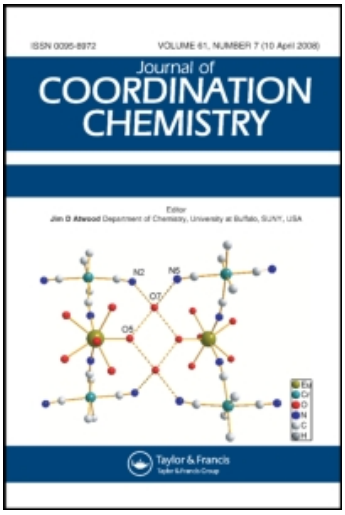

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Electrochemical and spectral behavior of mononuclear oxo-vanadium(IV)salicyldiimine complexes

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Electrochemical and spectral behavior of mononuclear oxo-vanadium(IV)salicyldiimine complexes

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Electrochemical and spectroscopic data of unsymmetrical and symmetrical mononuclear oxo-vanadium(IV)salicyldiimine complexes [VO(*x*,*y*-Sal)(*x*′,*y*′-Sal)Phen)] and [VO(*x*, *y*-Sal)(*x*′, *y*′-Sal)iPr)], where $x, x' = 5$-H, 5-Br, 5-NO_2 and $y, y' = 4$-H, 4-MeO, were prepared and studied. Our results show tetradentate SalPhen or SaliPr coordinated in the equatorial plane. The electrochemical behavior is related to UV–Vis and IR spectra. Electron-withdrawing groups affected vanadium through π-acceptor properties of imine and electron-donation groups through π- and σ-donation via phenolic oxygen.

Keywords: Oxo-vanadium(IV); Salicyldiimine complexes; Unsymmetrical tetradentate salicyldiimine; SalPhen; SaliPr

1. Introduction

Orally active vanadyl complexes with $VO(N_2O_2)$ coordination modes have applications in the fields of synthesis and catalysis [1–5] and as insulin-mimetic [6–13]. The oxo functionality of oxo-vanadium complexes has taken part in a number of interesting oxo-transfer reactions. Attention is still growing for modified and supported reagents for catalysis and materials chemistry [14–19].

Due to the structural rigidity combined with the ease of preparation and derivatization of salen, it is an attractive scaffold for the development of bi-functional complexes [19, 20]. Salen ligands bind metal ions through two nitrogens and two oxygens. This tetradentate binding resembles the porphyrin framework in the heme-based oxidative enzymes [21–25]. Salen derivatives are more easily synthesized than porphyrins and their structures are more easily manipulated to create an asymmetric environment around the active metal site.

Electrochemical and spectroscopic data (UV–Vis and IR) provide information regarding catalytic activities that are frequently accompanied by change in the structure of the complex and the oxidation state of the metal [27–34].

Here we report the preparation and characterization of substituted Schiff-base oxo-vanadium(IV) complexes with $VO(N_2O_2)$ coordination modes (figure 1) and their electrochemical and spectroscopic properties.

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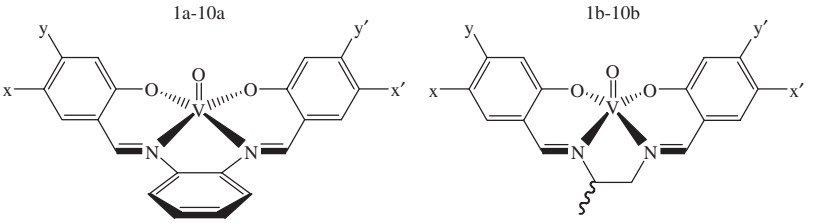

NOE	Complex Name[a]	Bridge	x	x′	y	y′
1a	*VO[(Sal)$_2$Phen]*	Phen	H	H	H	H
2a	*VO[(Sal)(5-Br–Sal)Phen]*	Phen	H	Br	H	H
3a	*VO[(Sal)(5-Br-4-MeO–Sal)Phen]*	Phen	H	Br	H	MeO
4a	*VO[(Sal)(5-NO$_2$–Sal)Phen]*	Phen	H	NO_2	H	H
5a	*VO[(5-Br–Sal)(5-NO$_2$–Sal)Phen]*	Phen	Br	NO_2	H	H
6a	*VO[(5-Br–Sal)$_2$Phen]*	Phen	Br	Br	H	H
7a	*VO[(5-Br–Sal)(5-Br-4-MeO–Sal)Phen]*	Phen	Br	Br	H	MeO
8a	*VO[(5-Br-4-MeO–Sal)$_2$Phen]*	Phen	Br	Br	MeO	MeO
9a	*VO[(5-NO$_2$–Sal)(5-Br-4-MeO–Sal)Phen]*	Phen	NO_2	Br	H	MeO
10a	*VO[(5-NO$_2$–Sal)$_2$Phen]*	Phen	NO_2	NO_2	H	H
1b	*VO[(Sal)$_2$iPr]*	iPr	H	H	H	H
2b	*VO[(Sal)(5-Br–Sal)iPr]*	iPr	H	Br	H	H
3b	*VO[(Sal)(5-Br-4-MeO–Sal)iPr]*	iPr	H	Br	H	MeO
4b	*VO[(Sal)(5-NO$_2$–Sal)iPr]*	iPr	H	NO_2	H	H
5b	*VO[(5-Br–Sal)(5-NO$_2$–Sal)iPr]*	iPr	Br	NO_2	H	H
6b	*VO[(5-Br–Sal)$_2$iPr]*	iPr	Br	Br	H	H
7b	*VO[(5-Br–Sal)(5-Br-4-MeO–Sal)iPr]*	iPr	Br	Br	H	MeO
8b	*VO[(5-Br-4-MeO–Sal)$_2$iPr]*	iPr	Br	Br	MeO	MeO
9b	*VO[(5-NO$_2$–Sal)(5-Br-4-MeO–Sal)iPr]*	iPr	NO_2	Br	H	MeO
10b	*VO[(5-NO$_2$–Sal)$_2$iPr]*	Phen	NO_2	NO_2	H	H

[a]Complexes **2a, 3a, 4a, 5a, 7a, 8a, 9a, 2b, 3b, 4b, 5b, 7b, 8b, 9b** are new.

