CHAPTER 4

VO(IV) Salicylaldimine Complexes.

4.1. Introduction

Schiff bases derived from substituted salicylaldehydes are very versatile ligands which form [N-O] chelates with many metals. The advantages of incorporating an imine functionality lie in the versatility, structural variety, ease of preparation, and derivatization of such groups. Metal complexes derived from salicylaldimines feature among the earliest and most widely studied class of metallomesogens. Ligands are obtained from the condensation of appropriate 4-substituted alkoxy aldehyde with 4-substituted aniline or other primary amines [Scheme-1].
Owing to unusual geometries, large birefringence, polarisability, paramagnetism leading to unique functional behaviours, metallomesogens incorporating transition metal ions is a focal theme of current research [34, 39, 96]. Mesophase formation depends mainly on the intermolecular interactions between ligand groups and their arrangements around metal ions. Precise understanding and the control of phase behaviour, though, is a function of molecular chain length, substituent on the ligands, spacer groups and nature of metal ions, their planned synthesis is quite a challenging task [36, 37]. Salicylaldimines have been extensively exploited to access metal complexes with anticipated liquid crystalline properties [34-42, 97-106]. Unlike other first row transition metals, weakened intermolecular V=O....V=O... nonpolar interaction in oxovanadium(IV) complexes often frustrates exhibition of mesogenic properties. Due to the paramagnetism induced by the VO(IV) centre, these metallomesogens show interesting chemical and physical properties, which can lead to potential applications [97-106]. However, when mesogenic, oxovanadium(IV) complexes exhibit lower melting and clearing temperature, compared to other transition metals. Despite the inherent difficulties in synthesizing mesogenic vanadyl(IV) complexes, a number of vanadyl(IV) liquid crystalline complexes have been documented [34, 111, 106, 115, 116-119, 131, 139, 140]. First report on mesogenic vanadyl complex with Schiff
base ligands were made by Galyametdinov et al [99]. A series of mesogenic oxovanadium(IV) complexes with varying alkyl or alkoxy chain length exhibiting smectic mesomorphism are documented [34, 97-99, 111, 131, 139, 140]. Rich but complex mesomorphism exhibited by the salicylaldimines and their metal complexes including vanadium has attracted considerable interests. In this chapter, we report a systematic investigation on a series of oxovanadium(IV) Schiff base complexes containing a both shorter as well as longer alkoxy/alkyl/polar substituent on either side of the ligand.

4.2 Synthesis and characterization

4.2.1. Synthesis

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-chloro or p-nitro substituted aniline. The vanadyl (IV) complexes, \( \text{VO}_2 \) (L=salicylaldimines) were synthesized by the interaction of hot ethanolic solution of the ligands and vanadyl sulphate in the presence of triethylamine under reflux.
**Scheme 2.** $C_nH_{2n+1}Br$, KHCO$_3$, KI, dry acetone, $\Delta$, 40h, and ii. glacial AcOH, absolute EtOH $\Delta$, 4h iii. VOSO$_4.5H_2O$, MeOH, TEA, $\Delta$, 1h.

### 4.2.2. Synthesis of 4-n-alkoxy salicylaldehydes:

2,4-dihydroxybenzaldehyde (0.1 mol), potassium bicarbonate KHCO$_3$ (0.1 mol, potassium iodide (catalytic amount 0.1 to 0.2 gm), and 1-bromoalkane (0.1 mol) mixed in 250 ml of dry acetone. The mixture was refluxed for 24 hrs and
filtered when hot, to remove insoluble solids. Dilute hydrochloric acid was added to neutralize the warm solution, which was then extracted twice with CHCl₃ (2X100 ml). The combined CHCl₃ extracts were concentrated to give a purple solid. The solid is purified by column chromatography first with hexane followed by a mixture of hexane/ CHCl₃ (1:1). The solvent was evaporated to give pale yellow liquid, in lower homologues and white solids in higher homologues. Yield 60-80%.

4.2.3. N-(4-n-decyloxysalicylidene)-4'-n-chloroaniline (L1)

Yield: 0.390g, 75%. Anal. Calc. for C₂₃H₃₀ClNO₂: C, 71.2; H, 7.7; N, 3.6. Found: C, 71.1; H, 7.5; N, 3.5%; FAB Mass (m/e, fragment): m/z: calc. 387.2; found: 388[M+H⁺]. HNMR (400MHZ, CDCl₃): 0.87(t, J=7.2, 6H, -CH₃), 1.25-1.58 (m, 30H, (-CH₂)₃₀), 4.02(t, J=6.4, 2H, -OCH₂), 8.29(d, J=8.0, 1H, H-aryl), 13.06(s, 1H, OH), 8.5(s, 1H, -CH=N). IR (vmax, cm⁻¹, KBr): 3424(vOH), 2913(vas(C-H), CH₃), 2918(vas(C-H), CH₂), 2869(vs(C-H), CH₃), 2845(vas(C-H), CH₂), 1603(vC=N), 1278(vC-O).
4.2.4. N-(4-n-octadecyloxy salicylidene)-4'-n-chloroaniline (L2)

