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# Rod shaped oxovanadium(IV) Schiff base complexes: Synthesis, mesomorphism and influence of flexible alkoxy chain lengths

Bishop Dev Gupta, Chitraniva Datta, Gobinda Das, Chira R. Bhattacharjee\*

Department of Chemistry, Assam University, Silchar 788011, Assam, India

### HIGHLIGHTS

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- A series of oxovanadium(IV) complexes of bidentate [N,O] donor Schiff-base ligands have been synthesized.
- The ligands and complexes are all thermally stable exhibiting smectic mesomorphism.
- The ligands show SmC and an unidentified SmX phase reminiscent of soft crystal.
- Oxovanadium complexes mostly showed SmA phase.
- Interestingly, the complexes with C<sub>10</sub> and C<sub>12</sub> alkoxy chain length exhibited additionally SmC phase also.

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### G R A P H I C A L A B S T R A C T

A series of oxovanadium(IV) complexes of bidentate [N,O] donor rod shaped Schiff base ligands containing flexible alkoxy arms on either side of the aromatic rings have been successfully synthesized. Of particular interest is that the ligands showed striated textures (SmX) reminiscent of soft crystal not observed in the case of complexes. The complexes with carbon chain length ( $C_{10}$ ,  $C_{12}$ ) interestingly showed SmC mesophase in addition to SmA phase.



### ABSTRACT

A series of oxovanadium(IV) complexes of bidentate [N,O] donor Schiff-base ligands of the type [VO(L)<sub>2</sub>], [L = N-(4-*n*-alkoxysalicylaldimine)-4'-octadecyloxyaniline, *n* = 8, 10, 12, 14, 16 and 18] have been synthesized. The compounds were characterized by elemental analyses, Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H, <sup>13</sup>C nuclear magnetic resonance (NMR), ultraviolet–visible spectroscopy (UV–Vis), and fast atom bombardment (FAB) mass spectrometry. The mesomorphic behavior of the compounds was studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The ligands and complexes are all thermally stable exhibiting smectic mesomorphism. The ligands 8-OR to16-OR show SmC phase at ~113–118 °C and an unidentified SmX phase reminiscent of soft crystal at ~77–91 °C whereas the complexes all showed SmA phases. Interestingly the complexes with C<sub>10</sub> and C<sub>12</sub> alkoxy chain length exhibited additionally SmC phases also. The melting points of the ligands linearly increases whereas mesophase to isotropic transition temperature decreases as a function of increasing carbon chain length of alkoxy arm while no trend was apparently noticeable for the complexes.

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### Introduction

Metallomesogens incorporating Schiff base ligands have triggered much research in recent years because of their potential application in multifarious areas [1–4]. The transdisciplinary nature of this field is evidenced by the pervasive nature of liquid–crystal science, extending from biology through chemistry to physics, mathematics and electronic engineering. Schiff base ligands due to their flexible coordination donor sites, diverse structures and properties generate a variety of stereochemistries and a wide range of bonding interactions [4–8]. Their complexes with various transition metals lead to a distinctive class of metallomesogens with novel physical properties [7–9]. Coordination of metals





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<sup>\*</sup> Corresponding author. Tel.: +91 03842 270848; fax: +91 03842 270342. *E-mail address*: crbhattacharjee@rediffmail.com (C.R. Bhattacharjee).

to functionalised organic liquid crystals induce color, magnetism, polarisability and provide various new structural motifs including square planar, octahedral, square pyramidal, lantern types often unaccessible with conventional organic materials. Salicylaldimines have been extensively utilized to access metal complexes through stabilized azomethine moiety with anticipated liquid crystalline properties [9-12]. A great potential of metallomesogens as advanced molecular materials is recognized which led to a steady increase in interest towards liquid crystals incorporating transition metal element [13–16]. Mesogens containing transition metal ions such as copper(II), nickel(II) and palladium(II) [12,17] with salicylaldimine moiety are well documented. Almost all metallic elements of the d-block have been explored to generate metallomesogens yet liquid crystals containing vanadyl(IV) have not been adequately addressed. Owing to paramagnetism of VO(IV), such metallomesogens show quite interesting chemical and physical properties with potential for applications [18–20]. Oxovanadium(IV) complexes serve as interesting models for several biochemical processes such as haloperoxidation [21,22], nitrogen fixation [23], phosphorylation [24], glycogen metabolism [25–27] and insulin mimicking [28,29]. To devise synthetic strategy for the oxovanadium(IV) complexes associated with multifunctional properties such as magnetic, electronic or mesogenic properties desirable for technological applications is quite a challenging task. Further, oxovanadium(IV) complexes with axial coordinative interaction(...V=0...V=0...) often inhibit exhibition of mesomorphism or provide an additional control on the liquid crystalline behavior, ferroelectric/piezoelectric and non-linear optical (NLO) properties over and above the variation in the flexibility of ligand tails [30–32]. Liquid crystals with transition metal core groups such as VO(IV) are a fascinating branch of material science, because the self-assemblies of coordinated metal complexes enhances the physico-chemical properties with new functionalities thereby increasing their potential range of applications [33,34]. A series of copper(II) and vanadyl(IV) complexes of N-(4-alkoxysalicylidene)-4'-alkylaniline with shorter alkyl chain earlier reported by Ghedini and co-workers shows smectic mesomorphism [8]. Recently we reported a systematic investigation on a series of oxovanadium(IV) Schiff base complexes containing a both shorter as well as longer alkoxy substituent on either side of the ligand [35,36]. In the present paper we report a new series of rod-shaped mesomorphic vanadium(IV) complexes of [N,O] donor Schiff base ligands and the effect of flexible alkoxy chain length on the mesomorphism.

