

## Research Article

# Synthesis, Structural Characterization, and Electrochemical Studies of New Oxovanadium(V) Complexes Derived from 2-Furanoylhydrazon Derivatives

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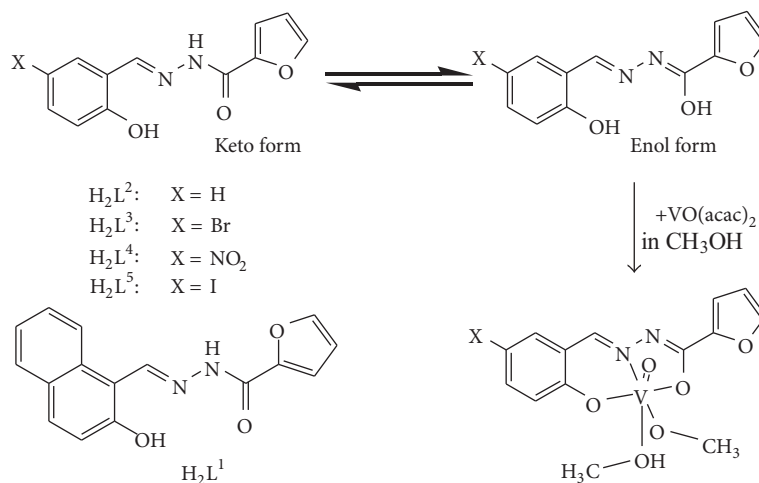
Five monooxovanadium(V) complexes [VO(L<sup>1</sup>)(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] (1), [VO(L<sup>2</sup>)(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] (2), [VO(L<sup>3</sup>)(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] (3), [VO(L<sup>4</sup>)(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] (4), and [VO(L<sup>5</sup>)(OCH<sub>3</sub>)(OHCH<sub>3</sub>)] (5) were synthesized and characterized by IR, NMR UV-Vis, and single-crystal structure analysis [H<sub>2</sub>L<sup>1</sup> = (E)-N'-(2-hydroxynaphthalen-1-yl)methylenefuran-2-carbohydrazide, H<sub>2</sub>L<sup>2</sup> = (E)-N'-(2-hydroxybenzylidene)furan-2-carbohydrazide, H<sub>2</sub>L<sup>3</sup> = (E)-N'-(5-bromo-2-hydroxybenzylidene)furan-2-carbohydrazide, H<sub>2</sub>L<sup>4</sup> = (E)-N'-(2-hydroxy-5-nitrobenzylidene)furan-2-carbohydrazide, H<sub>2</sub>L<sup>5</sup> = (E)-N'-(2-hydroxy-5-iodobenzylidene)furan-2-carbohydrazide]. In all 1–3 structures the vanadium atom has a distorted octahedral coordination with the three meridional donor atoms from the Schiff base dianion (L<sup>1-3</sup>)<sup>2-</sup> and one methoxylato group occupying the sites of the equatorial plane. The oxo group and one methanol molecule occupy the apical sites. In the complexes 1, 2, and 3 the conformation of 2-furanyl oxygen atom relative to the carbohydrazide oxygen atom is *s*-anti, *s*-anti/*s*-syn, and *s*-syn at 293 K, respectively. Cyclic voltammetric experiments of the solution species 1–5 in DMSO revealed a quasi-reversible behavior.

## 1. Introduction

The chemistry of vanadium has received considerable attention due to the discovery that vanadium is an essential element in biological systems [1]. There is continuous interest in the chemistry of vanadium complexes due to its inhibitory capabilities for various enzymes [2], its ability to catalyze oxidation and oxo-transfer reactions [3], and its occurrence in many biological systems [4]. This is particularly related with the discoveries of several medicinal properties of vanadium complexes, that is, insulin mimetic [5–7], antifungal/antibacterial [8], antitumor [9], anticancer activities [10], and the presence of vanadium in the prosthetic group of certain haloperoxidases and nitrogenases [11]. Structural and functional models for vanadate-dependent haloperoxidases, for vanadium nitrogenases and other biologically active

vanadium compounds, have further stimulated vanadium coordination chemistry [12]. Vanadium complexes are also important catalysts for several chemical reactions such as oxidation, epoxidation, and hydroxylation [13]. Schiff base complexes of V (III, IV and V) have been used as catalysis for the electroreduction of O<sub>2</sub> to H<sub>2</sub>O in acetonitrile [14]. Because of electrochemical reversibility of V-Schiff base complex derivations, they can be used as electron transfer mediator for modification of different electrode materials, and preparation of chemically modified electrodes with these compounds has been received increasing interest in the field of electroanalysis [15].

On the other hand, hydrazone ligands, a class of Schiff base, derived from the condensation of acid hydrazides (R-CO-NH-NH<sub>2</sub>) with aromatic 2-hydroxy carbonyl compounds are important tridentate O, N, O-donor ligands.



SCHEME 1: Tridentate hydrazone Schiff base ligands and their oxovanadium complexes.

The coordination chemistry and biochemistry of aroylhydrazones,  $R-CO-NH-N=CH-R'$ , have attracted increasing interest due to their chelating ability and their pharmacological applications [16]. Hydrazone ligands create environment similar to biological systems by usually making coordination through oxygen and nitrogen atoms [17]. Furthermore, hydrazones have wide spread applications in fields such as coordination chemistry [18, 19], analytical chemistry [20, 21], bioinorganic chemistry [22–24], and also in magnetic, electronic, nonlinear optically active, and fluorescent [25] compounds.

As part of our research in the study of the coordinating capabilities of aroylhydrazones and their coordination compounds [26–30], here, we report the synthesis, structure, and electrochemistry behavior of monooxovanadium(V) complexes of furancarbohydrazone Schiff bases (Scheme 1).

## 2. Experimental

**2.1. Materials and Instrumentations.** Vanadyl bis(acetylacetonate), 2-furancarboxylic acid hydrazide, 2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, and 2-hydroxy-1-naphthaldehyde were purchased from Merck and used as received. 2-hydroxy-5-iodobenzaldehyde was synthesized according to the reported literature procedure [31]. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer. UV-Vis spectra of solution were recorded on a thermospectronic, Helios Alpha spectrometer.  $^1H$  and  $^{13}C$  NMR spectra of ligands and their complexes in DMSO- $d_6$  solution were recorded on a Bruker 250 and 62.9 MHz spectrometer, and chemical shifts are indicated in ppm relative to tetramethylsilane. Voltammetric experiments were performed using an autolab voltammetric analyzer.

## 2.2. Synthesis of the Ligands

**2.2.1. General Procedure.** All ligands were prepared in a similar manner by refluxing a mixture of 2-furancarboxylic acid hydrazide and *o*-hydroxybenzaldehyde with equivalent molar ratio in 20 mL methanol. The mixture was refluxed for 2–3 h. The solution was then evaporated on a steam bath to 5 mL and cooled to room temperature. The obtained solids were separated and filtered off, washed with 5 mL of cooled methanol, and then dried in air. Completion of the reactions was checked by TLC on silica gel plates.