An ethanolic solution of (4-n-octadecyloxy)salicyaldehyde (0.3g, 1mmol) was added to an ethanolic solution of 4-chloroaniline (0.1g, 1mmol). The solution mixture was refluxed with few drops of acetic acid as catalyst for 3h to yield the Schiff base N-(4-n-octadecyloxy salicylidene)-4'-n-chloroaniline. The solid was collected by filtration and recrystallised several times from absolute ethanol to give a pure compound. Yield: 0.4g, 75%.

Yield: 0.4g, 75%. Anal. Calc. for C₃₁H₄₆ClNO₂: C, 74.4; H, 9.2; N, 2.8. Found: C, 74.1; H, 9.3; N, 2.7%; FAB Mass (m/e, fragment): m/z: calc. 499.3; found: 500[M+H⁺]. ¹H NMR (400MHZ, CDCl₃): 0.87(t, J=5.7, 6H, CH₃), 1.25-1.78 (m, 30H, (CH₂)₁₅), 3.95(t, J=5.9, 2H, OCH₂), 7.3(d, J=7.2, 1H, H-aryl), 13.06(s, 1H, OH), 8.5(s, 1H, CH=N); ¹³C NMR (75.45 MHz; CDCl₃; Me₄Si at 25°C, ppm) δ= 106.3 (-C1), 131.1 (-C2), 104.9 (-C3), 161.6 (-C4), 109.3 (-C5), 122.7 (-C6), 132.1(-C7), 122.6 (-C8), 131.4 (-C9), 159.8(-C10).
4.2.5. N-(4-n-decyloxysalicylidene)-4'-n-nitroaniline (L\textsubscript{3})

![Chemical Structure Image]

Yield: 0.316g, 76%. Anal. Calc. for C\textsubscript{23}H\textsubscript{30}N\textsubscript{2}O\textsubscript{4}: C, 69.3; H, 7.5; N, 7.0. Found: C, 70.1; H, 7.3; N, 7.3%; FAB Mass (m/e, fragment): m/z: calc. 398.2; found: 399[M+H\textsuperscript{+}]. \textsuperscript{1}HNMR (400MHZ, CDCl\textsubscript{3}): 0.87(t, J=7.2, 6H, CH\textsubscript{3}), 1.25-1.58 (m, 30H, (CH\textsubscript{2})\textsubscript{15}), 4.02(t, J=6.4, 2H, OCH\textsubscript{2}), 8.29(d, J=8.0, 1H, H-aryl), 13.06(s, 1H, OH), 8.5(s, 1H, CH= N). IR (\textit{v}_\text{max}, cm\textsuperscript{-1}, KBr): 3433(\textit{vOH}), 2915(\textit{vas}(C-H), CH\textsubscript{3}), 2917(\textit{vas}(C-H), CH\textsubscript{2}), 2867(\textit{vs}(C-H), CH\textsubscript{3}), 2844(\textit{vas}(C-H), CH\textsubscript{2}), 1602(\textit{vC=N}), 1276(\textit{vC-O}), 1516(\textit{vs}(NO)), 1351(\textit{vs}(NO)),

4.2.6. N-(4-n-octadecyloxysalicylidene)-4'-n-nitroaniline (L\textsubscript{4})

![Chemical Structure Image]

Yield: 0.418g, 78%. Anal. Calc. for C\textsubscript{31}H\textsubscript{46}N\textsubscript{2}O\textsubscript{4}: C, 72.9; H, 9.0; N, 5.4. Found: C, 71.8; H, 9.1; N, 5.3%; FAB Mass (m/e, fragment): m/z: calc. 510.3; found: 511[M+H\textsuperscript{+}]. \textsuperscript{1}HNMR (400MHZ, CDCl\textsubscript{3}): 0.87(t, J=7.2, 6H, CH\textsubscript{3}), 1.25-1.58 (m, 30H, (CH\textsubscript{2})\textsubscript{15}), 4.02(t, J=6.4, 2H, OCH\textsubscript{2}), 8.29(d, J=8.0, 1H, H-aryl), 13.06(s, 1H, OH), 8.5(s, 1H, CH= N); \textsuperscript{13}C NMR (75.45 MHZ; CDCl\textsubscript{3}; Me\textsubscript{4}Si at 25\textdegree C, ppm) 8= 107.2 (-C1), 130.1 (-C2), 102.4 (-C3), 161.5 (-C4), 109.8 (-C5), 122.9 (-C6), 122.3(-C7), 123.6 (-C8), 122.4 (-C9), 147.8(-C10). IR (\textit{v}_\text{max}, cm\textsuperscript{-1},
4.3. Synthesis of oxovanadium (IV) complexes