### **Experimental section**

### Physical measurements

The C, H and N analyses were carried out using a Carlo Erba 1108 elemental analyzer (USA). Molar conductance of the compounds was determined in dichloromethane (ca  $10^{-3}$  mol L<sup>-1</sup>) at room temperature using MAC-554 conductometer (Macroscientific Works, India). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance II –400 MHz (Bruker, India) spectrometer in CDCl<sub>3</sub> (chemical shift in  $\delta$ ) solution with tetramethylsilane (TMS) as internal standard. Ultraviolet-visible absorption spectra of the compounds in dichloromethane were recorded on a Shimadzu UV-1601PC spectrophotometer (Shimadzu, Asia pacific, Pte. Ltd., Singapore). Infrared spectra were recorded on a Perkin-Elmer BX series spectrometer (Perkin Elmer, USA) on a KBr disc. Mass spectra were recorded on a JEOL SX-102 (JEOL, Japan) spectrometer with fast atom bombardment. The optical textures of the different phase of the compounds were studied using a polarizing microscope (Nikon optiphot-2-Pol, Nikon Corporation, Tokyo, Japan) attached with Instec hot and cold stage HCS302, with STC200 temperature controller of 0.1 °C accuracy. The thermal behavior of the compounds were studied using a Perkin–Elmer differential scanning calorimeter (Perkin Elmer International, Switzerland) Pyris-1 spectrometer with a heating or cooling rate of 10 °C/min in the temperature range from 20 to 160 °C.

### Materials

The materials were procured from Tokyo Kasei, Japan and Lancaster Chemicals, USA. All solvents were purified and dried using standard procedures. Silica (60–120 mesh) from Spectrochem was used for chromatographic separation. Silica gel G (E-Merck, India) was used for thin layer chromatography (TLC).

### Synthesis and analysis

The general preparative route for salicylaldimine based Schiff bases are presented in Scheme 1. The two step procedure involves alkylation of 2,4-dihydroxybenzaldehyde followed by condensation with p-alkoxy substituted aniline. The vanadyl(IV) complexes,  $VO(LH)_2$  (LH = N-(4-*n*-alkoxysalicylaldimine)-4'-octadecyloxyaniline, *n* = 8, 10, 12, 14, 16, 18) were synthesized by the interaction of hot ethanolic solution of the ligands and vanadyl sulfate in the presence of triethylamine under reflux.

### *Synthesis of n-alkoxysalicyldehyde (n = 8, 10, 12, 14, 16, 18)*

Alkoxysalicyldehyde derivatives were prepared following the general method reported in literature [32]. 2,4-Dihydroxybenzaldehyde (10 mmol, 1.4 g), KHCO<sub>3</sub> (10 mmol, 1 g), KI (catalytic amount) and 1-bromooctane (10 mmol, 1.9 g), 1-bromodecane (10 mmol, 2.2 g), 1-bromododecane (10 mmol, 2.4 g), 1-bromotetradecane (10 mmol, 2.7 g), 1-bromohexadecane (10 mmol, 3.0 g) and 1-bromooctadecane (10 mmol, 3.3 g) were mixed in 250 mL of dry acetone. The mixture was heated under reflux for 24 h, and then filtered, while hot, to remove any insoluble solids. Dilute HCl was added to neutralize the warm solution, which was then extracted with chloroform (100 mL). The combined chloroform extract was concentrated to give a purple solid. The solid was purified by column chromatography using a mixture of chloroform and hexane (v/v, 1/1) as eluent. Evaporation of the solvents afforded a white solid product.

### Synthesis of octadecyloxy aniline

p-Hydroxy acetanilide (5 g, 0.03 mol) is refluxed with equimolar amount of octadecyl bromide (9.9 g, 0.03 mol) for 36 h in dry acetone using  $K_2CO_3$  (4.6 g) as the base and KI as the catalyst, acetone was then dried off and the product was dissolved in dichloromethane and the solution was washed with saturated NaCl solution. The solution was then treated with  $Na_2SO_4$  to absorb the moisture present in the solution. Dichloromethane was then distilled off to obtain the crude 4-octadecyloxy acetanilide. 4-Octadecyloxy acetanilide was then hydrolyzed for 4 h with 35% HCl in ethanol. After that the solution was treated with 2 mol dm<sup>-3</sup> of NaOH solution and a large amount of water up to pH ~12. The product was then filtered, recrystallised with alcohol using animal charcoal.