**2.3. Synthesis of (*E*)-*N'*-((2-Hydroxynaphthalen-1-yl)methylene)furan-2-carbohydrazone ( $H_2L^1$ ).** Yield: 85%. Anal Calc. for  $C_{16}H_{12}N_2O_3$  (280.28 g/mol) C: 68.56, H: 4.32, N: 9.99%. Found C: 68.50, H: 4.36, N: 10.11%. Selected IR data ( $cm^{-1}$ ): 1650 (vs, C=O); 1591 (m, C=N<sub>azomethine</sub>); 951 (m, N-N); 1288, 1321 (s, C-O enolate); 3167 (m, NH); 3612 (m, O-H)  $cm^{-1}$ .  $^1H$  NMR (250.13 MHz; DMSO- $d_6$ ):  $\delta$  12.68 (s, 1H, CO-NH-); 12.24 (s, 1H, -OH); 9.48 (s, 1H); 8.18 (d, 1H,  $J = 8.25$ ); 7.96 (s, 1H); 7.89 (d, 1H,  $J = 9.5$  Hz); 7.85 (d, 1H,  $J = 9.0$  Hz); 7.56 (t, 1H,  $J = 8.0$  Hz); 7.34 (m, 2H); 7.19 (d, 1H,  $J = 9.0$  Hz); 6.70 (t, 1H,  $J = 1.5$  Hz) ppm.  $^1H$  NMR (250.13 MHz; DMSO- $d_6$  +  $D_2O$ ):  $\delta = 9.36$  (s, 1H); 8.15 (s, 1H); 7.85 (s, 3H); 7.52 (s, 1H); 7.30 (s, 2H); 7.14 (s, 1H); 6.66 (s, 1H) ppm.  $^{13}C$  NMR (DMSO- $d_6$ ; 62.90 MHz): 109.0, 112.7, 115.9, 119.3, 121.1, 124.0, 128.2, 128.2, 129.4, 132.0, 133.2, 146.5, 146.6, 147.5, 154.2, and 158.4 ppm. UV/Vis ( $CH_3OH$  solution,  $\epsilon_{max}$  in  $10^3 dm^3 mol^{-1} cm^{-1}$ ): 233 (44 870), 266 (22 980), 314 (16 740<sup>sh</sup>), 326 (26 420), 365 nm (23 240).

**2.4. Synthesis of (*E*)-*N'*-((2-Hydroxybenzylidene)furan-2-carbohydrazone ( $H_2L^2$ ).** Yield: 88%. Anal Calc. for  $C_{12}H_9BrN_2O_3$  (230.22 g/mol) C: 62.60, H: 4.38, N: 12.17%.

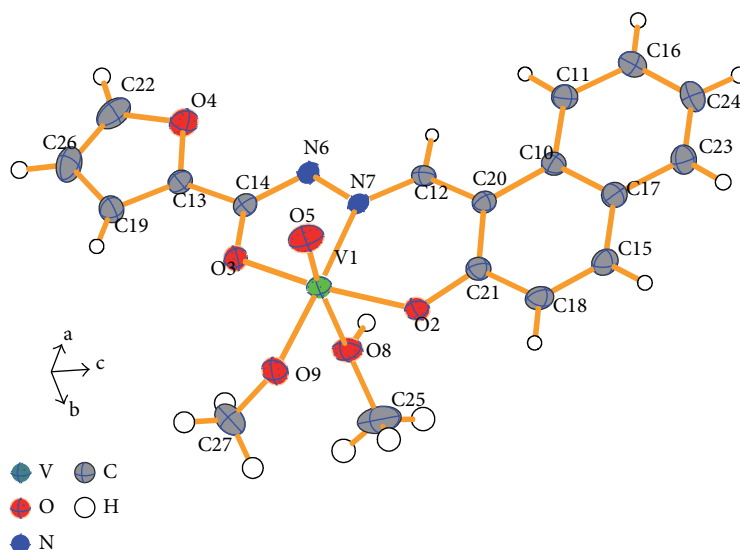


FIGURE 1: Thermal ellipsoid plot of  $[\text{VO}(\text{L}^1)(\text{OCH}_3)(\text{OHCH}_3)]$  (1) at 30% probability level; bond lengths and angles in Table 4.

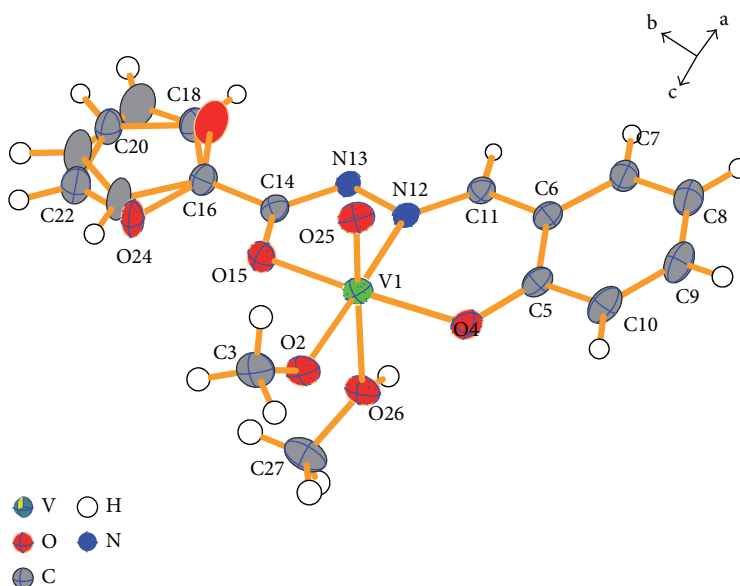


FIGURE 2: Thermal ellipsoid plot of  $[\text{VO}(\text{L}^2)(\text{OCH}_3)(\text{OHCH}_3)]$  (2) at 30% probability level, bond lengths and angles in Table 5.

Found C: 62.51, H: 4.34, N: 12.22%. Selected IR data ( $\text{cm}^{-1}$ ): 1660 (vs, C=O); 1593 (s, C=N<sub>azomethine</sub>); 947 (m, N-N); 1286 (vs, C-O enolate); 3145 (m, NH); 3621 (m, O-H)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  12.13 (s, 1H, CO-NH-); 11.16 (s, 1H, -OH); 8.26 (s, 1H); 7.92 (s, 1H); 7.51 (d, 1H,  $J = 7.0$  Hz); 7.27 (m, 2H); 6.89 (m, 2H); 6.68 (s, 1H) ppm.  $^1\text{H}$  NMR (250.13 MHz; DMSO- $d_6$  + D $_2$ O):  $\delta = 8.52$  (s, 1H); 7.78 (s, 1H); 7.44 (d, 1H,  $J = 7.25$ ); 7.24 (m, 2H); 6.84 (m, 2H); 6.62 (t, 1H,  $J = 1.25$ ) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ; 62.90 MHz): 112.7, 115.7, 116.9, 119.1, 120.0, 129.8, 131.9, 146.45, 146.6, 148.7, 154.5, and 157.8 ppm. UV/Vis (CH $_3$ OH solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 239 (6400<sup>sh</sup>), 290 (14080), 300 (15280), 332 nm (10980).

