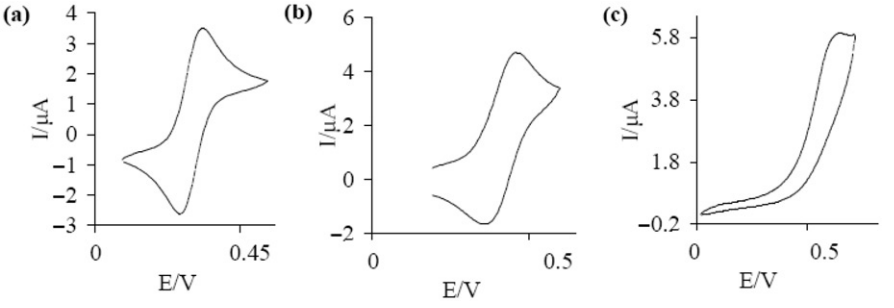


Figure 2. Cyclic voltammograms of selected oxo-vanadium complexes (a) VO[(5-Br-Sal)(5-Br-6-MeO-Sal)en], **7E**; (b) VO[(5-Br-6-MeO-Sal)$_2$en], **8E**; (c) VO[(5-Br-6-MeO-Sal)(5-NO$_2$-Sal)Pn], **9P** in DMF and presence 0.1 mM of supporting electrolyte (TBAHP) in RT. Potential are *vs.* SCE as reference electrode at scan rate 50 mvs$^{-1}$.



V(IV/V) redox couple correspond to electronic properties of ligands. In fact, a clear correlation was found between electron donating or electron withdrawing of the substituent and the value of $E_{pa}$ for the V(IV)/V(V) redox couples, in agreement with those of Jacobsen [30] and Rajagopal [31]. The cyclic voltammograms of **7E**, **8E** and **9P** are shown in figure 2. While most monomeric (green) complexes show reversible electrochemical behavior, orange-brown polymeric ones have irreversible voltammograms, suggesting that oxo-vanadium(V) as electrochemical intermediate is more stable than oxo-vanadium(IV). The partial bond via oxo group donation of each complex to vanadium of other complexes ($\cdots$V=O$\cdots$V=O$\cdots$) stabilize V(V) making irreversible electrochemistry.

As expected from electronic effects of the substituents, the trend of oxidation potentials ($E_{pa}$) increases 5-H < 5-Br < 5-NO$_2$ or 6-MeO < 6-H, with increasing electron-withdrawing and acceptor qualities of the substituents.

This significant electronic effect on the reactivity of oxo-metal may be ascribed to: (1) effect of substituent on the metal-oxo bond length, (2) non-bonding ligand interactions in the relevant states [32], (3) metal-oxo $\pi$-interaction.

Electron-withdrawing substituents on the ligand destabilize the metal-oxo through $\pi$-interaction making it a more reactive oxidant; strong electron-withdrawing effects with high $\pi$-acceptor nature stabilize the lower oxidation state, while electron-donating groups with low $\pi$-acceptor quality have a reverse effect [33, 34]. Another possibility is decreasing donor ability of the ligands decreases stabilities of both V(IV) and V(V) through phenoxy groups [34] as the results show decreasing in the basicity of the phenoxy group through the trend of MeO > H > Br > NO$_2$. The electrochemical studies support this supposition [35].

## 4. Conclusion

The systematic variation in the reactivity of oxo-vanadium complexes with the change of substituent in the ligand can be rationalized in terms of redox potentials. While electron withdrawing decreases the electron density of vanadium by electron-withdrawing groups as strong $\pi$-acceptors and increases it via the electron-donating groups as weak $\pi$-acceptors, the $\sigma$-donor decreases or increases the electron density on

the metal center via $\sigma$-donation. Both $\sigma$- and $\pi$-interactions have the same effect on the oxidation and reduction potentials.

Electron-withdrawing groups are weak $\sigma$-donors and the electron-donating groups are strong $\sigma$-donors. Complexes with en and pn bridges have similar trends by varying substituents, but Salpn ligands are better $\pi$-acceptors than Salen type ligands. Therefore, Salpn complexes are oxidized at higher potentials. Electrochemical results agree with electronic interactions between metal center and ligand by the UV–Vis and IR measurements.

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