The ligand $L_4$ (0.10 g, 0.2 mmol) or $L_2$ (0.07 g, 0.2 mmol) or $L_7$ (0.10 g, 0.2 mmol) or $L_6$ (0.08 g, 0.2 mmol) was dissolved in minimum volume of absolute ethanol and vanadyl sulphate, $\text{VOSO}_4\cdot\text{H}_2\text{O}$ (0.01 g, 0.1 mmol) dissolved in methanol was added to it followed by addition of triethylamine and refluxed for 2h. A greenish solid formed immediately was filtered, washed with diethyl ether and recrystallized from chloroform-ethanol.

4.3.1. Oxovanadium (IV) complex $L_4\text{VO}$

\[
\begin{array}{c}
\text{C}_{10}\text{H}_{21}\text{O} \\
\text{O} \\
\text{N} \\
\text{Cl} \\
\text{Cl} \\
\text{OC}_{10}\text{H}_{21} \\
\end{array}
\]

Yield=0.06 g, 75%. Anal. Calc. for $\text{C}_{46}\text{H}_{58}\text{Cl}_2\text{N}_2\text{O}_5\text{V}$: C, 65.7; H, 6.9; N, 3.3. Found: C, 65.2; H, 6.8; N, 3.1%; FAB Mass (m/e, fragment): m/z: calc. 839.3; found: 840$\text{[M+H]}^+$. IR (vmax, cm$^{-1}$, KBr): 2919(vas(C-H), CH$_3$), 2851(vas(C-H), CH$_2$), 1589(vC=N), 1516(vas(NO)), 1350((v$\delta$(NO))).
4.3.2. Oxovanadium (IV) complex ($L_2VO$)

Yield = 0.08 g, 75%. Anal. Calc. for $C_{62}H_{90}Cl_2N_2O_5V$: C, 69.9; H, 8.5; N, 2.6.
Found: C, 70.1; H, 8.3; N, 2.5%; FAB Mass ($m/e$, fragment): $m/z$: calc. 1063.6;
found: 1064[$M+H^+$]. IR ($v_{max}$, cm$^{-1}$, KBr): 2920($v_{as}(C-H)$, CH$_3$),
2850($v_{as}(C-H)$, CH$_2$), 1612($v_{C=N}$), 981($v_{V=O}$).

4.3.3. Oxovanadium (IV) complex ($L_3VO$)

Yield = 0.07 g, 79%. Anal. Calc. for $C_{46}H_{58}N_4O_9$: C, 64.1; H, 6.7; N, 6.5.
Found: C, 64.2; H, 6.6; N, 6.4%; FAB Mass ($m/e$, fragment): $m/z$: calc. 861.4;
found: 862[$M+H^+$]. IR ($v_{max}$, cm$^{-1}$, KBr): 2920($v_{as}(C-H)$, CH$_3$), 2850($v_{as}(C-H)$, CH$_2$),
1595($v_{C=N}$), 988($v_{V=O}$).
4.3.4. Oxovanadium (IV) complex (L₄VO)

![Oxovanadium (IV) complex (L₄VO)](image)

Yield=0.08g, 77%. Anal. Calc. for C₆₂H₉₀N₄O₉ V: C, 68.5; H, 8.3; N, 5.1.

Found: C, 68.1; H, 8.1; N, 5.2%; FAB Mass (m/e, fragment): m/z: calc. 1085.6; found: 1086[M+H⁺]. IR (vmax, cm⁻¹, KBr): 2919(vas(C-H), CH₃), 2851(vas(C-H), CH₂), 1584(vC=N), 991(vo=O).

4.4. Results and discussions

4.4.1. Synthesis

The Schiff bases were obtained as yellow microcrystalline solids in good yields. The mononuclear light green vanadyl (IV) complexes were prepared in good yields by the direct reaction of the VOSO₄.5H₂O with the chosen ligand (Scheme 2). Obtained as bis-chelates, the complexes are readily recrystallised from methanol/CH₂Cl₂. The compounds were characterized by ¹H and ¹³C NMR, FT-IR, UV-Vis spectroscopy and elemental analysis. Solution electrical conductivity measurements in CH₂Cl₂ revealed non-ionic nature of the complexes.
4.4.2. IR Study

The shift of vCN vibrational stretching frequency at ca.1625 cm\(^{-1}\) to lower wave number (\(\Delta v\sim 30 \text{ cm}^{-1}\)) and absence of vOH mode and phenolate oxygen upon chelation, clearly suggested the coordination of azomethine N and phenolate oxygen to the metal. The vC=N stretching frequency is rather independent of the length of alkoxy side chain in both ligands and their complexes. The vanadyl(V=O) stretching at ca.980 cm\(^{-1}\) is suggestive of the absence of any intermolecular (...V=O...V=O...) interaction indicating the monomeric nature of the complexes. The presence of linear chain interactions usually cause vV=O to shift to lower wave no (ca.870 cm\(^{-1}\)). The IR data also showed V=O stretching frequency to be insensitive to the length of the alkoxy side chain.