2.5. Synthesis of (*E*)-*N*<sup>1</sup>-(5-Bromo-2-hydroxybenzyl-idene) furan-2-carbohydrazide ( $\text{H}_2\text{L}^3$ ). Yield: 91%. Anal. Calc. for  $\text{C}_{12}\text{H}_9\text{BrN}_2\text{O}_3$  (309.12 g/mol) C: 46.63, H: 2.93, N: 9.06%. Found C: 46.98, H: 2.89, N: 9.02%. Selected IR data ( $\text{cm}^{-1}$ ): 1665 (vs, C=O); 1611 (s, C=N<sub>azomethine</sub>); 956 (m, N-N); 1273, 1306 (s, C-O enolate); 3129 (m, NH); 3397 (m, O-H)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  12.17 (s, 1H, CO-NH-); 11.15 (s, 1H, -OH); 8.58 (s, 1H); 7.92 (s, 1H); 7.74 (s, 1H); 7.39 (dd, 1H,  $J = 8.75$  Hz,  $J = 2.25$  Hz); 7.30 (s, 1H); 6.88 (d, 1H,  $J = 8.5$  Hz); 6.68 (s, 1H) ppm.  $^1\text{H}$  NMR (250.13 MHz; DMSO- $d_6$  + D $_2$ O):  $\delta = 8.50$  (s, 1H); 7.83 (s, 1H); 7.68 (d, 1H,  $J = 2.0$ ); 7.84 (dd, 1H,  $J = 8.75$  Hz,  $J = 2.5$  Hz); 7.27 (d, 1H,  $J = 2.5$ ); 6.85

TABLE 1: Crystallographic data of **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Net formula	C <sub>18</sub> H <sub>17</sub> N <sub>2</sub> O <sub>6</sub> V	C <sub>14</sub> H <sub>15</sub> N <sub>2</sub> O <sub>6</sub> V	C <sub>14</sub> H <sub>14</sub> BrN <sub>2</sub> O <sub>6</sub> V
$M_r/\text{g mol}^{-1}$	408.28	358.22	437.12
Crystal size/mm	0.049 × 0.300 × 0.455	0.270 × 0.360 × 0.450	0.053 × 0.136 × 0.565
$T/\text{K}$	293 K	293 K	293 K
Radiation	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$
Crystal system	Monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
$a/\text{\AA}$	7.8995 (7)	8.418 (2)	10.6835 (3)
$b/\text{\AA}$	20.3400 (10)	16.228 (3)	7.8198 (3)
$c/\text{\AA}$	10.9949 (8)	11.902 (2)	20.1460 (6)
$\alpha^\circ$	90	90	90
$\beta^\circ$	91.577 (7)	104.34 (2)	104.940 (3)
$\gamma^\circ$	90	90	90
$V/\text{\AA}^3$	1765.95 (2)	1575.2 (6)	1626.16
$Z$	4	4	4
Calc. density/ $\text{g cm}^{-3}$	1.536	1.51	1.785
$\mu/\text{mm}^{-1}$	0.601	0.66	3.100
Absorption correction	Analytical	analytical	analytical
Refls. measured	7800	7393	6829
$R_{\text{int}}$	0.035	0.031	0.038
$\theta$ range	3.266–29.248	3.3913–28.9660	3.1354–29.2307
Observed refls.	2740	2732	2402
Hydrogen refinement	None	none	none
Refls in refinement	4028	3602	3736
Parameters	244	245	218
Restraints	0	40	0
$R(F_{\text{obs}})$	0.0450	0.0519	0.0404
$R_w(F_2)$	0.1399	0.1052	0.1106
$S$	0.9120	0.9714	0.9785
Shift/error <sub>max</sub>	0.0004097	0.0007320	0.0003961

(d, 1H,  $J = 8.75$ ); 6.64 (t, 1H,  $J = 1.75$ ) ppm. <sup>13</sup>C NMR (DMSO- $d_6$ ; 62.90 MHz): 110.9, 112.6, 115.9, 119.1, 121.8, 130.6, 134.0, 146.0, 146.7, 154.6, and 156.7 ppm. UV/Vis (CH<sub>3</sub>OH solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 217 (23 020), 246 (16 140), 291 (31 020), 303 (31 460), 340 (18 220).

**2.6. Synthesis of (E)-N<sup>1</sup>-(2-Hydroxy-5-nitrobenzylidene)furan-2-carbohydrazide (H<sub>2</sub>L<sup>4</sup>).** Yield: 93%. Anal Calc. for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub> (275.22 g/mol) C: 52.37, H: 3.30, N: 15.27%. Found C: 52.43, H: 3.35, N: 15.12%. Selected IR data (cm<sup>-1</sup>): 1671 (vs, C=O); 1612 (m, C=N<sub>azomethine</sub>); 965 (m, N-N); 1293, 1344 (vs, C-O enolate); 3274 (m, NH); 3448 (w, O-H) cm<sup>-1</sup>. <sup>1</sup>H NMR (250.13 MHz; DMSO- $d_6$ ):  $\delta$  12.22 (2H, CO-NH- and -OH); 8.66 (s, 1H); 8.48 (d, 1H,  $J = 2$  Hz); 8.10 (dd, 1H,  $J = 9.25$  Hz,  $J = 2.5$  Hz); 7.91 (s, 1H); 7.31 (s, 1H); 7.03 (d, 1H,  $J = 9.0$  Hz); 6.67 (d, 1H,  $J = 1.25$  Hz) ppm. <sup>1</sup>H NMR (250.13 MHz; DMSO- $d_6$  + D<sub>2</sub>O):  $\delta$  = 8.59 (s, 1H); 8.45 (s, 1H); 8.01 (s, 1H); 7.82 (s, 1H); 7.26 (s, 1H); 7.04 (s, 1H); 6.64 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO;

62.90 MHz): 112.6, 115.9, 117.4, 120.4, 124.0, 126.9, 140.3, 144.7, 146.6, 154.6, and 162.9. UV/Vis (CH<sub>3</sub>OH solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 210 (11 680), 295 (28 160), 325 nm (19 400).