Figure 1. Oxo(Salphen)vanadium(IV) **1a**–**10a** and oxo(SaliPr)vanadium(IV) **1b**–**10b** complexes.

2. Experimental

2.1. *Reagents*

2-Hydroxybenzaldehyde, 5-nitro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, vanadyl acetylacetonate and 1,2-diaminobenzene were used as received from commercial suppliers (Merck, Aldrich) and 1,2-diaminopropane was purified by distillation under vacuum. The solvents CH_3Cl, CH_2Cl_2, CH_3CN and EtOH 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. All chemicals were reagent grade and used without further purification. 4-Methoxy-5-bromo-2-hydroxybenzaldehyde 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 a Bruker FT-NMR AC-250 (250 MHz) spectrophotometer 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). Melting points were determined by 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)/3 M KCl reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode were employed for the electrochemical studies. Voltammetric 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*

Symmetrical Schiff bases H_2[(Sal)$_2$Phen] (**1a**), H_2[(5-Br–Sal)$_2$Phen] (**6a**), H_2[(5-NO_2–Sal)$_2$Phen] (**10a**) [26], H_2[(Sal)$_2$iPr] (**1b**) [27], H_2[(5-Br–Sal)$_2$iPr] (**6b**) and H_2[(5-NO_2–Sal)$_2$iPr] (**10b**) were obtained by conventional one-step condensation of 1,2-diamine with appropriate aldehyde in 1 : 2 molar ratio in methanol or ethanol [28–30] as previously described [27, 31–33].

2.3.1. Preparation of 5-bromo-4-methoxy-2-hydroxybenzaldehyde. A solution of Br_2 (3.94 g, 25 mmol) in CH_2Cl_2 (45 mL) was slowly added to 4-methoxy-2-hydroxybenzaldehyde (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. After the organic phases were dried over $MgSO_4$, 5-bromo-4-methoxy-2-hydroxybenzaldehyde (3.16 g, 97%) 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, 41.40; H, 2.85. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 11.18(s, 1H; OH), 9.77 (s, 1H; C*H*O), 7.50 (d, $J = 2.2$ Hz, 1H; 1 arom. H), 7.48 (d, $J = 2.2$ Hz, 1H; 1 arom. H), 2.25 (s, 3H; CH_3); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 195.98, 159.40, 140.53, 133.42, 130.04, 121.39, 111.24, 15.33; IR (KBr): ν(cm^{-1}) = 2883, 1654, 1608, 1452, 1415, 1378, 1303, 1272, 1236, 1199, 1024, 968, 865, 705.

2.3.2. Synthesis of *N,N′*-phenylene *bis*(salicylideneiminato) ligands

2.3.2.1. *Synthesis of H$_2$[(Sal)(5-Br–Sal)Phen].* To a vigorously stirred and cool (2–5°C) dilute solution of 20 mmol (216 mg) of 1,2-diaminobenzene in 30 mL of anhydrous ethanol was added dropwise a cooled solution of 10 mmol 2-hydroxybenzaldehyde in 40 mL anhydrous ethanol. After the addition was complete, the mixture was stirred for 15 min and then refluxed for 30 min. The resulting solution was used in the next step without purification. To a stirred solution, was added a solution of 10 mmol 5-bromo-2-hydroxybenzaldehyde in 40 mL anhydrous ethanol and it was refluxed for 90 min. The mixture was concentrated by solvent evaporation in a vacuum until an orange solid, H_2[(Sal)(5-Br–Sal)Phen], precipitated. The product was filtered

and recrystallized from ethanol until pure product was obtained. Yield 80%, based on 1,2-diaminobenzene, m.p. 178–180°C. Elemental analysis for $C_{20}H_{15}BrN_2O_2$, M.W. 395.25; Calcd (%): C, 60.78; H, 3.83; N, 7.09. Found: C, 60.72; H, 3.93; N, 7.25. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.68–7.43 (m, 11H), 8.67 (s, 1H), 9.35 (s, 1H), 10.65 (s, 1H), 12.35 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 110.35(2), 118.80(2), 121.62(2), 124.32(2), 129.33(2), 133.62, 135.22, 136.45, 141.08, 143.82(2), 158.91(2), 167.55(2); IR (KBr): ν(cm^{-1}) = 1603.

2.3.2.2. *Synthesis of H$_2$[(Sal)(5-Br-4-MeO–Sal)Phen].* The ligand was prepared from 5-bromo-4-methoxy-2-hydroxybenzaldehyde (10 mmol) by a similar procedure to that employed for H_2[(Sal)(5-Br–Sal)Phen]. Yield 65%, a light yellow solid, m.p. 251–253°C. Elemental analysis for $C_{21}H_{17}BrN_2O_3$, M.W. 425.28; Calcd (%): C, 59.31; H, 4.03; N, 6.59. Found: C, 59.05; H, 3.89; N, 6.69. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.86 (s, 3H), 6.59–7.51 (m, 10H), 8.49 (s, 1H), 8.64 (s, 1H), 12.97 (s, 1H), 13.62 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 59.43, 101.30, 103.10, 112.90, 115.21, 118.42, 122.21(2), 126.50, 127.95, 129.83, 136.72, 142,63(2), 154.47, 159.35, 161.15(2), 164.46, 186.24; IR (KBr): ν(cm^{-1}) = 1606.