## N-(4-n-octadecyloxysalicylidene)-4'-n-octadecyloxy aniline (4-18-OR)

An ethanolic solution of (4-n-octadecyloxy)-salicyaldehyde (0.3 g, 1 mmol) was added to an ethanolic solution of 4-octadecyloxy aniline (0.3 g, 1 mmol). The solution mixture was refluxed with few drops of acetic acid as catalyst for 3 h to yield the Schiff base N-(4-n-octadecyloxysalicylidene)-4'-n-octadecyloxy aniline. The



**Scheme 1.** The synthetic route to the ligands, N-[(4-*n*-alkoxysalicylidene)-4'-octadecyloxy aniline] and the mononuclear oxovanadium(IV) complexes (VO-*n*-OR); n = 8,10,12,14,16,18; (OR) = OC<sub>18</sub>H<sub>37</sub>. Note: (i) Dry K<sub>2</sub>CO<sub>3</sub>, dry acetone, KI (catalyst); (ii) H<sup>\*</sup>/H<sub>2</sub>O, EtOH; (iii) glacial acetic acid (catalyst), EtOH, reflux, 2 h; (iv) VOSO<sub>4</sub>·2H<sub>2</sub>O, TEA, methanol reflux 1 h.

solid was collected by filtration and recrystallised several times from absolute ethanol to give a pure compound.

Yield: 0.45 g, 75%. Anal. Calc. for C<sub>49</sub>H<sub>83</sub>NO<sub>3</sub>: C, 80.2; H, 11.4; N, 1.9. Found: C, 80.1%; H, 11.3%; N, 1.8%; FAB Mass (*m/e*, fragment): *m/z*: calc. 733.6; found: 733 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.87 (t, *J* = 6.3 Hz, 6H, --CH<sub>3</sub>), 1.2-1.5 (m, 56H, (CH<sub>2</sub>)<sub>28</sub>), 3.9 (q, *J* = 6.3, 4H, OCH<sub>2</sub>), 6.4 (s, <sup>1</sup>H), 6.4 (d, 8.4 Hz, <sup>2</sup>H), 6.9 (d, 8.7 Hz, <sup>5.6</sup>H), 7.2 (d, 8.7 Hz, <sup>3</sup>H), 7.2 (d, 8.7 Hz, <sup>4.7</sup>H), 8.5 (s, 1H, CH=N), 13.9 (s, 1H, OH); <sup>13</sup>C NMR (75.45 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si at 25 °C, ppm)  $\delta$  = 102.2 (--C1), 107.1 (--C2), 131.2 (--C3), 122.9 (--C4), 115.7 (--C5), 115.7 (--C6), 122.9 (--C7); IR (v<sub>max</sub>, cm<sup>-1</sup>, KBr):3435 (v<sub>OH</sub>), 2917 (v<sub>as</sub>(C-H), CH<sub>3</sub>), 2919 (v<sub>as</sub>(C-H), CH<sub>2</sub>), 2868 (v<sub>s</sub>(C-H), CH<sub>3</sub>), 2845 (v<sub>as</sub>(C-H), CH<sub>2</sub>), 1630 (v<sub>C=N</sub>), 1277 (v<sub>C-O</sub>).

### *N*-(4-*n*-hexadecyloxysalicylidene)-4'-*n*-octadecyloxy aniline (4-16-OR)

Yield: 0.46 g, 78%. Anal. Calc. for  $C_{47}H_{79}NO_3$ : C, 79.9; H, 11.2; N, 1.9. Found: C, 79.8%; H, 11.1%; N, 1.9%; FAB Mass (m/e, fragment): *m/z*: calc. 705.6; found: 706 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, *J* = 6.3 Hz, 6H, --CH<sub>3</sub>), 1.2-1.4 (m, 52H, (CH<sub>2</sub>)<sub>27</sub>), 3.8 (q, *J* = 6.2, 4H, OCH<sub>2</sub>), 6.3 (d, 8.5 Hz, <sup>2</sup>H), 6.4 (s, <sup>1</sup>H), 6.9 (d, 8.7 Hz, <sup>2</sup>H), 6.9 (d, 8.7 Hz), <sup>2</sup>H), 6.9 (d, 8.7 Hz), <sup>3</sup>H), 6.9 (d, 8.7 Hz), <sup>3</sup>H), <sup>3</sup>H)</sup>

 $^{5.6}$ H), 7.1 (d, 8.6 Hz,  $^{3}$ H), 7.2 (d, 8.7 Hz,  $^{4.7}$ H), 8.4 (s, 1H, CH=N), 13.4 (s, 1H, OH); IR ( $\nu_{max}, \, cm^{-1}, \, KBr$ ):3435 ( $\nu_{OH}$ ), 2917 ( $\nu_{as}$ (C–H), CH<sub>3</sub>), 2919 ( $\nu_{as}$ (C–H), CH<sub>2</sub>), 2869 ( $\nu_{s}$ (C–H), CH<sub>3</sub>), 2845 ( $\nu_{as}$ (C–H), CH<sub>2</sub>), 1626 ( $\nu_{C=N}$ ), 1278 ( $\nu_{C-O}$ ).