**2.7. Synthesis of (E)-N<sup>1</sup>-(2-Hydroxy-5-iodobenzylidene)furan-2-carbohydrazide (H<sub>2</sub>L<sup>5</sup>).** Yield: 86%. Anal Calc. for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub> (275.22 g/mol) C: 40.47, H: 2.55, N: 7.87%. Found C: 40.41, H: 2.61, N: 7.79%. Selected IR data (cm<sup>-1</sup>): 1668 (vs, C=O); 1609 (s, C=N<sub>azomethine</sub>); 952 (m, N-N); 1274, 1351 (vs, C-O enolate); 3262 (m, NH); 3447 (w, O-H) cm<sup>-1</sup>. <sup>1</sup>H NMR (250.13 MHz; DMSO- $d_6$ ):  $\delta$  12.16 (s, 1H, CO-NH-); 11.15 (s, 1H, -OH); 8.57 (s, 1H); 7.92 (s, 1H); 7.88 (s, 1H); 7.51 (d, 1H,  $J = 8.5$  Hz); 7.30 (s, 1H); 7.74 (d, 1H,  $J = 8.75$  Hz); 6.67 (s, 1H) ppm. <sup>1</sup>H NMR (250.13 MHz; DMSO- $d_6$  + D<sub>2</sub>O):  $\delta$  = 8.85 (s, 1H); 7.83 (s, 1H); 7.382 (s, 1H); 7.24 (s, 1H); 6.72 (d, 1H,  $J = 8.75$  Hz); 6.64 (s, 1H) ppm. <sup>13</sup>C NMR (DMSO; 62.90 MHz): 81.72, 112.61, 115.82, 119.48, 122.35, 136.62, 139.76, 145.99, 146.52, 146.63, 154.56, and 157.35. UV/Vis (CH<sub>3</sub>OH solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ):

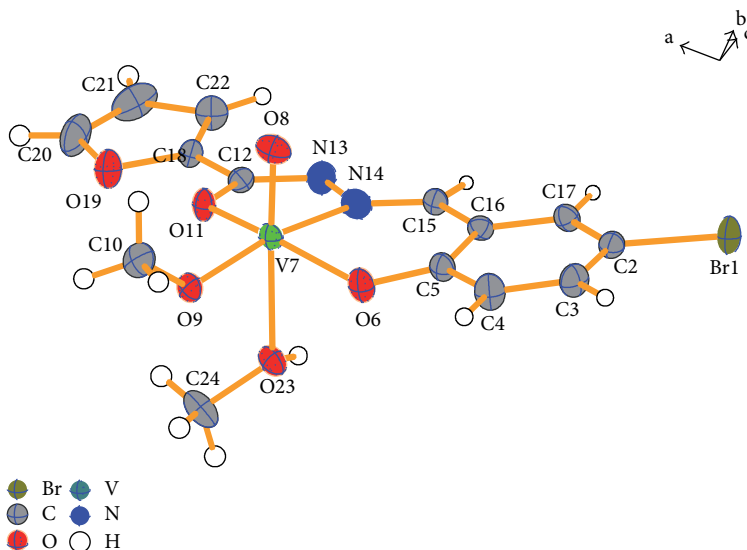


FIGURE 3: Thermal ellipsoid plot of  $[\text{VO}(\text{L}^3)(\text{OCH}_3)(\text{OHCH}_3)]$  (**3**) at 30% probability level, bond lengths and angles in Table 6.

223 (18 200), 250 (15 600), 293 (27 740), 305 (27 680), 344 (14 420).

**2.8. Synthesis of the Complexes  $[\text{VO}(\text{L}^{1-5})(\text{OCH}_3)(\text{CH}_3\text{OH})]$  (**1**–**5**).** These complexes were synthesized by the same method. General method: the appropriate ligand ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ ,  $\text{H}_2\text{L}^3$ ,  $\text{H}_2\text{L}^4$ , or  $\text{H}_2\text{L}^5$ ) (1.0 mmol) was dissolved in a solution of methanol (20 mL) then  $\text{VO}(\text{acac})_2 \cdot 0.265 \text{ g}$ , 1.0 mmol) was added and the solution was refluxed for 4 h. After cooling, the resulting solid was filtered off, washed with cooled absolute ethanol, and dried at  $100^\circ\text{C}$ . Single crystals of  $[\text{VO}(\text{L}^1)(\text{OCH}_3)(\text{OHCH}_3)]$  (**1**),  $[\text{VO}(\text{L}^2)(\text{OCH}_3)(\text{OHCH}_3)]$  (**2**), and  $[\text{VO}(\text{L}^3)(\text{OCH}_3)(\text{OHCH}_3)]$  (**3**) were prepared by the thermal gradient method.

**2.9. Synthesis of  $[\text{VO}(\text{L}^1)(\text{OCH}_3)(\text{OHCH}_3)]$  (**1**).** Yield: 82%. Anal. Calc. for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_6\text{V}$  (408.28 g/mol) C: 52.95, H: 4.20, N: 6.86, V: 12.48%. Found C: 53.02, H: 4.13, N: 3.91, V: 12.39%. Selected IR data ( $\text{cm}^{-1}$ ): 3384 (m); 1609 (vs); 1510 (s); 1330 (s); 1264 (m); 1061 (vs); 973 (vs); 762 (s); 625 (m); 592 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250.13 MHz;  $\text{DMSO-d}_6$ ):  $\delta$  3.15 (s, 6H); 5.27 (s, 1H); 6.67 (s, 1H); 7.08 (m, 2H); 7.45 (s, 1H); 7.63 (s, 1H); 7.91 (s, 2H); 8.06 (d, 1H,  $J = 9.25 \text{ Hz}$ ); 8.51 (s, 1H), 9.76 (s, 1H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ; 62.90 MHz): 49.0, 74.4, 111.6, 112.7, 115.3, 115.9, 119.8, 122.1, 124.5, 128.6, 128.7, 129.4, 132.8, 135.5, 146.4, 148.7, 162.9, and 164.7 ppm. UV/Vis ( $\text{CH}_3\text{OH}$  solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 221 (39 640), 239 (38 280), 280 (28 280<sup>sh</sup>), 301 (26 840), 336 (24 880<sup>sh</sup>), 436 nm (6 920<sup>sh</sup>).

**2.10. Synthesis of  $[\text{VO}(\text{L}^2)(\text{OCH}_3)(\text{OHCH}_3)]$  (**2**).** Yield: 75%. Anal. Calc. for  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_6\text{V}$  (358.22 g/mol) C: 46.94, H: 4.22, N: 7.82, V: 14.22%. Found C: 47.04, H: 4.17, N: 7.79, V: 14.25%. Selected IR data ( $\text{cm}^{-1}$ ): 3445 (m); 1612 (vs); 1513 (s); 1351 (m); 1275 (m); 963 (s); 750 (s); 629 (s); 586 (m)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (250.13 MHz;  $\text{DMSO-d}_6$ ):  $\delta$  3.15 (s, 6H), 5.26 (s, 1H); 6.64 (s, 1H); 6.90 (m, 2H); 6.90 (m, 2H); 7.11 (s, 1H); 7.4 (d, 1H,  $J = 5.5 \text{ Hz}$ ); 7.66 (s, 1H); 7.86 (s, 1H); 8.83 (d, 1H,  $J = 4 \text{ Hz}$ ) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ; 62.90 MHz): 49.0, 74.9, 112.6, 115.3, 116.6, 120.3, 120.7, 133.3, 134.6, 146.0, 146.4, 152.4, 163.5, and 163.8 ppm. UV/Vis ( $\text{CH}_3\text{OH}$  solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 206 (34 260), 280 (24 880<sup>sh</sup>), 304 (26 120), 326 (26 040<sup>sh</sup>), 410 nm (5 940<sup>sh</sup>).