2.3.2.3. *Synthesis of H$_2$[(Sal)(5-NO$_2$–Sal)Phen].* The ligand was prepared from 5-nitro-2-hydroxybenzaldehyde (10 mmol) with the procedures used for H_2[(Sal)(5-Br–Sal)Phen]. Yield 58%, an orange solid, m.p. 283–285°C. Elemental analysis for $C_{20}H_{15}N_3O_4$, M.W. 361.35; Calcd (%): C, 66.48; H, 4.18; N, 11.63. Found: C, 66.39; H, 4.07; N, 11.38. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.27–7.68 (m, 11H), 8.57 (s, 1H), 9.78 (s, 1H), 10.93 (s, 1H), 13.63 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 111.35(2), 119.80(2), 121.72, 124.32, 129.33(2), 135.62, 139.68, 141.82(2), 159.11, 163.54 (2), 167.55, 195.42; IR (KBr): ν(cm^{-1}) = 1616.

2.3.2.4. *Synthesis of H$_2$[(5-Br–Sal)(5-NO$_2$–Sal)Phen].* The ligand was prepared from 5-bromo-2-hydroxybenzaldehyde (10 mmol) and 5-nitro-2-hydroxybenzaldehyde (10 mmol) with similar procedures as employed for H_2[(Sal)(5-Br–Sal)Phen]. Yield 62%, a yellow-orange solid, m.p. 257–260°C. Elemental analysis for $C_{20}H_{14}BrN_3O_4$, M.W. 440.25; Calcd (%): C, 54.56; H, 3.21; N, 9.54. Found: C, 54.43; H, 3.28; N, 9.52. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.71–8.28 (m, 11H), 8.97 (s, 1H), 9.67 (s, 1H), 11.92 (s, 1H), 13.50 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 112.32, 115.95, 118.85, 120.03(2), 121.65(2), 126.21, 128.01, 129.83(2), 135.41, 139.38, 143.05, 148.17(2), 159.22, 164.11(2), 184.56; IR (KBr): ν(cm^{-1}) = 1615.

2.3.2.5. *Synthesis of H$_2$[(5-Br–Sal)(5-Br-4-MeO–Sal)Phen].* as prepared from 5-bromo-2-hydroxybenzaldehyde (10 mmol) and 5-bromo-4-methoxy-2-hydroxybenzaldehyde (10 mmol) with similar procedure to that used for H_2[(Sal)(5-Br–Sal)Phen]. Yield 45%, a yellow solid. M.p. 216–218°C. Elemental analysis for $C_{21}H_{16}Br_2N_2O_3$, M.W. 504.17 Calcd (%): C, 50.03; H, 3.20; N, 5.56. Found: C, 50.26; H, 2.97; N, 5.62. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.89 (s, 3H), 6.21–7.33 (m, 9H), 8.51 (s, 1H), 8.93 (s, 1H), 13.04 (s, 1H), 13.43 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 57.03, 101.31, 103.00, 112.14, 116.11, 119.22, 121.08, 122.97(2), 127.83, 129.03, 134.51(2), 135.92, 147,05(2), 157.01, 157.67, 164.15(2), 181.11; IR (KBr): ν(cm^{-1}) = 1605.

2.3.2.6. *Synthesis of H_2[(5-NO_2–Sal)(5-Br-4-MeO–Sal)Phen].* The ligand was prepared from 5-bromo-4-methoxy-2-hydroxybenzaldehyde (10 mmol) and 5-nitro-2-hydroxybenzaldehyde (10 mmol) using similar procedures as for H_2[(Sal)(5-Br–Sal)Phen]. Yield 60%, an orange solid, m.p. 256–259 °C. Elemental analysis for $C_{21}H_{16}BrN_3O_5$, M.W. 470.27; Calcd (%): C, 53.63; H, 3.43; N, 8.94. Found: C, 53.44; H, 3.59; N, 9.06. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.93 (s, 3H), 6.53–7.63 (m, 9H), 8.49 (s, 1H), 8.78 (s, 1H), 13.55 (s, 1H), 14.21 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 59.43, 101.41, 103.90, 112.93, 116.81, 19.72, 122.64(2), 126.15, 127.83, 129.03(2), 135.22, 140.33, 147,53(2), 159.05, 162.35(2), 164.26, 184.31; IR (KBr): ν(cm^{-1}) = 1612.

2.3.2.7. *Synthesis of H_2[(5-Br-4-MeO–Sal)$_2$Phen].* To a stirred solution of 10 mmol (216 mg) of 1,2-diaminobenzene in 40 mL of anhydrous ethanol, was added a cooled solution of 20 mmol 5-bromo-4-methoxy-2-hydroxybenzaldehyde in 80 mL anhydrous ethanol. After the addition was completed, the mixture was stirred for 30 min and then refluxed for 120 min. The mixture was concentrated by solvent evaporation in a vacuum until yellow H_2[(5-Br-4-MeO–Sal)$_2$Phen] precipitated. The product was filtered and recrystallized from ethanol until pure product was obtained. Yield 95%, based on 5-bromo-4-methoxy-2-hydroxybenzaldehyde, m.p. 249–251°C. Elemental analysis for $C_{22}H_{18}Br_2N_2O_4$, M.W. 534.20; Calcd (%): C, 49.46; H, 3.40; N, 5.24. Found: C, 49.70; H, 3.55; N, 5.31. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.97 (s, 6H), 6.58–7.51 (m, 8H), 8.56 (s, 2H), 13.64 (s, 2H); IR (KBr): ν(cm^{-1}) = 1605.

2.3.2.8. *Synthesis of H_2[(Sal)$_2$Phen], H_2[(5-Br–Sal)$_2$Phen], H_2[(5-NO_2–Sal)$_2$Phen].* The ligands were prepared from 2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde or 5-nitro-2-hydroxybenzaldehyde, respectively, with similar procedures to those employed for H_2[(5-Br-4-MeO–Sal)$_2$Phen and characterized by comparing to the literature [27–34].