### *N*-(4-*n*-tetradecyloxysalicylidene)-4'-*n*-octadecyloxy aniline (4-14-*OR*)

Yield: 0.48 g, 80%. Anal. Calc. for  $C_{45}H_{75}NO_3$ : C, 79.7; H, 11.1; N, 2.0. Found: C, 79.6%; H, 11.1%; N, 2.2%; FAB Mass (*m*/*e*, fragment): *m*/*z*: calc. 677.5; found: 678 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.89 (t, *J* = 6.3 Hz, 6H, --CH<sub>3</sub>), 1.2-1.4 (m, 48H, (CH<sub>2</sub>)<sub>24</sub>), 3.7 (q, *J* = 6.2, 4H, OCH<sub>2</sub>), 6.1 (d, 8.5 Hz, <sup>2</sup>H), 6.4 (s, <sup>1</sup>H), 6.9 (d, 8.7 Hz, <sup>5.6</sup>H), 7.1 (d, 8.6 Hz, <sup>3</sup>H), 7.2 (d, 8.7 Hz, <sup>4.7</sup>H), 8.5 (s, 1H, CH=N), 13.4 (s, 1H, OH); IR ( $v_{max}$ , cm<sup>-1</sup>, KBr):3434 ( $v_{OH}$ ), 2916 ( $v_{as}$ (C-H), CH<sub>3</sub>), 2918 ( $v_{as}$ (C-H), CH<sub>2</sub>), 2867 ( $v_{s}$ (C-H), CH<sub>3</sub>), 2840 ( $v_{as}$ (C-H), CH<sub>2</sub>), 1628 ( $v_{C=N}$ ), 1276 ( $v_{C-O}$ ).

### *N*-(4-*n*-dodecyloxysalicylidene)-4'-*n*-octadecyloxy aniline (4-12-OR)

Yield: 0.38 g, 77%. Anal. Calc. for C<sub>43</sub>H<sub>71</sub>NO<sub>3</sub>: C, 79.4; H, 11.0; N, 2.1. Found: C, 79.2%; H, 10.8%; N, 2.1%; FAB Mass (*m/e*, fragment): *m/z*: calc. 649.5; found: 650 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

0.91 (t, J = 6.2 Hz, 6H,  $-CH_3$ ), 1.2–1.6 (m, 44H,  $(CH_2)_{22}$ ), 3.7 (q, J = 6.2, 4H, OCH<sub>2</sub>), 6.2 (d, 8.5 Hz, <sup>2</sup>H), 6.3 (s, <sup>1</sup>H), 6.9 (d, 8.7 Hz, <sup>5.6</sup>H), 7.1 (d, 8.6 Hz, <sup>3</sup>H), 7.2 (d, 8.7 Hz, <sup>4.7</sup>H), 8.5 (s, 1H, CH=N), 13.4 (s, 1H, OH); IR ( $v_{max}$ , cm<sup>-1</sup>, KBr):3431 ( $v_{OH}$ ), 2915 ( $v_{as}$ (C–H), CH<sub>3</sub>), 2918 ( $v_{as}$ (C–H), CH<sub>2</sub>), 2867 ( $v_s$ (C–H), CH<sub>3</sub>), 2841 ( $v_{as}$ (C–H), CH<sub>2</sub>), 1620 ( $v_{C=N}$ ), 1277 ( $v_{C-O}$ ).

### N-(4-n-decyloxysalicylidene)-4'-n-octadecyloxy aniline (4-10-OR)

Yield: 0.38 g, 77%. Anal. Calc. for  $C_{41}H_{67}NO_3$ : C, 79.1; H, 10.8; N, 2.2. Found: C, 79.0%; H, 10.7%; N, 2.2%; FAB Mass (m/e, fragment): *m/z*: calc. 621.5; found: 622 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.87 (t, *J* = 6.4 Hz, 6H, --CH<sub>3</sub>), 1.2-1.5 (m, 40H, (CH<sub>2</sub>)<sub>20</sub>), 3.7 (q, *J* = 6.2, 4H, OCH<sub>2</sub>), 6.2 (d, 8.5 Hz, <sup>2</sup>H), 6.3 (s, <sup>1</sup>H), 6.9 (d, 8.7 Hz, <sup>5.6</sup>H), 7.1 (d, 8.6 Hz, <sup>3</sup>H), 7.2 (d, 8.7 Hz, <sup>4.7</sup>H), 8.5 (s, 1H, CH=N), 13.4 (s, 1H, OH); IR ( $v_{max}$ , cm<sup>-1</sup>, KBr):3431 ( $v_{OH}$ ), 2915 ( $v_{as}$ (C-H), CH<sub>3</sub>), 2918 ( $v_{as}$ (C-H), CH<sub>2</sub>), 2867 ( $v_s$ (C-H), CH<sub>3</sub>), 2841 ( $v_{as}$ (C-H), CH<sub>2</sub>), 1625 ( $v_{C=N}$ ), 1277 ( $v_{C-O}$ ).

### N-(4-n-octayloxysalicylidene)-4'-n-octadecyloxy aniline (4-8-OR)

Yield: 0.37 g, 75%. Anal. Calc. for  $C_{39}H_{63}NO_3$ : C, 78.8; H, 10.6; N, 2.4. Found: C, 78.7%; H, 10.4%; N, 2.3%; FAB Mass (*m/e*, fragment): *m/z*: calc. 593.5; found: 594 [M + H<sup>+</sup>]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.92 (t, *J* = 6.3 Hz, 6H, -CH<sub>3</sub>), 1.2–1.6 (m, 36H, (CH<sub>2</sub>)<sub>18</sub>), 3.7 (q, *J* = 6.2, 4H, OCH<sub>2</sub>), 6.2 (d, 8.5 Hz, <sup>2</sup>H), 6.3 (s, <sup>1</sup>H), 6.9 (d, 8.7 Hz, <sup>5.6</sup>H), 7.1 (d, 8.6 Hz, <sup>3</sup>H), 7.2 (d, 8.7 Hz, <sup>4.7</sup>H), 8.5 (s, 1H, CH=N), 13.4 (s, 1H, OH); IR (v<sub>max</sub>, cm<sup>-1</sup>, KBr):3430 (v<sub>OH</sub>), 2915 (v<sub>as</sub>(C-H), CH<sub>3</sub>), 2918 (v<sub>as</sub>(C-H), CH<sub>2</sub>), 2867 (v<sub>s</sub>(C-H), CH<sub>3</sub>), 2841 (v<sub>as</sub>(C-H), CH<sub>2</sub>), 1628 (v<sub>C=N</sub>), 1277 (v<sub>C-O</sub>).