4.4.3. UV-vis study

The electronic absorption spectra (Fig. 4.1.) of the ligand (L\(_1\)) exhibited two bands one at ~246 nm (\(\varepsilon=3,400 \text{ llmol}^{-1}\text{cm}^{-1}\)) due to \(\pi-\pi^*\) transition of the aromatic rings and another at ~337 nm, (\(\varepsilon=5,400 \text{ llmol}^{-1}\text{cm}^{-1}\)) attributed to \(\pi-\pi^*\) transition of imine (-C=N) chromophores. The latter band is blue shifted to lower wavelength at ~328 nm on complexation with VO(IV) centre (Fig. 4.1.). In addition, a strong band at ~400 nm, (\(\varepsilon=2,400 \text{ llmol}^{-1}\text{cm}^{-1}\)) for vanadyl complex is assigned to MLCT transition. A similar observation (Table. 1.) was also noted for the nitro series.
Fig. 4.1. Absorption spectra of L₄ and L₄VO.

Table 4.1. UV-visible absorption data of the ligand and complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\max}$(nm)</th>
<th>$\pi\rightarrow\pi^*$ (ε, 1 mol⁻¹ cm⁻¹)</th>
<th>MLCT (ε, 1 mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>246 (3,500), 337(2,300)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₁VO</td>
<td>245(5,400), 328(2,200)</td>
<td>400(2,500)</td>
<td></td>
</tr>
<tr>
<td>L₂</td>
<td>246(3,600), 336(2,400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₂VO</td>
<td>244(5,300), 328(2,300)</td>
<td>398(2,400)</td>
<td></td>
</tr>
<tr>
<td>L₃</td>
<td>245(5,500), 334(2,400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₃VO</td>
<td>241(5,400), 328(2,400)</td>
<td>398(2,400)</td>
<td></td>
</tr>
<tr>
<td>L₄</td>
<td>244(5,400), 334(2,400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L₄VO</td>
<td>242(5,300), 328(2,400)</td>
<td>402(2,400)</td>
<td></td>
</tr>
</tbody>
</table>
4.4.4. NMR study

$^1$H NMR spectra of ligands showed a signal at $\delta=13.4$-$13.8$ ppm, corresponding to the OH proton. The imine proton appeared at 8.5 ppm. Multiplets in the range of 6.4-$7.3$ ppm is attributable to aromatic proton. $^{13}$C-NMR spectra for both the ligands showed a signal at $\sim$163 ppm is attributed to azomethine carbon. Carbon atoms in the benzene ring showed signals at 102-$151$ ppm.

4.4.5. Variable temperature magnetic susceptibility study

The variable temperature magnetic susceptibility measurements were carried out for a representative complex L$_2$VO (Fig. 4.2.). The compound follows Curie-Weiss law. Absence of any maximum in $\chi M$ vs $T$ infers that nonexistence of strong exchange interactions between the spin centers. The strength of efficient super exchange path is presumably hindered by coordinating ability of metal ion. Hence the vanadium complex can be considered as magnetically isolated spin centres.

![Graph](image)

Fig. 4.2. Variation of magnetic susceptibility of with temperature.
4.4.6. Mesomorphic properties

Owing to the viscous nature of the complexes, DSC thermograms often did not show sharp peaks. Typical fan-like textures (Fig.4.3. and Fig.4.4) characteristic of SmA dominated the phase sequence of all the ligands and their complexes. The thermal data (Table.4.2) show interesting trend as a function of the electron withdrawing substituent (Cl, or NO2) and carbon chain length (C10 or C18). For the C10 ligand, both melting point and clearing point of chloro substituted compound (L1) is about 20°C higher than the nitro substituted compound (L6). For the corresponding complexes, the melting point of the chloro substituted one (L1VO) is about 45°C lower while the clearing point is ~50°C higher than that of the nitro substituted compound (L3VO). Quite different trend however, was observed for the C-18 ligand and its complexes. The melting point of both chloro and nitro substituted ligand were almost the same (~57.3°C) while the clearing point of the former was ~20°C lower than the later. The nitro-substituted C10 ligand also melted at 57.3°C. In this case, therefore neither the substituent nor the carbon chain length had any effect on the melting temperatures. The C-18-complexes, on the other hand, showed a difference of ~35°C between the chloro and nitro substituted ones, for both melting and clearing temperatures. On the whole the melting temperatures of the complexes were always substantially higher than the ligands with no definitive trends with regards to chloro or nitro substituent or carbon chain length. Crystal to crystal phase transitions were often encountered and are one of the redeeming features of phase sequences observed for the compounds. The ligands and complexes all showed enantiotropic phase transitions. The enthalpies of transitions for SmA→
I and vice versa for all the compounds expectedly are < 10 kJ mol\(^{-1}\). For the ligand L\(_4\), as many as three low enthalpy crystal-crystal transitions could be seen on the heating run. The DSC thermogram for the typical compounds L\(_1\) and L\(_1\)VO are shown in the **Fig.4.5.** and **Fig.4.6.**