2.3.3. Synthesis of *N,N*-isopropylene *bis*(salicylideneiminato) ligands

2.3.3.1. *Synthesis of H_2[(Sal)(5-Br–Sal)iPr].* To a vigorously stirred and cooled dilute solution (2–5°C) of 10 mmol (74 mg) of 1,2-diaminopropane in 40 mL of anhydrous ethanol, was added dropwise a cooled solution of 8 mmol 2-hydroxybenzaldehyde in 40 mL anhydrous ethanol. 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 solvent and excess diamine, and was used as a precursor for the next step without further purification. To a stirred solution of this precursor in 30 mL anhydrous ethanol was added a solution of 8 mmol 5-bromo-2-hydroxybenzaldehyde in 30 mL anhydrous ethanol, and the mixture was refluxed for 60 min and concentrated by solvent evaporation in a vacuum until oily yellow H_2[(Sal)(5-Br–Sal)iPr] was obtained. Yield 70%, based on 2-hydroxybenzaldehyde. 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, 56.32; H, 4.66; N, 7.98. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.41 (d, 3), 3.71 (d, 2H), 3.89 (m, 1H), 6.18–7.39 (m, 7H), 8.27 (s, 1H), 9.82 (s, 1H), 12.65 (s, 1H), 13.15 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 20.29, 64.97, 65.67,

118.99, 119.02, 119.90, 128.99, 133.54, 135.07(2), 158.26, 160.01, 163.31, 165.20; IR (KBr): $\nu(cm^{-1}) = 1627$.

2.3.3.2. *Synthesis of H$_2$[(Sal)(5-Br-4-MeO–Sal)iPr].* was prepared from 5-bromo-4-methoxy-2-hydroxybenzaldehyde (8 mmol) using the procedure employed for H$_2$[(Sal)(5-Br–Sal)iPr]. Yield 55%, an oily yellow product. Elemental analysis for $C_{18}H_{19}BrN_2O_3$, M.W. 391.26; Calcd (%): C, 55.26; H, 4.89; N, 7.16. Found: C, 54.98; H, 5.02; N, 7.33. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.49 (d, 3), 3.64 (d, 2H), 3.89 (m, 1H), 3.98 (s, 3H), 6.38–7.59 (m, 6H), 8.38 (s, 1H), 9.63 (s, 1H), 12.25 (s, 1H), 13.35 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 20.49, 58.37, 63.23, 65.67, 101.99, 103.11, 118.92, 121.92, 127.44(2), 132.35(2), 135.27, 159.26, 161.01, 162.93, 164.37, 179.22; IR (KBr): $\nu(cm^{-1}) = 1627$.

2.3.3.3. *Synthesis of H$_2$[(Sal)(5-NO$_2$–Sal)iPr].* To a vigorously stirred and cooled dilute solution (10–15°C) of 10 mmol (74 mg) of the 1,2-diaminopropane in 40 mL of anhydrous ethanol, was added dropwise a cooled solution of 8 mmol 2-hydroxybenzaldehyde in 40 mL anhydrous ethanol. After the addition was complete, the mixture was stirred for 15 min and then refluxed for 15 min. The resulting solution was evaporated in vacuum to remove the solvent and the excess diamine and was used as a precursor for the next step without further purification. To a stirred solution of this precursor in 30 mL anhydrous ethanol was added a solution of 8 mmol 5-bromo-2-hydroxybenzaldehyde in 30 mL anhydrous ethanol and refluxed for 60 min. The mixture was concentrated by solvent evaporation in a vacuum until yellow H$_2$[(Sal)(5-NO$_2$–Sal)iPr] precipitated. The product was filtered and recrystallized from ethanol until pure product was obtained. Yield 60%, based on 2-hydroxybenzaldehyde, m.p. 230–232°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, 62.17; H, 5.41; N, 12.92. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.45 (d, 3H), 3.82 (d, 2H), 3.95 (m, 1H), 6.97–7.29 (m, 7H), 8.20 (s, 1H), 8.45 (s, 1H), 12.99 (s, 1H), 14.50 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 19.87, 54.01, 65.3, 115.8, 118.7, 122.25, 124.45, 126.52(2), 128.43, 130.4, 132.21, 139.11, 156.68, 162.51(2), 163.52; IR (KBr): $\nu(cm^{-1}) = 1630$.

2.3.3.4. *Synthesis of H$_2$[(5-Br–Sal)(5-NO$_2$–Sal)iPr].* The ligand was prepared from 5-bromo-2-hydroxybenzaldehyde (8 mmol) and 5-nitro-2-hydroxybenzaldehyde (8 mmol) by the procedure used for H$_2$[(Sal)(5-NO$_2$–Sal)iPr]. Yield 45%, a yellow solid, m.p. 80–82°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, 50.01; H, 4.18; N 10.11. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.49 (d, 3H), 3.66 (m, 1H), 3.95 (d, 2H), 6.65–8.45 (m, 6H), 9.84 (s, 1H), 10.92 (s, 1H), 12.95 (s, 1H), 14.21 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 19.99, 64.01, 65.3, 115.09, 117.87, 119.08, 124.45, 125.02, 126.52, 128.41, 134.4, 135.2, 139.91, 156.68, 163.31(2), 165.32; IR (KBr): $\nu(cm^{-1}) = 1668$.

2.3.3.5. *Synthesis of H$_2$[(5-Br–Sal)(5-Br-4-MeO–Sal)iPr].* The ligand was prepared from 5-bromo-2-hydroxybenzaldehyde (8 mmol) and 5-bromo-4-methoxy-2-hydroxybenzaldehyde (8 mmol) with similar procedure to that employed for H$_2$[(Sal)(5-Br–Sal)iPr]. Yield 50%, an oily yellow product. 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, 46.20; H, 3.89; N, 5.85.