### Synthesis of oxovanadium(IV) complexes

The ligands, 4-18-OR (0.7 g, 1 mmol), 4-16-OR (0.7 g, 1 mmol), 4-14-OR (0.6 g, 1 mmol), 4-12-OR (0.6 g, 1 mmol), 4-10-OR (0.6 g, 1 mmol) and 4-8-OR (0.5 g, 1 mmol) was dissolved in minimum volume of absolute ethanol and vanadyl sulfate,  $VOSO_4.2H_2O$  (0.08 g, 0.5 mmol) dissolved in methanol was added to it followed by addition of triethylamine and refluxed for 2 h. A greenish solid formed immediately was filtered, washed with diethyl ether and recrystallized from chloroform–ethanol.

*VO-18-OR.* Yield: 0.58 g (75%) Anal. Calc. for  $C_{98}H_{164}N_2O_7V$ : C, 76.7; H, 10.7; N, 1.8. Found: C, 76.6%; H, 10.6%; N, 1.8%; FAB Mass (*m/e*, fragment): *m/z*: calc.1533.2; found: 1533 [M+H<sup>\*</sup>]; IR (KBr, cm<sup>-1</sup>): 1613 ( $v_{C=N}$ ), 1144 ( $v_{C-O}$ , phenolic), 981 ( $v_{V=O}$ ).

*VO-16-OR.* Yield: 0.51 g (76%) Anal. Calc. for  $C_{94}H_{156}N_2O_7V$ : C, 76.4; H, 10.6; N, 1.9. Found: C, 76.1%; H, 10.6%; N, 1.8%; FAB Mass (*m*/*e*, fragment): *m*/*z*: calc.1477.1; found: 1477 [M+H<sup>+</sup>]; IR (KBr, cm<sup>-1</sup>): 1610 ( $v_{C=N}$ ), 1140 ( $v_{C=O}$ , phenolic), 980 ( $v_{V=O}$ ).

*VO-14-OR.* Yield: 0.77 g (70%) Anal. Calc. for  $C_{90}H_{148}N_2O_7V$ : C, 76.0; H, 10.5; N, 1.9. Found: C, 75.9%; H, 10.4%; N, 1.9%; FAB Mass (*m/e*, fragment): *m/z*: calc.1420; found: 1421 [M+H<sup>+</sup>]; IR (KBr, cm<sup>-1</sup>): 1615 ( $v_{C=N}$ ), 1141 ( $v_{C-O}$ , phenolic), 982 ( $v_{V=O}$ ).

*VO-12-OR.* Yield: 0.82 g (75%) Anal. Calc. for  $C_{86}H_{140}N_2O_7V$ : C, 75.6; H, 10.3; N, 2.0. Found: C, 75.5%; H, 10.2%; N, 1.9%; FAB Mass (*m/e*, fragment): *m/z*: calc. 1364; found: 1364 [M+H<sup>+</sup>]; IR (KBr, cm<sup>-1</sup>): 1612 ( $v_{C=N}$ ), 1138 ( $v_{C-O}$ , phenolic), 982 ( $v_{V=O}$ ).

*VO-10-OR.* Yield: 0.74 g (74%) Anal. Calc. for  $C_{82}H_{132}N_2O_7V$ : C, 75.2; H, 10.1; N, 2.1. Found: C, 75.1%; H, 9.8%; N, 2.1%; FAB Mass (*m/e*, fragment): *m/z*: calc.1307.9; found: 1308 [M+H<sup>+</sup>]; IR (KBr, cm<sup>-1</sup>): 1612 ( $v_{C=N}$ ), 1139 ( $v_{C=O}$ , phenolic), 980 ( $v_{V=O}$ ).

*VO-8-OR.* Yield: 0.73 g (73%) Anal. Calc. for C<sub>78</sub>H<sub>124</sub>N<sub>2</sub>O<sub>7</sub>V: C, 74.7; H, 9.9; N, 2.2. Found: C, 74.6%; H, 9.6%; N, 2.2%; FAB Mass (*m*/*e*,

fragment): *m/z*: calc.1251.8; found: 1252 [M+H<sup>+</sup>]; IR (KBr, cm<sup>-1</sup>): 1615 (v<sub>C=N</sub>), 1141 (v<sub>C=O</sub>, phenolic), 982 (v<sub>V=O</sub>).