Interesting mesomorphic observation was noted for lower homologous series. The ligand L\(_{1a}\) with chloro substituent exhibits a SmA phase (**Fig. 4.7**), whereas with nitro substituent lacks the mesomorphism. The DSC thermogram of L\(_{1a}\) is shown in the **Fig.4.8.** Upon complexation, mesomorphism was lost. Quite surprisingly the ligand L\(_4\) showed a nematic phase, whereas analogous compounds with chloro substituent showed SmA phase. The complexes did not exhibit any mesomorphism. Ligand L\(_{3a}\) showed SmA phase (**Fig.4.9**), DSC thermogram (**Fig.4.10**) also showed two transition in heating and cooling cycle.
Fig. 4.5. DSC thermogram of L₁

Fig. 4.6. DSC thermogram of L₁VO

Fig. 4.7. Fanlike texture (SmA).

Fig. 4.8. DSC thermogram of L₁a.

Fig. 4.9. Focal conic texture (SmA).

Fig. 4.10. DSC thermogram of L₃a.
Table 4.2. DSC and POM data.

<table>
<thead>
<tr>
<th></th>
<th>Heating (°C)</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_{1a}</td>
<td>Cr 93.2(7.5) Cr, 96.0(12.9) SmA</td>
<td>116.7(3.4) SmA 72.9(6.0) Cr, 71.8(5.5) Cr</td>
</tr>
<tr>
<td></td>
<td>118.7(3.8) l</td>
<td>1119.2(4.6) SmA 45.6(20.2) Cr</td>
</tr>
<tr>
<td>L_{1}</td>
<td>Cr 75.8(34.9) SmA 120.9(4.6) l</td>
<td>1110.4(5.5) SmA 63.9(55.0) Cr</td>
</tr>
<tr>
<td>L_{3a}</td>
<td>Cr 912.9(59.4) SmA 112.2(5.8) l</td>
<td>95.6(3.2) SmA 75.8(61.9) Cr, 50.6(62.2) Cr</td>
</tr>
<tr>
<td>L_{2}</td>
<td>Cr 57.3(2.9) Cr, 90.6(57.4) SmA</td>
<td>916.5(2.0) l</td>
</tr>
<tr>
<td></td>
<td>96.5(2.0) l</td>
<td>1 54.1(30.3) Cr</td>
</tr>
<tr>
<td>L_{5}</td>
<td>Cr 92.3(0.31) N 99.3(17.3) l</td>
<td>1 82.9(29.9) SmA 43.9(39.2) Cr</td>
</tr>
<tr>
<td>L_{3}</td>
<td>Cr 57.3(36.4) SmA 104.8(9.1) l</td>
<td>1 116.3(2.7) SmA 66.8(46.3) Cr, 44.0(5.4) Cr</td>
</tr>
<tr>
<td>L_{4}</td>
<td>Cr 57.2(1.5) Cr, 60.5(1.5) Cr, 78.8(16.2) Cr, 81.8(27.8) SmA</td>
<td>116.5(2.6) l</td>
</tr>
<tr>
<td></td>
<td>1178.8(16.2) l</td>
<td>1 54.1(30.3) Cr</td>
</tr>
<tr>
<td>L_{1}VO</td>
<td>Cr 107.8(4.8) Cr, 146.5(4.5) SmA</td>
<td>1 231.5(4.3) SmA</td>
</tr>
<tr>
<td></td>
<td>233.7(3.4) l</td>
<td>1 1231.5(4.3) SmA</td>
</tr>
<tr>
<td>L_{2}VO</td>
<td>Cr 114.1(34.2) Cr, 116.6(8.1) SmA</td>
<td>1 60.5(21.7) 21.7 Cr</td>
</tr>
<tr>
<td></td>
<td>135.2(7.8) l</td>
<td>1 116.1(16.3) SmA</td>
</tr>
<tr>
<td>L_{3}VO</td>
<td>Cr 124.1(18.7) SmA 185.5(16.7) l</td>
<td>116.1(16.3) SmA</td>
</tr>
<tr>
<td>L_{4}VO</td>
<td>Cr 75.2(1.0) Cr, 157.2(35.1) SmA</td>
<td>1159.2(1.5) SmA 139.9(20.6) Cr</td>
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<tr>
<td></td>
<td>171.1(5.3) l</td>
<td>1 159.2(1.5) SmA 139.9(20.6) Cr</td>
</tr>
</tbody>
</table>