**2.11. Synthesis of  $[\text{VO}(\text{L}^3)(\text{OCH}_3)(\text{OHCH}_3)]$  (**3**).** Yield: 77%. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}_6\text{V}$  (437.12 g/mol) C: 38.47, H: 3.23, N: 6.41, V: 11.65%. Found C: 38.56, H: 3.32, N: 6.34, V: 11.73%. Selected IR data ( $\text{cm}^{-1}$ ): 3557 (w); 1609 (s); 1525 (s); 1341 (s); 1279 (s); 964 (s); 881 (vs); 750 (m); 626 (s); 597 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250.13 MHz;  $\text{DMSO-d}_6$ ):  $\delta$  3.14 (s, 6H); 5.30 (s, 1H); 6.64 (s, 1H); 6.82 (d, 1H,  $J = 8.5 \text{ Hz}$ ); 7.11 (s, 1H); 7.56 (d, 1H,  $J = 8.75 \text{ Hz}$ ); 7.87 (s, 2H); 8.78 (s, 1H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ; 62.90 MHz): 49.0, 75.4, 110.8, 112.7, 115.67, 119.2, 122.7, 134.8, 136.6, 145.8, 146.6, 151.3, 162.4, and 164.2 ppm. UV/Vis ( $\text{CH}_3\text{OH}$  solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 203 (27 680), 248 (21 100<sup>sh</sup>), 293 (22 480), 304 (22 760), 327 (22 180), 412 nm (4200).

**2.12. Synthesis of  $[\text{VO}(\text{L}^4)(\text{OCH}_3)(\text{OHCH}_3)]$  (**4**).** Yield: 71%. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_8\text{V}$  (403.22 g/mol) C: 41.70, H: 3.50, N: 10.42, V: 12.63%. Found C: 41.85, H: 3.56, N: 10.51, V: 12.60%. Selected IR data ( $\text{cm}^{-1}$ ): 3415 (m), 1614 (vs); 1515 (s); 1339 (vs); 1289 (s); 968 (s); 749 (m); 580 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250.13 MHz;  $\text{DMSO-d}_6$ ):  $\delta$  3.14 (s, 6H); 5.41 (s, 1H); 6.68 (s, 1H); 7.06 (m, 2H); 7.94 (s, 1H); 8.15 (s, 1H); 8.70 (s, 1H); 9.00 (s, 1H) ppm.  $^{13}\text{C}$  NMR spectrum could not be taken because of the solubility limitations. UV/Vis ( $\text{CH}_3\text{OH}$  solution,  $\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 215 (18 600), 238 (16 060<sup>sh</sup>), 324 (33 600 very broad) and 429 nm (2 420<sup>sh</sup>).

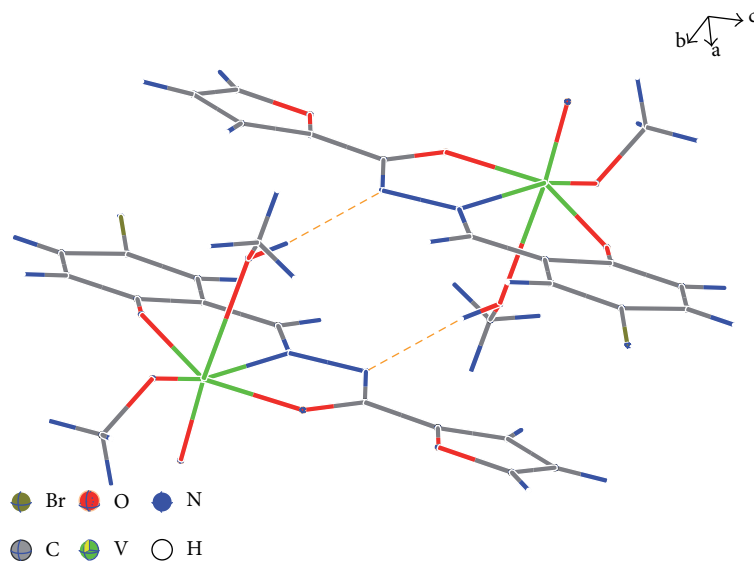


FIGURE 4: The hydrogen-bonded structure of the complex 3.

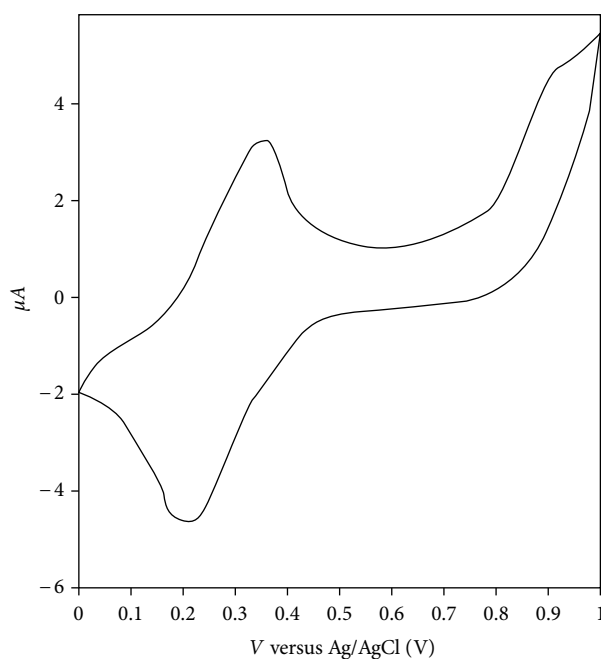


FIGURE 5: Cyclic voltammogram of  $10^{-3} \text{ mol L}^{-1}$  complex 2 in DMSO and  $\text{LiClO}_4$  ( $0.1 \text{ mol L}^{-1}$ ); scan rate  $50 \text{ mVs}^{-1}$ .

2.13. *Synthesis of  $[\text{VO}(\text{L}^5)(\text{OCH}_3)(\text{OHCH}_3)]$  (5).* Yield: 70%. Anal. Calc. for  $\text{C}_{14}\text{H}_{14}\text{IN}_2\text{O}_6\text{V}$  (484.12 g/mol) C: 34.73, H: 2.91, N: 5.79, V: 10.52%. Found C: 34.67, H: 2.88, N: 5.90, V: 10.68%. Selected IR data ( $\text{cm}^{-1}$ ): 3415 (s); 1614 (vs); 1516 (s); 1350 (m); 1273 (s); 1051 (vs); 970 (s); 745 (m); 626 (s); 591 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (250.13 MHz;  $\text{DMSO-d}_6$ ):  $\delta$  3.15 (s, 6H); 5.30 (s, 1H); 6.64 (s, 1H); 6.71 (d, 1H,  $J = 8.5 \text{ Hz}$ ); 7.12 (s, 1H); 7.69 (m d, 1H,  $J = 8.0 \text{ Hz}$ ); 7.85 (s, 1H); 8.00 (s, 1H); 8.76 (s, 1H) ppm.  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ; 62.90 MHz): 48.8, 75.3, 81.4, 112.6, 115.6, 119.5, 123.4, 140.8, 142.3, 145.8, 146.4, 151.1, 163.0, and 164.2 ppm. UV/Vis ( $\text{CH}_3\text{OH}$  solution,

$\epsilon_{\text{max}}$  in  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 240 (21 560), 285 (21 680), 306 (23 040), 334 (20 280<sup>sh</sup>), 426 nm (2 900<sup>sh</sup>).