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.39 (d, 3), 3.74 (d, 2H), 3.83 (m, 1H), 3.96 (s, 3H), 6.28–7.68 (m, 5H), 8.48 (s, 1H), 10.02 (s, 1H), 13.25 (s, 1H), 13.65 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 20.07, 56.43, 64.12, 65.71, 100.77, 102.41, 112.89, 118.03, 119.96, 127.06, 133.75(2), 136.07, 160.12, 160.91, 163.29, 164.87, 172.31; IR (KBr): ν(cm^{-1}) = 1623.

2.3.3.6. *Synthesis of H$_2$[(5-NO$_2$–Sal)(5-Br-4-MeO–Sal)iPr].* was prepared from 5-bromo-4-methoxy-2-hydroxybenzaldehyde (8 mmol) and 5-nitro-2-hydroxybenzaldehyde (8 mmol) with similar procedures as for H_2[(Sal)(5-Br–Sal)iPr]. Yield 55%, an oily yellow product. 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, 49.47; H, 4.23; N, 9.50. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.39 (s, 3H), 3.73 (d, 2H), 3.82 (m, 1H), 3.97 (s, 3H), 6.62–8.21 (m, 5H), 8.34 (s, 1H), 9.83 (s, 1H), 13.45 (s, 1H), 14.23 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 20.25, 57.32, 64.082, 65.83, 100.62, 102.91, 115.02, 118.66, 125.61(2), 128.01, 135.34, 142.11, 159.20, 163.14(2), 163.92, 173.02; IR (KBr): ν(cm^{-1}) = 1620.

2.3.3.7. *Synthesis of H$_2$[(5-Br-4-MeO–Sal)$_2$iPr].* To a stirred solution of 10 mmol (74 mg) of 1,2-diaminopropane in 40 mL of anhydrous ethanol, was added a cooled solution of 18 mmol 5-bromo-4-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 solvent and excess diamine. The product was dissolved in 30 mL anhydrous ethanol and concentrated by solvent evaporation in a vacuum until yellow-orange H_2[(5-Br-4-MeO–Sal)$_2$iPr] precipitated. The product was filtered and recrystallized from ethanol until pure product was obtained. Yield 90%, based on 5-bromo-4-methoxy-2-hydroxybenzaldehyde, m.p. 169–171°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, 45.71; H, 4.30; N, 5.74. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.37 (s, 3H), 3.63 (d, 2H), 3.76 (m, 1H), 3.90 (s, 6H), 6.44 (m, 2H), 7.30 (m, 2H), 8.14 (s, 2H), 13.70 (s, 2H). ^{13}C NMR (250 MHz, $CDCl_3$): δ (ppm) = 20.15, 56.32(2), 64.08(2), 100.15(2), 100.86(2), 113.00, 135.00(2), 159.20(2), 162.54, 163.85, 164.32(2); IR (KBr): ν(cm^{-1}) = 1619.

2.3.3.8. *Synthesis of H$_2$[(Sal)$_2$iPr], H$_2$[(5-Br–Sal)$_2$iPr], H$_2$[(5-NO$_2$–Sal)$_2$iPr].* The ligands were prepared from 2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde or 5-nitro-2-hydroxybenzaldehyde, respectively, using similar procedures as for H_2[(5-Br-4-MeO–Sal)$_2$iPr] and characterized by literature comparison [27–34].

2.3.4. Synthesis of *N,N*-phenylene *bis*(salicylideneiminato)oxo-vanadium(IV) complexes

2.3.4.1. *Synthesis of VO[(Sal)(5-Br–Sal)Phen] (***2a***).* To a stirred and hot solution of 2 mmol H_2[(5-Br–Sal)(Sal)Phen] in 25 mL ethanol was added a hot solution of 2 mmol (530 mg) VO(acac) in 10 mL methanol. The reaction mixture was then refluxed for 45 min. The colored solution was concentrated and cooled to yield green powder, which was filtered and recrystallized from ethanol until pure product was obtained. Yield 92%. Elemental analysis for $C_{20}H_{13}BrN_2O_3V$, M.W. 460.17; Calcd (%): C, 52.20; H, 2.85; N, 6.09. Found: C, 51.88; H, 2.56; N, 5.79.

2.3.4.2. *Synthesis of VO[(Sal)(5-Br–4–MeO–Sal)Phen]* (**3a**). The complex was prepared from H_2[(Sal)(5-Br–MeO–Sal)Phen] by the same procedure for **2a**. Yield 80%. Elemental analysis for $C_{21}H_{15}BrN_2O_4V$, M.W. 490.20; Calcd (%): C, 51.45; H, 3.08; N, 5.71. Found: C, 51.34; H, 2.87; N, 5.92.

2.3.4.3. *Synthesis of VO[(Sal)(5-NO_2–Sal)Phen]* (**4a**). The complex was prepared from H_2[(Sal)(5-NO_2–Sal)Phen] using the procedure for **2a**. Yield 85%. Elemental analysis for $C_{20}H_{13}N_3O_5V$, M.W. 426.28; Calcd (%): C, 56.35; H, 3.07; N, 9.86. Found: C, 56.02; H, 3.30; N, 9.71.

2.3.4.4. *Synthesis of VO[(5-Br–Sal)(5-NO_2–Sal)Phen]* (**5a**). was prepared from H_2[(5-Br–Sal)(5-NO_2–Sal)Phen] by the same procedure used for **2a**. Yield 85%. Elemental analysis for $C_{20}H_{12}BrN_3O_5V$, M.W. 505.17; Calcd (%): C, 47.55; H, 2.39; N, 8.32. Found: C, 47.87; H, 2.61; N, 8.12.

2.3.4.5. *Synthesis of VO[(5-Br–Sal)(5-Br-4-MeO–Sal)Phen]* (**7a**). The complex was prepared from H_2[(5-Br–Sal)(5-Br-4-MeO–Sal)Phen] using the procedure employed for **2a**. Yield 75%. Elemental analysis for $C_{21}H_{14}Br_2N_2O_4V$, M.W. 569.10; Calcd (%): C, 44.32; H, 2.48; N, 4.92. Found: C, 44.51; H, 2.24; N, 5.11.