4.4.7. DFT study

As efforts to obtain single crystal of the complexes proved futile, density functional theory (DFT) calculation is performed to investigate the electronic structure of the VO(IV) complexes (Fig. 4.11. and Fig. 4.12). Full geometry optimization of the complexes without symmetry constrain has been carried out with DMol3 program package [272] using Kohn–Sham Theory [273, 274]. The generalized gradient approximation (GGA) was used in the calculations. At the GGA level, we have chosen the BLYP functional [275, 276] which incorporates Becke’s exchange and Lee–Yang–Parr correlation. The DNP basis functions, chosen in the present study, are the double-numerical atomic orbitals
augmented by polarization functions, i.e., functions with angular momentum one higher than that of the highest occupied orbital in the free atom\[277\]. The DNP basis set is believed to be more accurate than a Gaussian basis set 6-31G** of similar size. In our calculations, self consistent field procedures are performed with a convergence criterion of \(2 \times 10^{-5}\) a.u. on the total energy and \(10^{-6}\) a.u. on electron density. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) diagram of the complexes L\(_2\)VO and L\(_6\)VO are shown in (Fig.4.13a, Fig.4.13b, and Fig.4.14a, Fig. 4.14b). In both the complexes electron density of the HOMO is localized mainly on the vanadium atom while the LUMO of L\(_2\)VO complex is localized on the alkoxy chain bearing aromatic ring and that of L\(_6\)VO complex is distributed on the nitro-substituted aromatic ring. Noticeable differences in the distribution of electron density on LUMO of L\(_2\)VO and L\(_6\)VO may be ascribed to the chemical nature of the electronegative substituents (-Cl and -NO\(_2\)). The HOMO and LUMO energies of the complex 2a-10 are calculated to be -4.18 eV and -2.59 eV, respectively, \(\Delta E=1.59\) eV. Corresponding energies for the complex 2b-10 were -4.58 eV and -3.44 eV respectively, \(\Delta E=1.14\). Some of the selective geometric parameters of optimized vanadium complexes, evaluated by DFT calculation at BLYP/DNP level are shown in Table 4.3. The calculated bond distances of the complexes are in good agreement with a related structurally characterised [N\(_2\)O\(_2\)] donor bis(salicylaldiminato)vanadyl complexes [159]. The bond angles of 129.50 and 161.90 for O1—V—O2 and N1—V—N2, respectively, in both the complexes suggest a distorted square pyramidal geometry.
Fig. 4.11. DFT structure of $L_2VO$.  
Fig. 4.12. DFT structure of $L_6VO$.

Fig. 13a. HOMO of $L_2VO$.

Fig. 4.13b. HOMO of $L_6VO$.

Fig. 4.14a. LUMO of $L_2VO$.

Fig. 4.14b. LUMO of $L_6VO$.

Table 4.3. Selective geometric parameters of optimized vanadium complexes

<table>
<thead>
<tr>
<th>Structure parameter</th>
<th>$L_2VO$</th>
<th>$L_6VO$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V-O(3)$</td>
<td>1.622</td>
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<td>$N(2)-V-O(2)$</td>
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4.5. Oxovanadium(IV) complexes of the type [VO(L)$_2$],
[L=N-(4-n-alkoxysalicylaldimine)-4'-hexadecyloxyaniline.

There is no report on the vanadium salicylaldimine complexes with long alkoxy tail on both aryl moieties till date. Accordingly we report here in 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.

4.5.1. Synthesis and analysis

The general preparative route for salicylaldimine based Schiff bases are presented in Scheme 3. 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'-hexadecyloxyaniline, n=8, 10, 12, 14, 16, 18]) were synthesized by the interaction of hot ethanolic solution of the ligands and vanadyl sulphate in the presence of triethylamine under reflux.
Schemes. $C_{n}H_{2n+1}Br$, KHCO$_3$, KI, dry acetone, $\Delta$, 40h, and ii. glacial AcOH, absolute EtOH $\Delta$, 4h iii. VOSO$_4$·5H$_2$O, MeOH, TEA. $\Delta$, 1h.

4.5.2 Synthesis of n-alkoxysalicyldehyde ($n=8, 10, 12, 14, 16, 18$)

2, 4-Dihydroxybenzaldehyde (10 mmol, 1.38g), KHCO$_3$ (10 mmol, 1g), KI (catalytic amount) and 1-bromooctane (10mmol, 1.9g), 1-bromodecane (10mmol, 2.2g), 1-bromododecane (10mmol, 2.4g), 1-bromotetradecane (10 mmol, 2.7 g), 1-bromohexadecane (10mmol, 3.0g) and 1-bromooctaadecane (10 mmol, 3.3g) 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.