### **Results and discussion**

The synthetic protocol for the ligands N-[4-n-alkoxysalicylaldimine)-4'-octadecyloxyaniline] and the corresponding mononuclear oxovanadium(IV) complexes (VO-n-OR) (-OR = OC<sub>18</sub>H<sub>37</sub>; *n* = 8, 10,12,14, 16, 18) are summarized in Scheme 1. The compounds were all obtained as stable colored solids. The characterizations of the compounds were made by elemental analyses, FT-IR, UV-VIS, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry. The elemental analyses are in good agreements with composition of the compounds. The Schiff bases exhibited  $v_{CN}$  at 1635–1625 cm<sup>-1</sup>; this band shifts to a lower wave number (1610–1620 cm<sup>-1</sup>) upon chelation, reflecting coordination of azomethine. Occurrence of vanadyl (V=O) stretching mode at  $\sim$ 975 cm<sup>-1</sup> indicates the absence of any intermolecular  $(\dots V=0\dots V=0\dots)$  interaction confirming monomeric complexes. The <sup>1</sup>H NMR spectra of ligands show signal at 13.4–13.8 ppm, corresponding to the –OH proton and a signal at 8.5 ppm due to the proton of imine group. FAB-mass spectra of the compounds are concordant with their formula weights. Solution electrical conductivities of the complexes recorded in dichloromethane ( $10^{-3}$  M) were found to be <10  $\Omega^{-1}$  cm<sup>-1</sup> mol<sup>-1</sup> confirming the non-electrolytic nature of the complexes.

The UV–visible spectra (Fig. 1) of ligands (10–OR and18–OR) in dichloromethane and their complexes (VO–10–OR and VO–18–OR) exhibited two bands in the  $\pi$ – $\pi$ \* region. The observed bands in the ligands were almost invariant in the corresponding complexes and also as a function of alkoxy chain lengths of the homologues (Table 1).

The phase transition behavior of the compounds was monitored using DSC and polarizing optical microscopy (POM). Thermal traces of the ligands and the complexes are summarized in Table 2. Both the ligands and their complexes exhibited liquid crystalline behavior. The ligands all showed enantiotropic SmC mesomorphism. Upon cooling the sample from isotropic melt, a focal conic texture of SmC phase (Fig. 2) at ~113–118 °C was observed. Remarkably a striated focal conic texture of an unidentified smectic mesophase (SmX/soft crystal) (Fig. 3) is observed at ~77–91 °C on further cooling of the compounds 8-OR to16-OR. Differential scanning calorimetry (DSC) also supports these observations.

The DSC thermogram for a typical compound (10-OR) is shown in Fig. 4, which exhibited two transitions in heating and three in cooling cycle. The transition at 118 °C ( $\Delta H$  = 8.2 kJ mol<sup>-1</sup>) is due to the isotropic–smectic C phase, and that at 81 °C



Fig. 1. UV-visible spectrum of ligands and complexes.

UV-visible spectral data of ligands (4-n-OR) and complexes (VO-n-OR).

Compounds	UV-visible, $\lambda_{\max}$ (nm) ( $\epsilon$ , l mol <sup>-1</sup> cm <sup>-1</sup> ) ( $\pi \rightarrow \pi^*$ transition)
C40He2NO2	285 (9300)
$(4-18-0C_{18}H_{37})$	350 (20,660)
$C_{98}H_{164}N_2O_6V$	286 (6340)
(VO-18-OC <sub>18</sub> H <sub>37</sub> )	352 (13,230)
C <sub>47</sub> H <sub>79</sub> NO <sub>3</sub>	284 (9350)
(4-16-OC <sub>18</sub> H <sub>37</sub> )	350 (20,530)
C <sub>94</sub> H <sub>156</sub> N <sub>2</sub> O <sub>6</sub> V	284 (9250)
(VO-16-OC <sub>18</sub> H <sub>37</sub> )	349 (22,500)
C <sub>45</sub> H <sub>75</sub> NO <sub>3</sub>	282 (6350)
(4-14-OC <sub>18</sub> H <sub>37</sub> )	352 (21,730)
C <sub>90</sub> H <sub>148</sub> N <sub>2</sub> O <sub>6</sub> V	280 (6550)
(VO-14-OC <sub>18</sub> H <sub>37</sub> )	349 (27,500)
C <sub>43</sub> H <sub>71</sub> NO <sub>3</sub>	285 (6350)
(4-12-OC <sub>18</sub> H <sub>37</sub> )	350 (25,630)
C <sub>86</sub> H <sub>140</sub> N <sub>2</sub> O <sub>6</sub> V	280 (8450)
(VO-12-OC <sub>18</sub> H <sub>37</sub> )	352 (21,450)
$C_{41}H_{67}NO_3$	284 (10,505)
(4-10-OC <sub>18</sub> H <sub>37</sub> )	350 (23,595)
$C_{82}H_{132}N_2O_6V$	286 (10,900)
(VO-10-OC <sub>18</sub> H <sub>37</sub> )	353 (18,483)
$C_{39}H_{63}NO_3$	282 (10,515)
(4-8-OC <sub>18</sub> H <sub>37</sub> )	352 (22,595)
C <sub>78</sub> H <sub>124</sub> N <sub>2</sub> O <sub>6</sub> V	284 (10,800)
(VO-8-OC <sub>18</sub> H <sub>37</sub> )	355 (24,483)

### Table 2

DSC data of ligands (4-n-OR) and complexes (VO-n-OR).