2.3.4.6. *Synthesis of VO[(5-Br-4-MeO–Sal)$_2$Phen]* (**8a**). The complex was prepared from H_2[(5-Br-4-MeO–Sal)$_2$Phen] with the procedure for **2a**. Yield 90%. Elemental analysis for $C_{22}H_{16}Br_2N_2O_5V$, M.W. 599.12; Calcd (%): C, 44.10; H, 2.69; N, 4.68. Found: C, 44.00; H, 2.60; N, 4.66.

2.3.4.7. *Synthesis of VO[(5-NO_2–Sal)(5-Br-4-MeO–Sal)Phen]* (**9a**). was prepared from H_2[(5-NO_2-Sal)(5-Br-4-MeO-Sal)phen] using the same procedure employed for **2a**. Yield 95%. Elemental analysis for $C_{21}H_{14}Br_2N_2O_4V$, M.W. 569.10; Calcd (%): C, 44.32; H, 2.48; N, 4.92. Found: C, 44.51; H, 2.24; N, 5.11.

2.3.5. Synthesis of N,N′-isopropylene bis(salicylideneiminato) complexes

2.3.5.1. *Synthesis of VO[(Sal)(5-Br–Sal)iPr]* (**2b**). To a stirred and hot solution of 2 mmol H_2[(5-Br–Sal)(Sal)iPr] in 25 mL ethanol was added a hot solution of 2 mmol (530 mg) VO(acac) in 15 mL methanol and the reaction mixture was refluxed for 60 min. The colored solution was concentrated and cooled to yield green powder. The product was recrystallized from ethanol/acetonitrile. Yield 88%. Elemental analysis for $C_{17}H_{15}BrN_2O_3V$, M.W. 426.16; Calcd (%): C, 47.91; H, 3.55; N, 6.57. Found: C, 47.67; H, 3.41; N, 6.28.

2.3.5.2. *Synthesis of VO[(Sal)(5-Br-4-MeO–Sal)iPr]* (**3b**). The complex was prepared from H_2[(Sal)(5-Br-4-MeO–Sal)iPr] by the same procedure used for **2b**. Yield 80% of green crystals. Elemental analysis for $C_{18}H_{17}BrN_2O_4V$, M.W. 456.18; Calcd (%): C, 47.39; H, 3.76; N, 6.14. Found: C, 47.09; H, 3.50; N, 6.24.

2.3.5.3. *Synthesis of VO[(Sal)(5-NO_2–Sal)iPr]*(**4b**). It is prepared by use of H_2[(Sal)(5-NO_2–Sal)iPr] with the procedure employed for **2b**. Yield 75%.

Elemental analysis for $C_{17}H_{15}N_3O_5V$, M.W. 392.26; Calcd (%): C, 52.05; H, 3.85; N, 10.71. Found: C, 51.72; H, 3.97; N, 11.00.

2.3.5.4. *Synthesis of VO[(5-Br–Sal)(5-NO_2–Sal)iPr]* (**5b**). The complex was prepared using H_2[(5-Br–Sal)(5-NO_2–Sal)iPr] with the same procedure as used for **2b**. Yield 80%. Elemental analysis for $C_{17}H_{14}BrN_3O_5V$, M.W. 471.16; Calcd (%): C, 43.34; H, 3.00; N, 8.92. Found: C, 43.63; H, 2.83; N, 9.08.

2.3.5.5. *Synthesis of VO[(5-Br–Sal)(5-Br-4-MeO–Sal)iPr]* (**7b**). The complex was prepared by use of H_2[(5-Br–Sal)(5-Br-4-MeO–Sal)iPr] with the procedure for **2b**. Yield 85%. Elemental analysis for $C_{18}H_{16}Br_2N_2O_4V$, M.W. 535.08; Calcd (%): C, 40.40; H, 3.01; N, 5.24. Found: C, 40.34; H, 3.17; N, 5.39.

2.3.5.6. *Synthesis of VO[(5-Br-4-MeO–Sal)$_2$iPr]* (**8b**). The complex was prepared from H_2[(5-Br-4-MeO–Sal)$_2$iPr] using the procedure employed for **2b**. Yield 90%. Elemental analysis for $C_{19}H_{18}Br_2N_2O_5V$, M.W. 565.11; Calcd (%): C, 40.38; H, 3.21; N, 4.96. Found: C, 40.53; H, 3.47; N, 4.78.

2.3.5.7. *Synthesis of VO[(5-NO_2–Sal)(5-Br-4-MeO–Sal)iPr]* (**9b**). was prepared from H_2[(5-NO_2–Sal)(5-Br-4-MeO–Sal)iPr] with the procedure employed for **2a**. Yield 85%. Elemental analysis for $C_{18}H_{16}BrN_3O_6V$, M.W. 501.18; Calcd (%): C, 43.14; H, 3.22; N, 8.38. Found: C, 42.81; H, 3.31; N, 8.45.

3. Results and discussion

Symmetrical Schiff-base ligands incorporating either a phenyl or isopropyl (*i*Pr) bridge and corresponding oxo-vanadium(IV) complexes **1a**, **6a**, **10a** and **1b**, **6b, 10b** were synthesized by literature methods. The Schiff-base ligands and corresponding vanadium(IV) complexes **2a**, **3a**, **4a**, **5a**, **7a**, **8a**, **9a**, **2b**, **3b**, **4b**, **5b**, **7b**, **8b** and **9b** are new. Vanadium complexes were obtained through mixing $VO(acac)_2$ with the tetradentate ligand in ethanolic solution and characterized by electrochemical, microanalyses, UV-Vis and NMR spectra. Some of the results are summarized in table 1. Single crystals of oxo-vanadium complexes for X-ray diffraction measurements could not be obtained.