4.5.3. Synthesis of hexadecyloxy aniline

P-hydroxy acetanilide (5g, 0.03mol) is refluxed with equimolar amount of hexadecyl bromide (10.9g, 0.03 mol0 for 36 hours in dry acetone using K₂CO₃ (4.6g) as the base and KI as the catalyst acetone was then dried off and the product was dissolved in CH₂Cl₂ and the solution was washed with saturated NaCl solution. The solution was then treated with Na₂SO₄ to absorb the moisture present in the solution. CH₂Cl₂ was then distilled off to obtain the crude 4-hexadecyloxy acetanilide. 4-hexadecyloxy acetanilide was then hydrolised for 4 hours with 35% HCl in ethanol. After that the solution was treated with 2mol dm⁻³ of NaOH solution and a large amount of water upto pH=12. The product was then filtered, recystallised with alcohol using animal charcoal, to absorb any colored impurity present.
4.5.4 N-(4-n-octadecyloxyosalicylidene)-4'-n-hexadecyloxy aniline (4-18-OR)

An ethanolic solution of (4-n-octadecyloxy)-salicyaldehyde (0.3g, 1mmol) was added to an ethanolic solution of 4-decyloxy aniline (0.3g, 1mmol). The solution mixture was refluxed with few drops of acetic acid as catalyst for 3h to yield the Schiff base N-(4-n-octadecyloxyosalicylidene)-4'-n-decyloxy aniline. The solid was collected by filtration and recrystallised several times from absolute ethanol to give a pure compound.

Yield: 0.45g, 75%. 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, 1.8%; FAB Mass (m/e, fragment): m/z: calc. 705.6; found: 706[M+H^+]; \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}): 0.87(t, J=6.3 Hz, 6H, -CH\textsubscript{3}), 1.2-1.5 (m, 56H, (CH\textsubscript{2})\textsubscript{28}), 3.9(q, J=6.3, 4H, OCH\textsubscript{2}), 6.4(s,1H), 6.4(d, 8.4 Hz, \textsuperscript{2}H), 6.9(d, 8.7Hz, \textsuperscript{5,6}H), 7.2(d, 8.7 Hz, \textsuperscript{3}H), 7.2(d, 8.7 Hz, \textsuperscript{4,7}H), 8.5(s, 1H, CH=N), 13.9(s, 1H, OH); \textsuperscript{13}C NMR (75.45 MHz; CDCl\textsubscript{3}; Me\textsubscript{4}Si at 25\textdegree C, ppm) \delta= 102.4 (-C1), 107.2 (-C2), 132.4 (-C3), 122.5 (-C4), 115.8 (-C5), 115.8 (-C6), 122.5(-C7); IR (vmax, cm\textsuperscript{-1}, KBr):3435(vOH), 2917(vas(C-H), CH\textsubscript{3}), 2919(vas(C-H), CH\textsubscript{2}), 2869(vs(C-H), CH\textsubscript{3}), 2845(vas(C-H), CH\textsubscript{2}), 1630(vC=N), 1278(vC-O).
4.5.5. \( N-(4\text{-}n\text{-hexadecyloxysalicylidene})\)-4/\(n\text{-hexadecyloxy aniline (4-16-OR)}\)

\[
\begin{align*}
\text{Yield: } & \quad 0.46\text{g, 78\%. Anal. Calc. for } C_{45}H_{75}NO_3: \text{C, 79.7; H, 11.1; N, 2.0. Found: } \\
& \quad C, 79.8; H, 11.1; N, 1.9\%; \text{FAB Mass (m/e, fragment): } m/z: \text{calc. } 677.6; \text{found: } 678[M+H^+]; \text{ } \\
& \quad ^1\text{HNMR (400MHz, CDCl}_3\text{): } 0.89(t, J=6.3 \text{ Hz, } 6\text{H, } -\text{CH}_3\text{), 1.2-1.4 } \\
& \quad (\text{m, 52H, } (\text{CH}_2)_{27}\text{), 3.8(q, J=6.2, 4H, } \text{OCH}_2\text{), 6.3(d, 8.5 Hz, } ^2\text{H), 6.4(s,1H), } \\
& \quad 6.9(d, 8.7Hz, ^5\text{H}), 7.1(d, 8.6 Hz, } ^3\text{H), 7.2(d, 8.7 Hz, 4, 7H), 8.4(s, 1H, CH=N), } \\
& \quad 13.5(s, 1H, OH); \text{IR (vmax, cm}^{-1}\text{, KBr): } 3435(\text{vOH}), 2917(\text{vas(C-H), CH}_3\text{), } \\
& \quad 2919(\text{vas(C-H), CH}_2\text{), 2869(\text{vs(C-H), CH}_3\text{), 2845(\text{vas(C-H), CH}_2\text{), } } \\
& \quad 1626(\text{vC=N), 1278(\text{vC-O).})}
\end{align*}
\]