2.14. *Electrochemical Properties.* For cyclic voltammetry studies, a conventional three-electrode system was used with a polished glassy carbon electrode (area  $3.14 \text{ mm}^2$ ) as working electrode and a platinum wire counter electrode. The reference was an aqueous  $\text{Ag}/\text{AgCl}$  saturated electrode, separated from the bulk of the solution by a bridge with solvent and supporting electrolyte. The solutions in the bridge



TABLE 2: Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths	
V1–O2	1.8480 (18)
V1–O3	1.9430 (17)
V1–O5	1.585 (2)
V1–N7	2.078 (2)
V1–O8	2.569 (2)
V1–O9	1.7652 (18)
O3–C14(C–O)	1.307 (3)
O2–C21(C–O)	1.337 (3)
N6–C14(C=N)	1.305 (3)
N7–C12(C=N)	1.297 (3)
N6–N7	1.396 (3)
O8–H81	0.837
Bond angles	
O2–V1–O3	152.03 (8)
O2–V1–O5	99.87 (11)
O3–V1–O5	101.00 (10)
O2–V1–N7	84.07 (8)
O3–V1–N7	75.18 (7)
O5–V1–N7	96.74 (9)
O2–V1–O8	78.99 (8)
O3–V1–O8	77.77 (7)
O5–V1–O8	172.09 (9)
N7–V1–O8	75.37 (7)
O2–V1–O9	103.01 (8)
O3–V1–O9	89.51 (8)
O5–V1–O9	104.61 (11)
N7–V1–O9	155.81 (9)
O8–V1–O9	83.24 (8)
V1–O2–C21	133.69 (16)
V1–O3–C14	117.39 (15)
V1–N7–N6	116.56 (14)
V1–N7–C12	127.44 (17)

were changed periodically to avoid aqueous contamination from entering the cell via the Ag/AgCl electrode. The electrolytic medium consisted of 0.1 mol/L lithium perchlorate (LiClO<sub>4</sub>) as supporting electrolyte in dimethyl sulfoxide, and all experiments were carried out at room temperature. The solutions were freshly prepared before use and were purged with N<sub>2</sub> saturated with solvent for 10 min prior to taking measurements in order to remove dissolved O<sub>2</sub>. Voltammograms were recorded in the range from 0.0 to +1.0 V versus Ag/AgCl.

**2.15. X-Ray Crystallography Data Collection and Refinement.** Dark brown crystals of **1**, **2**, and **3** were investigated by X-ray diffraction at 200 K on an Oxford-Diffraction Xcalibur Nova E diffractometer equipped with a molybdenum microsource ( $\lambda = 0.7107$  Å). The structures were solved by Direct Methods with SIR97 [32] and refined with full-matrix least-squares techniques on  $F^2$  with CRYSTALS [33]. The crystal data and refinement parameters are presented in Table 1. The hydrogen atoms were found in successive Fourier difference

TABLE 3: Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths	
V1–O2	1.7649 (19)
V1–O4	1.848 (2)
V1–N12	2.121 (2)
V1–O15	1.9726 (19)
V1–O25	1.593 (2)
V1–O26	2.329 (2)
C14–O15	1.292 (3)
O4–C5	1.333 (3)
C11–N12	1.286 (3)
N13–C14	1.310 (3)
N12–N13	1.393 (3)
O26–H261	0.825
Bond angles	
O2–V1–O4	102.81 (9)
O2–V1–N12	160.64 (9)
O2–V1–O26	81.50 (8)
O2–V1–O15	93.40 (9)
O2–V1–O25	102.97 (10)
O4–V1–O15	152.49 (8)
O4–V1–O25	99.60 (10)
O4–V1–O26	80.65 (9)
N12–V1–O15	74.38 (7)
N12–V1–O25	93.74 (9)
N12–V1–O26	81.60 (7)
O15–V1–O25	98.18 (10)
O15–V1–O26	79.96 (8)
O25–V1–O26	175.30 (8)
V1–O2–C3	131.02 (19)
O4–V1–N12	83.65 (8)

analysis. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were first refined with restraints on the bond lengths and angles (C–H in the range 0.93–0.98 Å and O–H = 0.82 Å) and  $U_{\text{iso}}$  (in the range 1.2–1.5 times  $U_{\text{eq}}$  of the parent atom), after which they were refined with riding constraints. The molecular structure plots were drawn with ORTEPIII [34–36].

### 3. Results and Discussion

The reaction of 2-furancarboxylic acid hydrazide with several aromatic *o*-hydroxy aldehydes with different substituents in methanol gave the desired tridentate Schiff base ligands in excellent yields and purity. Oxovanadium(V) complexes with tridentate hydrazone Schiff base ligands were prepared by treating a methanolic solution of the appropriate ligand with equimolar amount of VO(acac)<sub>2</sub> (Scheme 1).

**3.1. Description of the Structures (1, 2, and 3).** In order to define the coordination sphere conclusively, a single-crystal X-ray diffraction study was made. A list of some crystallographic data of **1**, **2**, and **3** is given in Table 1. An ORTEP diagram with the atom numbering scheme of the **1**, **2**, and **3** is shown in Figures 1, 2, and 3 and selected bond lengths

TABLE 4: Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths	
V7–O6	1.847 (3)
V7–O8	1.584 (4)
V7–O9	1.767 (3)
V7–O11	1.957 (3)
V7–N14	2.130 (3)
V7–O23	2.372 (4)
O11–C12 (C–O)	1.287 (5)
C5–O6 (C–O)	1.341 (5)
C12–N13 (C=N)	1.314 (5)
N14–C15 (C=N)	1.289 (5)
N13–N14	1.399 (5)
Bond angles	
O6–V7–O8	99.77 (19)
O6–V7–O9	100.85 (14)
O8–V7–O9	103.06 (17)
O6–V7–O11	152.96 (15)
O8–V7–O11	97.74 (17)
O9–V7–O11	95.04 (14)
O6–V7–N14	83.93 (13)
O8–V7–N14	94.85 (16)
O9–V7–N14	160.28 (16)
O8–V7–O23	174.55 (15)
O9–V7–O23	81.83 (14)
O11–V7–O23	79.28 (14)
N14–V7–O23	79.97 (13)
O6–V7–O23	81.48 (15)
V7–N14–N13	115.8 (2)
V7–N14–C15	127.4 (3)
V7–O11–C12	118.6 (3)
O11–V7–N14	74.17 (13)

and angles are given in Tables 2, 3, and 4, respectively. In **1**, **2**, and **3**, the vanadium atom has a six-coordinated structure as a  $\text{VO}_5\text{N}$  with nitrogen and two oxygen atoms provided by the Schiff base ligand and three oxygen atoms from methoxy, methanol, and oxo ligands. An axial position is occupied by the oxygen atom from methanol, and another axial position is occupied by the oxygen atom from the oxo ligand.