V=O stretching frequencies in the solid state are given in table 1. A sharp band at 1596–1637 cm^{-1} due to azomethine ν(C=N) stretch of the ligands, shifts to lower wavenumber by 1–20 cm^{-1} indicating coordination of azomethine nitrogen to the metal [34]. Monomeric green five-coordinate oxo-vanadium complexes have higher V=O stretching frequencies than polymeric orange-brown six-coordinate complexes, around 950 ± 50 and $850 \pm 30\,cm^{-1}$, respectively [35], providing a criterion for discriminating the coordination number of oxo-vanadium complexes [36–38]. Thus, the green complexes **1a**, **2a**, **3a**, **6a**, **7a**, **8a**, **9a**, **1b**, **2b**, **3b**, **4b**, **6b**, **7b**, **8b**, **9b**, **10b** whose ν(V=O) values are 911–993 cm^{-1} are monomeric five-coordinate with square-pyramidal geometries, and the orange-brown complexes **4a**, **5a**, **10a**, **4b**, **5b** whose ν(V=O) values are 841–873 cm^{-1} are polymeric six-coordinate polynuclear linear chain structures (V=O···V=O···) [35] with octahedral geometries [39, 40]. The symmetrical

Table 1. Spectral and physical properties of oxo-vanadium complexes **1a**–**10a** and **1b**–**10b**.

NOE	Color	m.p. (°C)[a]	$\lambda_{max}(\varepsilon)$ nm	$\lambda_{CT}(\varepsilon)$ nm[b]	$\nu_{V=O}$ (cm^{-1})	$\nu_{C=N}$ (cm^{-1})[c]
1a	Green	343–345	545(390)	419(10700)	982	**1603**
2a	Light green	400*	582(180)	408(20400)	986	**1601, 1602w**
3a	Green-yellow	350*	423(sh)	389(14500)	984	**1596, 1602**
4a	Brown	378*	533(310)	367(10600)	872	**1612, 1603w**
5a	Brown	389*	536(121)	392(15600)	873	**1609, 1600**
6a	Green	400*	744(5)	405(4070)	911	**1600**
7a	Green-yellow	360*	744(10)	398(3290)	980	**1596, 1600**
8a	Green-yellow	400*	746(20)	393(12400)	985	**1596**
9a	Green-yellow	400	744(16)	420(2560)	982	**1598, 1610w**
10a	Dark orange	300*	538(241)	432(3578)	841	**1614**
1b	Green	155–156	583(100)	359(7870)	976	**1611**
2b	Dark green	95*	558(116)	364(5600)	980	**1632, 1609w**
3b	Dark green	–	–	361(sh)	984	**1611, 1602w**
4b	Brown-red	350*	743(19)	399(17500)	868	**1637, 1598w**
5b	Brown-red	330*	741(12)	434(2109)	867	**1636, 1618w**
6b	Green	400*	576(51)	371(4526)	977	**1621**
7b	Dark green	198–203	737(13)	–	993	**1610, 1616w**
8b	Green	400*	–	397(2530)	987	**1603**
9b	Green	340*	579(120)	359(13700)	987	**1602, 1595w**
10b	**Green-brown**	**80**	**743 (12)**	**420(sh)**	**970**	**1590**

[a]*Decomposition point.
[b]CT is charge transfer peak in UV-Vis spectra obtained from 0.0001 M of oxo-vanadium complex in DMF.
[c]w – weak.

and unsymmetrical complexes with electron-withdrawing substituent on the ligand, due to increase of partial positive charge on vanadium, are six coordinate, except for **9a** and **9b**. In **9a** and **9b**, in addition to withdrawing nitro substitute, donating substituents –Br and –MeO on the phenyl ring exist. Therefore, vanadium does not coordinate other ligands or the oxo group of other complexes and remains five-coordinate. Electrochemical behavior of the vanadium center in these complexes provides corroborating data.

While electron density of the metal center decreases by electron-withdrawing groups as strong π-acceptors, it increases by reducing π-accepting property of electron donating ligand, via C=N band. Evidence for this is the similarity of C=N bond stretch upon complex formation when it should be expected to decrease further. Evidently, the electron-withdrawing properties of ligand to vanadium transfer through the π bond, not a σ interaction, and electron-donating properties occur through both σ and π donating interactions of phenoxy.

By change of the bridge from phenyl (**1a**–**10a**) to isopropyl (**1b**–**10b**), because of more electron donation of *i*-Pr, the C=N band stretching frequency increases about 20 cm^{-1} and partial positive charge on the vanadium decreases. This is observed for green monomeric complex **10b** relative to orange polymeric complex **10a** with ν(V=O) values 970 and 841 cm^{-1}, respectively.

Table 1 also provides electronic spectral data of complexes. The electronic spectra of both kinds of ligands in DMF exhibit two bands around 250 ± 30 and 330 ± 30 nm. Based on their extinction coefficients these are assigned as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. Both bands shift to lower energy in complexes indicating coordination to the metal. This is supported by appearance of a lower intensity band around 400 ± 30 nm due to ligand to metal charge transfer (LMCT).

Complexes display a weak broad band at 500–700 nm and a shoulder around 450 nm due to expected d–d transitions. In some cases the shoulder overlaps with the intense LMCT transition [41].