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Compo	ounds	Heating ( $\Delta H$ , kJmol <sup>-1</sup> )	Cooling ( $\Delta H$ , kJ mol <sup>-1</sup> )
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	18-OR		Cr 100.1 (89.1) SmC 114.0	I 113.3 (16.4) SmC 97.5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			(17.4) I	(88.0) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16-OR		Cr 96.7 (74.4) SmC 116.8	I 116.1 (13.8) SmC 91.7 (4.1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			(14.5) I	SmX 88.3 (47.0) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14-OR		Cr 95.1 (26.5) SmC 117.8 (13.7)	I 115.5 (12.8) SmC 87.3 (3.7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			Ι	SmX 78.3 (40.0) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	12-OR		Cr 92.1 (68.5) SmC 118.4 (11.3)	I 117.4 (8.2) SmC 85 (3.2) SmX
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			I	68.1 (38.6) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10-OR		Cr 89.4 (57.5) SmC 118.8 (8.7) I	I 118 (8.2) SmC 81 (2.6) SmX
$      \begin{array}{rlllllllllllllllllllllllllllllll$				67.4 (39.5) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8-OR		Cr 87.3 (77.5) SmC 119.0	I 118.2 (10.9) SmC 77.3 (5.5)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			(11.8) I	SmX 71.6 (50.1) Cr
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	VO-18	-OR	Cr 99.1 (111.3) SmA 119.0	I 118.0 (19.1) SmA 89.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			(19.4) I	(119.9) Cr
$ \begin{array}{c} (6.0) \ {\rm I} \\ {\rm VO-14-OR} & {\rm Cr}\ 103.2\ (2.6)\ {\rm Cr}_1\ 127.6\ (34.0) & {\rm I}\ 141.8\ (2.8)\ {\rm SmA}\ 80.8\ (13.9)\ {\rm Cr} \\ {\rm SmA}\ 145.1\ (7.8)\ {\rm I} \\ {\rm VO-12-OR} & {\rm Cr}\ 131.7\ (24.0)\ {\rm SmA}\ 158.7 & {\rm I}\ 148.8\ (7.0)\ {\rm SmA}\ 74.2\ (8.9) \\ {\rm (10)\ {\rm I}} & {\rm SmC}\ 45.5\ (6.8)\ {\rm Cr} \\ {\rm VO-10-OR} & {\rm Cr}\ 89.7\ (81.2)\ {\rm SmA}\ 122.9\ (9.2)\ {\rm I}\ 122.8\ (12.1)\ {\rm SmA}\ 64.8\ (25.7) \\ {\rm SmC}\ 57.5\ (6.1)\ {\rm Cr} \\ {\rm VO-8-OR} & {\rm Cr}\ 81.9\ (2.3)\ {\rm Cr}_1\ 96.2\ (20.0) \\ {\rm SmA}\ 155.2\ (5.0)\ {\rm I} \end{array} $	VO-16	-OR	Cr 132.5 (25.4) SmA 143.9	I 143.8 (5.1) SmA 83.6 (11.7) Cr
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			(6.0) I	
$\begin{array}{c} & {\rm SmA}\ 145.1\ (7.8)\ {\rm I} \\ {\rm VO-12\text{-}OR} & {\rm Cr}\ 131.7\ (24.0)\ {\rm SmA}\ 158.7 & {\rm I}\ 148.8\ (7.0)\ {\rm SmA}\ 74.2\ (8.9) \\ (10)\ {\rm I} & {\rm SmC}\ 45.5\ (6.8)\ {\rm Cr} \\ {\rm VO-10\text{-}OR} & {\rm Cr}\ 89.7\ (81.2)\ {\rm SmA}\ 122.9\ (9.2)\ {\rm I}\ 1\ 122.8\ (12.1)\ {\rm SmA}\ 64.8\ (25.7) \\ {\rm SmC}\ 57.5\ (6.1)\ {\rm Cr} \\ {\rm VO-8\text{-}OR} & {\rm Cr}\ 81.9\ (2.3)\ {\rm Cr}_1\ 96.2\ (20.0) & {\rm I}\ 154.3\ (6.6)\ {\rm SmA}\ 49.6\ (6.7)\ {\rm Cr} \\ {\rm SmA}\ 155.2\ (5.0)\ {\rm I} \end{array}$	VO-14	-OR	Cr 103.2 (2.6) Cr <sub>1</sub> 127.6 (34.0)	I 141.8 (2.8) SmA 80.8 (13.9) Cr
$ \begin{array}{cccc} \mbox{VO-12-OR} & Cr \ 131.7 \ (24.0) \ \mbox{SmA} \ 158.7 & I \ 148.8 \ (7.0) \ \mbox{SmA} \ 74.2 \ (8.9) \\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $			SmA 145.1 (7.8) I	
$ \begin{array}{cccc} (10) \ I & SmC \ 45.5 \ (6.8) \ Cr \\ \mbox{VO-10-OR} & Cr \ 89.7 \ (81.2) \ SmA \ 122.9 \ (9.2) \ I & I \ 122.8 \ (12.1) \ SmA \ 64.8 \ (25.7) \\ & SmC \ 57.5 \ (6.1) \ Cr \\ \mbox{VO-8-OR} & Cr \ 81.9 \ (2.3) \ Cr_1 \ 96.2 \ (20.0) & I \ 154.3 \ (6.6) \ SmA \ 49.6 \ (6.7) \ Cr \\ & SmA \ 155.2 \ (5.0) \ I \\ \end{array} $	VO-12	-OR	Cr 131.7 (24.0) SmA 158.7	I 148.8 (7.0) SmA 74.2 (8.9)
VO-10-OR         Cr 89.7 (81.2) SmA 122.9 (9.2) I         I 122.8 (12.1) SmA 64.8 (25.7) SmC 57.5 (6.1) Cr           VO-8-OR         Cr 81.9 (2.3) Cr <sub>1</sub> 96.2 (20.0)         I 154.3 (6.6) SmA 49.6 (6.7) Cr           SmA 155.2 (5.0) I         I			(10) I	SmC 45.5 (6.8) Cr
SmC 57.5 (6.1) Cr VO-8-OR Cr 81.9 (2.3) Cr <sub>1</sub> 96.2 (20.0) I 154.3 (6.6) SmA 49.6 (6.7) Cr SmA 155.2 (5.0) I	VO-10	-OR	Cr 89.7 (81.2) SmA 122.9 (9.2) I	I 122.8 (12.1) SmA 64.8 (25.7)
VO-8-OR Cr 81.9 (2.3) Cr <sub>1</sub> 96.2 (20.0) I 154.3 (6.6) SmA 49.6 (6.7) Cr SmA 155.2 (5.0) I				SmC 57.5 (6.1) Cr
SmA 155.2 (5.0) I	VO-8-0	OR	Cr 81.9 (2.3) Cr <sub>1</sub> 96.2 (20.0)	I 154.3 (6.6) SmA 49.6 (6.7) Cr
			SmA 155.2 (5.0) I	