In these compounds the Schiff base ligands form a six-membered and a five-membered chelate ring with bite angles of about  $84^\circ$  ( $\text{O}_{\text{phenolat}}-\text{V}-\text{N}$ ) and  $74^\circ$  ( $\text{N}-\text{V}-\text{O}_{\text{enolat}}$ ), respectively. These angles are the same with previously reported naphthohydrazone oxovanadium complexes [29]. The double deprotonated form of the N-arylidene fouranohydrazone ligands is consistent with the observed  $\text{O}-\text{C}_{\text{carbonyl}}$  and  $\text{N}=\text{C}_{\text{carbonyl}}$  bond lengths of 1.29 and 1.31 Å, respectively in **1**, **2**, and **3**. This is in agreement with the reported complexes containing the enolate form of N-arylidene hydrazone ligands [29, 30, 37], whereas the  $\text{C}=\text{O}$  bond is considerably short for reported complexes with the coordinated keto form of the N-arylidene benzohydrazone system [28, 38]. In furancarbohydrazone ligands the  $\text{C}-\text{N}$  and  $\text{C}=\text{O}$  bond

TABLE 5: Hydrogen bonding interactions for **1**, **2** and **3**.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (deg)
Complex 1				
O8–H81...N6	0.84	2.01	2.842 (4)	176
Complex 2				
O26–H261...N13	0.82	2.01	2.817 (8)	165
Complex 3				
O23–H231...N13	0.82	2.06	2.876 (7)	171

lengths are about 1.35 Å and 1.23 Å, respectively [39–41]. The corresponding bond lengths in complex **1–3** are about 1.31 Å and 1.29 Å, respectively. Comparison of these bond lengths indicates the shortening of the  $\text{C}-\text{N}$  bond length and lengthening of the  $\text{C}=\text{O}$  bond due to coordination in enol form. The vanadium to oxygen bond lengths follows the order  $\text{V-oxo oxygen} < \text{V-methoxy oxygen} < \text{V-phenolate oxygen} < \text{V-enolate oxygen} < \text{V-methanol oxygen}$ . The oxovanadium (V) complexes under consideration crystallize in the monoclinic crystal system. In **1** and **2** the space group is  $P2_1/c$  but in **3**, the space group is  $P2_1/n$ .

In the complexes **1**, **2**, and **3** the conformation of 2-furanyl oxygen atom relative to the carbohydrazone oxygen atom is *s-anti*, *s-anti/s-syn*, and *s-syn* at 293 K, respectively. These findings suggest the presence of low barrier energy for rotation of the 2-furanyl group around the  $\text{C}-\text{C}$  bond between 2-furanyl and the carbohydrazone groups at room temperature. This rotation plausibly prevents 2-furanyl oxygen atom involvement in the coordination to the vanadium center of the adjacent molecule. In addition, the oxygen atom in furan is too poor for a donor to take part in metal binding. From steric consideration also, the furan group is not properly positioned to be involved in metal binding.

Hydrogen bonding is a common feature for vanadium(IV) and vanadium(V) compounds in the solid state, if appropriate hydrogen bonding donors are present [42, 43]. The type of complexes described in this work contains two major functionalities which can participate in intermolecular hydrogen bond interactions. These are the N atom of the hydrazine fragment of the tridentate ligand and the  $\text{O}-\text{H}$  group of the metal coordinated methanol. In these complexes two molecules of complex are connected together by strong intermolecular  $\text{O}_{(\text{methanol})}-\text{H}\cdots\text{N}_{(\text{amide})}$  hydrogen bonds and create a pseudodimer as depicted in Figure 4. This strong intermolecular hydrogen bond stabilizes the crystal structure of **1**, **2**, and **3**. These pseudodimers make a chain along *c* diagonal by intermolecular hydrogen bonds. Parameters of hydrogen bonding geometry are given in Table 5.

### 3.2. Spectroscopic Studies

**3.2.1. NMR Spectra of the Ligands and Complexes.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of the ligands in  $\text{DMSO}-d_6$  confirmed the proposed structure of the ligands (Scheme 1). The principal peaks of the  $^1\text{H}$  NMR spectra of ligands  $\text{H}_2\text{L}^1-\text{H}_2\text{L}^5$



TABLE 6:  $^1\text{H}$  NMR of ligands ( $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$ ) and complexes (1–5).

Compound	Solvent	–CH=N– (azomethine)	–NH–	–OH <sub>(phenol)</sub>	–OH <sub>(methanol)</sub>	–CH <sub>3</sub>
$\text{H}_2\text{L}^1$	$(\text{CD}_3)_2\text{SO}$	8.66	12.30	11.31	—	—
$\text{H}_2\text{L}^1$	$(\text{CD}_3)_2\text{SO} + \text{D}_2\text{O}$	8.58	—	—	—	—
Complex 1	$(\text{CD}_3)_2\text{SO}$	9.76	—	—	5.27	3.15
$\text{H}_2\text{L}^2$	$(\text{CD}_3)_2\text{SO}$	8.61	12.33	11.13	—	—
$\text{H}_2\text{L}^2$	$(\text{CD}_3)_2\text{SO} + \text{D}_2\text{O}$	8.57	—	—	—	—
Complex 2	$(\text{CD}_3)_2\text{SO}$	8.83	—	—	5.27	3.15
$\text{H}_2\text{L}^3$	$(\text{CD}_3)_2\text{SO}$	8.67	12.25	10.69	—	—
$\text{H}_2\text{L}^3$	$(\text{CD}_3)_2\text{SO} + \text{D}_2\text{O}$	8.58	—	—	—	—
Complex 3	$(\text{CD}_3)_2\text{SO}$	8.78	—	—	5.30	3.14
$\text{H}_2\text{L}^4$	$(\text{CD}_3)_2\text{SO}$	8.66	12.22	12.22	—	—
$\text{H}_2\text{L}^4$	$(\text{CD}_3)_2\text{SO} + \text{D}_2\text{O}$	8.59	—	—	—	—
Complex 4	$(\text{CD}_3)_2\text{SO}$	8.99	—	—	5.41	3.14
$\text{H}_2\text{L}^5$	$(\text{CD}_3)_2\text{SO}$	8.57	12.16	11.15	—	—
$\text{H}_2\text{L}^5$	$(\text{CD}_3)_2\text{SO} + \text{D}_2\text{O}$	8.85	—	—	—	—
Complex 5	$(\text{CD}_3)_2\text{SO}$	8.76	—	—	5.30	3.15

TABLE 7: Electrochemical data of the complexes 1–5 in DMSO solution at 298 K.