Vanadium(IV) complexes with d^1 electronic configuration suffer from distortion due to first-order Jahn-Teller effect [42] that causes tetragonal distortion to a structure with C_{4v} symmetry. The strong color of the complexes indicate low-energy CT bands that originate from the filled high-energy ligand π orbital to the metal orbitals [39]. The ground state structure of vanadium(IV) in VO(SaliPr) or VO(Salphen) is located slightly above the ONNO pseudo-plane of the ligand, as seen in the crystal structure [39]. These species seem to suffer from the second-order Jahn-Teller effect [43]. Increasing LMCT wavelength from 393 to 432 nm occur with increasing electron-withdrawing nature of ligands as **5a** < **7a** < **3a** < **6a** < **2a** < **1a** < **9a** < **5a** < **4a** < **10a** for complexes with a phenyl bridge and a similar trend for isopropyl bridge. The wavelength for d–d transitions, λ_{max}, as a function of electronic properties of ligands, decreases from 5-NO_2 substituent (**10a** or **10b**) as an electron-withdrawing group to 4-MeO or 5-Br as electron-donating groups. Two reasons are offered. First, V(IV) is a hard acid with good interaction with hard –O and –N donors and electron-withdrawing substituents, making them harder. Therefore, on the basis of LFT more energy gap between HOMO and LUMO occur. Second, on the basis of CFT and π donation of phenoxy, Δ decreases. These trends are supported by the electrochemical behavior. Thus, an electron-withdrawing group operates through π-acceptor properties of the imine and electron-donation group through both π- and σ- donation via phenolic oxygen.

Electrochemical behavior of complexes was studied by the voltammometric technique in DMF solution in presence of TBAHP at RT in the potential range 0.0 to 1.0 V (*vs.* Ag/AgCl). The formal potentials ($E_{1/2}$) for the V(IV/V) redox couple were calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials of CVs. The ligands were tuned electronically by variation of corresponding diamines and 2-hydroxybenzaldehyde ligand precursors.

Recent studies [44–46] revealed that substituents at the 5,5′-position of the ligand could have profound effects. To quantify the influence of 5,5′-substituent on oxidation, reduction potentials of oxo-vanadium salicylaldimine complexes with electron-donating and electron-withdrawing groups were evaluated (table 2). There is a clear correlation between σ_p of the 5,5′-substituent and the value of $E_{1/2}$ for the V(IV)/V(V) redox couples. The cyclic voltammograms of oxo-vanadium complexes are provided in Supplemental Data. The voltammograms of other oxo-vanadium derivatives are similar. In most cases ΔE_p was at 100 ± 20 mV for one-electron transfer according to Nernst's equation for the vanadyl Schiff-base complexes. Upon reversal of the scan direction, the V(V) complexes are reduced to V(IV) at lower potentials. Multiple scans show the five-coordinate geometry is stable at least on the cyclic voltammetry time scale. The results show that in each series of ligands with aliphatic and aromatic imine bridges, the anodic peak potential (E_{pa}) corresponding to the intramolecular reductive coupling of the imine groups varies, as would be expected from the electronic effects of the substituents at the 5,5′ positions. Thus, E_{pa} becomes more positive according to the sequence MeO < H < Br < NO_2. On the other hand, the cathodic peak potential (E_{pc}) becomes less negative in the sequence MeO < H < Br < NO_2, increasing in both electron-withdrawing and acceptor qualities of the substituents.

Table 2. Electrochemical data of oxo-vanadium(IV) complexes **1a**–**10a** and **1b**–**10b** for V(IV)/V(V) couples in the presence of electron releasing and withdrawing substituents on the ligand.[a]

NOE	E_{pc} (mV)	E_{pa} (mV)	E_p(mV)	$E_{1/2}$ (mV)
1a	635	525	110	580
2a	650	530	115	590
3a	735	625	110	682
4a	740	600	140	670
5a	760	660	100	710
6a	720	600	120	660
7a	710	600	110	655
8a	695	625	70	660
9a	795	610	185	702
10a	795	705	90	750
1b	495	390	105	442
2b	550	420	130	485
3b	385	270	115	327
4b	640	535	105	587
5b	760	555	205	657
6b	570	465	105	517
7b	750	610	140	680
8b	560	455	105	507
9b	423	339	84	381
10b	259	219	40	239

[a]Potentials are *versus* SCE, R.T., DMF as solvent and TBAHP as supporting electrolyte in 0.0001 molar concentration of analyst.

Substituents may change the metal-oxo bond length, altering the non-bonding ligand interactions, however, such effects on metal-oxo bond length are typically less pronounced [47].

For all series, Hammett type relationships are found between the E_{pa} values and the appropriate *para*-substituent [48], reflecting the variation of electrode potential as a function of the electron-withdrawing ability of the substituents at the 5,5′ positions. The results show that decrease in basicity of the phenoxy group $MeO > H > Br > NO_2$ would be determinant for the electrochemical sequences. These electrochemical studies provide credence to this supposition [44, 45, 49–51]. Strong electron-donating substituents stabilize the higher oxidation state V(V) through the phenoxy groups, while electron-withdrawing substituents have reverse effect [52, 53]. Thus, the systematic reactivity of the oxo-vanadium complexes can be rationalized in terms of redox potentials.

Electron withdrawing decreases the electron density of the metal center by strong π-acceptors and increases by reducing π-accepting of the ligand via the C=N band. The σ-donor property decreases or increases the electron density on the metal center via σ- and π-donation. The oxidation of V(IV) increases: **5a** < **7a** < **3a** < **6a** < **2a** < **1a** < **9a** < **5a** < **4a** < **10a** for complexes with phenyl or *i*-Pr bridges.

4. Concluding remarks

Complexes with aromatic and aliphatic bridges have similar potential trend with substituent, but due to extensions of the π-system on salphen-type ligands,

[H_2(x, y-Sal)(x', y'-Sal)Phen)], are better π-acceptors than salipn-type ligands, [H_2(x, y-Sal)(x', y'-Sal)iPr)]. Therefore, [VO(x, y-Sal)(x', y'-Sal)Phen)] type complexes are oxidized at higher potentials. These electrochemical results have good agreement with proposed electronic interaction between metal and ligand by the UV-Vis and IR measurements. The electrode potentials reflect the electron-withdrawing ability of substituents at 5,5′ positions. In fact, electron-donating substituents on the ligand stabilize the high valent oxo-vanadium and electron-withdrawing substituents on the ligand destabilize the oxo-vanadium through π-interactions, making it a more reactive oxidant.

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