 $(\Delta H = 2.6 \text{ kJ mol}^{-1})$  is due to the smectic C-smectic Xphase. The transition from smectic X phase to the crystalline phase was observed at 67.4 °C ( $\Delta H = 39.6 \text{ kJ mol}^{-1}$ ) during cooling. In polarizing optical microscopic (POM) study, all the complexes exhibited highly birefringent fan-like texture at ~118–154 °C typical of the SmA phase (Fig. 5). In addition to SmA mesophase, VO-10-OR and VO-12-OR, on further cooling, also showed schlieren textures characteristic of SmC phase (Fig. 6) at ~64–74 °C. The thermal events as observed in DSC for all the complexes are concordant with POM observations. The compound VO-10-OR for instance, showed two transitions in heating (Cr-SmA at 89.7 °C and SmA-I at122.9 °C) and three on cooling cycle (I-SmA at 122.8 °C, SmA-SmC at 64.8 °C and SmC-Cr at 57.5 °C) (Fig. 7). Reproducibility of the thermal behavior was confirmed by several heating and cooling runs.



Fig. 2. Focal conic texture of SmC phase of 10-OR.



Fig. 3. Striated focal conic texture of 'soft crystal' phase (SmX) of 10-OR.



Fig. 4. DSC thermogram of 10-OR.

Variation of carbon chain length of flexible alkoxy arms with transition temperatures are depicted in Figs. 8 and 9. The melting points of the ligands linearly varied as a function of increasing carbon chain length of alkoxy arm while no trend was apparently noticeable for the complexes. The complexes show significantly



Fig. 5. Fan-like texture of SmA phase of VO-10-OR.



Fig. 6. Schlieren texture of SmC phase of VO-10-OR.



Fig. 7. DSC thermogram of VO-10-OR.

higher mesophase-isotropic transition temperatures than those for the corresponding ligands. With increase in carbon chain length of alkoxy arm in ligands, the mesophase to isotropic transition temperature decreases. As for complexes, the higher homologues



Fig. 8. Variation of carbon chain length in ligands.



Fig. 9. Variation of carbon chain length in complexes.

(VO-14-OR to VO-18-OR) showed similar trends as that of the ligands whereas quite different thermal events were noted for the complexes of lower homologues.

In the present study we observed enantiotropic SmA phase for the complexes VO-8-OR to VO-18-OR and in addition to SmA phase, SmC phases were also encountered for VO-10-OR and VO-12-OR only, in cooling cycle. In our earlier reports, we have found that, the oxovanadium complexes of hexadecyloxyaniline chain, VO-*n*-OC<sub>16</sub>H<sub>33</sub> (n = 12-18) showed enantiotropic SmC phase whereas VO-10-OC<sub>16</sub>H<sub>33</sub> showed enantiotropic SmA phase and VO-8-OC<sub>16</sub>H<sub>33</sub> showed monotropic SmA phase [35] and oxovanadium complexes of dodecyloxyaniline chain VO-*n*-OC<sub>12</sub>H<sub>25</sub> (n = 6,8,16,18) showed SmA/SmX phase [36].

### Conclusion

A series of new oxovanadium(IV) complexes of bidentate [N,O] donor rod shaped Schiff base ligands containing flexible alkoxy arms on either side of the aromatic rings have been successfully synthesized and characterized. The ligands and their complexes both exhibited smectic mesomorphism. Of particular interest is that the ligands showed striated textures (SmX) reminiscent of soft crystal not observed in the case of complexes. The complexes with carbon chain length ( $C_{10}$ ,  $C_{12}$ ) interesting volved SmC mesophase in addition to SmA phase. An interesting correlation of phase behavior with the alkoxy chain length was made. These compounds are new addition to the wealth of related vanadium complexes showing smectic mesomorphism.

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