Compound	$E_{\text{p.a}}$ (V)	$I_{\text{p.a}}$	$E_{\text{p.c}}$ (V)	$I_{\text{p.c}}$	$\Delta E_{\text{p}}$ (V)
1	0.421	$3.04 \times 10^{-6}$	0.273	$-4.46 \times 10^{-6}$	0.148
2	0.349	$3.28 \times 10^{-6}$	0.211	$-4.61 \times 10^{-6}$	0.138
3	0.454	$2.94 \times 10^{-6}$	0.298	$-4.39 \times 10^{-6}$	0.156
4	0.498	$2.85 \times 10^{-6}$	0.313	$-4.31 \times 10^{-6}$	0.185
5	0.430	$3.01 \times 10^{-6}$	0.277	$-4.37 \times 10^{-6}$	0.153

are listed in Table 6. The signal at  $\delta$  12.12–12.33 in the spectra of  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$  is assigned to the common NH-group, concomitant with the observation of a rapid loss of these signals when  $\text{D}_2\text{O}$  is added to the solution. Also the signals between  $\delta$  10.62–12.22 in the spectra of  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$  are lost upon addition of  $\text{D}_2\text{O}$  to the solution. Hence, this signal is assigned to the phenolic OH group. The resonances between  $\delta$  8.57–8.67 are assigned to the azomethine (–CH=N–) in the spectra of  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$ . In all ligands other aromatic protons appear between  $\delta$  6.60–7.85. The chemical shifts for these complexes are comparable and very close to each other. On complexation the absence of N–H and O–H peaks of the ligands shows coordination of  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$  as dianionic ligands in enol form (Scheme 1). In these ligands, a triplet peak and two doublet peaks should have been observed around  $\delta$  6.5–7.5 ppm for furan's hydrogens but because of the low coupling constant (ca. 2 Hz.) [44] and also not using a powerful instrument, only a singlet peak is observed for these hydrogens; however, in three cases ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^4$ ) this splitting could be observed. We have also recorded  $^{13}\text{C}$  NMR of ligands and their complexes to provide diagnostic tools for the elucidation of the structures. Assignments of the peaks are similar and are based on the chemical shift and intensity patterns.  $\Delta\delta$  observed for carbon atoms in the vicinity of the phenolate, enolate, and azomethine groups suggests their involvement in coordination. Two new

signals in complexes appear at  $\delta$  about 49 and 75 ppm; these signals correspond to methanol and methoxy carbon atoms, respectively.

**3.2.2. Infrared Spectra.** A list of the important vibrational frequencies (IR spectra) of the free ligands ( $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$ ) and their oxovanadium complexes, which are useful for determining the mode of coordination of the ligands, are given in the experimental part. A comparison of the spectra of the complexes with the ligands provides evidence for the coordination mode of the ligands in the complexes. Hence significant frequencies are selected by comparing the IR spectra of the ligands with those of oxovanadium complexes. All hydrazone Schiff base ligands ( $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$ ) exhibit a broad band around  $3167$ – $3270\text{ cm}^{-1}$  due to NH-vibrations. Also in IR spectra of all the ligands very strong band appears around  $1650$ – $1680\text{ cm}^{-1}$  due to C=O-vibration. In addition a broad band is centered at  $3400$ – $3600\text{ cm}^{-1}$  in  $\text{H}_2\text{L}^1$ – $\text{H}_2\text{L}^5$  due to the O–H of the phenol, probably involved in intramolecular hydrogen bonding. The infrared spectra of complexes display IR absorption band around  $1610\text{ cm}^{-1}$  which can be assigned to the C=N stretching frequency of the coordinated hydrazone ligand, whereas for the free ligands the same band are observed around  $1600\text{ cm}^{-1}$ . Strong C=N stretch (around  $1600\text{ cm}^{-1}$ ) indicates the C=N group of the coordinated Schiff

base ligands [45, 46]. On complexation the absence of N–H and C=O bands and red shifts in azomethine (–C=N–) band [47] of the ligands shows coordination of  $H_2L^1$ – $H_2L^5$  as three dentate dianionic ligands in enol form (Scheme 1). In all complexes very broad band around 3380–3440  $cm^{-1}$  expresses presence of –OH and coordination of methanol to the vanadium. The band at 963–972  $cm^{-1}$  is assigned to  $\nu(V=O)$ ; this band is observed as a new peak for the complexes and is not present in the spectra of the free ligands. Similarity of the IR spectra of the complexes shows the similarity of their structures.

**3.2.3. Electronic Spectra.** These complexes are shiny dark brown in solid state, but their methanol solutions are brown in color. These solutions have been used to record the electronic spectra. For the oxovanadium(V) compounds, no d-d bands are expected because they have a  $3d^0$  configuration and there are no d electrons [12]. The hydrazone ligands have bands in the range 209–290 and 300–342 nm. Based on their extinction coefficients these are assigned as due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively [20, 48, 49]. The UV-Vis spectrum of  $H_2L^3$ ,  $H_2L^4$ , and  $H_2L^5$  which they have electron-withdrawing group (e.g., Br, I, and  $NO_2^-$ ) at the para position with respect to phenolic OH group in the aryloxy ring is very closet to each other and they have very similar shape (they have two  $\lambda_{max}$  in around 290 and 305 nm). The Oxovanadium(V) complexes have bands in the range 205–220 and 324–336 nm. These bands are assigned as due to intraligand transitions. All bands shift in complexes indicating the coordination of ligands to the metal ions [50, 51]. The shoulder appeared at about 280 nm for 1–5 corresponds to LMCT band of  $V=O$  which is appeared at 274 nm for  $[VO(acac)_2]$ . The lowest energy transition lying around 420 nm is assigned to LMCT transition of the type  $O_{(phenolic)} \rightarrow V^{5+}$  [52–55]. Electronic spectra for these complexes in MeOH solutions are akin similar electronic structure in solution of these compounds.

**3.2.4. Electrochemistry.** The electrochemical behaviors of the complexes were studied by cyclic voltammetry techniques in the range of 0.00 to +1.0 V at a scan rate of 50 mV/s in DMSO on a glassy carbon electrode (GCE) and Ag/AgCl reference electrode using lithium perchlorate ( $LiClO_4$ ) as the supporting electrolyte. All the complexes exhibit a quasi-reversible reduction peak due to  $VO^{3+}/VO^{2+}$  couple. Cyclic voltammetry data for these complexes are collected in Table 7 and the Figure 5 displays a representative cyclic voltammogram of 2. The effect of the electronic nature of the substituent present on the salicylidene fragment of tridentate ligand is clearly reflected on the trend of the  $E_{1/2}$  values for this reduction. For the strong electron withdrawing substituent ( $Y = NO_2$ , complex 4) the reduction of the metal centre occurs at the highest potential while for the least (or without any) electron withdrawing substituent ( $X = H$ , complex 2) it occurs at the lowest potential. Also for complex 4 the oxidation of the metal centre occurs at the lowest potential, while for complex 2 it occurs at the highest potential.

## 4. Conclusion

This work revealed that coordination complexes of  $V^{5+}$  and tridentate hydrazone Schiff base ligands obtained from the reaction of 2-furancarboxylic acid hydrazide and aromatic *o*-hydroxyaldehydes derivatives afford a new class of  $V^{5+}$  complexes. Five monooxovanadium(V) complexes of tridentate Schiff base ligands were synthesized and characterized by spectroscopic methods and single crystal X-ray analysis. The crystal structures of 1–3 suggest the presence of low-barrier energy for rotation of the 2-furanyl group around the C–C bond between 2-furanyl and the carbohydrazone groups at room temperature. Electrochemical studies by cyclic voltammetry technique indicated that these complexes are quasi-reversible electroactive.

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