4.5.6. \( N-(4\text{-}n\text{-tetradecyloxysalicylidene})\)-4/\(n\text{-hexadecyloxy aniline (4-14-OR)}\)

\[
\begin{align*}
\text{Yield: } & \quad 0.48\text{g, 80\%. Anal. Calc. for } C_{45}H_{71}NO_3: \text{C, 79.4; H, 11.0; N, 2.1. Found: } \\
& \quad C, 79.2; H, 11.1; N, 2.2\%; \text{FAB Mass (m/e, fragment): } m/z: \text{calc. } 650; \text{found: } 651[M+H^+]; \text{ } \\
& \quad ^1\text{HNMR (400MHz, CDCl}_3\text{): } 0.89(t, J=6.3 \text{ Hz, } 6\text{H, } -\text{CH}_3\text{), 1.2-1.4 } \\
& \quad (\text{m, 48H, } (\text{CH}_2)_{24}\text{), 3.7(q, J=6.2, 4H, } \text{OCH}_2\text{), 6.1(d, 8.5 Hz, } ^2\text{H), 6.4(s,1H), } \\
& \quad 6.9(d, 8.7Hz, ^5\text{H}), 7.1(d, 8.6 Hz, } ^3\text{H), 7.2(d, 8.7 Hz, 4, 7H), 8.5(s, 1H, CH=N), } \\
& \quad 13.4(s, 1H, OH); \text{IR (vmax, cm}^{-1}\text{, KBr): } 3433(\text{vOH}), 2917(\text{vas(C-H), CH}_3\text{), } \\
& \quad 2919(\text{vas(C-H), CH}_2\text{), 2869(\text{vs(C-H), CH}_3\text{), 2845(\text{vas(C-H), CH}_2\text{), } } \\
& \quad 1626(\text{vC=N), 1278(\text{vC-O).})}
\end{align*}
\]
H), CH2), 2867(vs(C-H), CH3), 2840(vas(C-H), CH2), 1628(vC=N), 1277 (vC-O).

4.5.7. N-(4-n-dodecyloxysalicylidene)-4'-n-hexadecyloxy aniline (4-12-OR)

\[
\text{C}_{12}\text{H}_{25}\text{O}^-\quad /\quad 1 \quad /\quad 4 \quad 5 \quad -\text{OC}_{16}\text{H}_{33}^\text{6}
\]

Yield: 0.38g, 77%. Anal. Calc. for C_{41}H_{67}NO_{3}: C, 79.1; H, 10.8; N, 2.2. Found: C, 79.2; H, 10.7; N, 2.1%; FAB Mass (m/e, fragment): m/z: calc. 622; found: 623[M+H^+]; \text{^1}HNMR (400MHZ, CDCl_3): 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_2), 6.2(d, 8.5 Hz, ^2H), 6.3(s, ^1H), 6.9(d, 8.7Hz, ^5,6H), 7.1(d, 8.6 Hz, ^3H), 7.2(d, 8.7 Hz, ^4,7H), 8.5(s, 1H, CH=N), 13.4(s, 1H, OH); IR (vmax, cm^{-1}, KBr):3431(vOH), 2915(vas(C-H), CH_3), 2918(vas(C-H), CH_2), 2867(vs(C-H), CH_3), 2841(vas(C-H), CH_2), 1620(vC=N), 1277(vC-O).

4.5.8. N-(4-n-decyloxysalicylidene)-4'-n-hexadecyloxy aniline (4-10-OR)

\[
\text{C}_{16}\text{H}_{21}\text{O}^-\quad /\quad 1 \quad /\quad 4 \quad 5 \quad -\text{OC}_{16}\text{H}_{33}^\text{6}
\]

Yield: 0.38g, 77%. Anal. Calc. for C_{39}H_{61}NO_{3}: C, 78.8; H, 10.6; N, 2.3. Found: C, 78.7; H, 10.4; N, 2.2%; FAB Mass (m/e, fragment): m/z: calc. 593.5; found:
594[M+H⁺]; ¹HNMR (400MHz, CDCl₃): 0.87(t, J=6.4 Hz, 6H, -CH₃), 1.2-1.6 (m, 40H, (CH₂)₂₀), 3.7(q, J=6.2, 4H, OCH₂), 6.2(d, 8.5 Hz, 2H), 6.3(s,¹H), 6.9(d, 8.7Hz, 5.6H), 7.1(d, 8.6 Hz, 3H), 7.2(d, 8.7 Hz, 4.7H), 8.5(s, 1H, CH=N), 13.4(s, 1H, OH); IR (vmax, cm⁻¹, KBr): 3431 (vOH), 2915 (vas(C-H), CH₃), 2918 (vas(C-H), CH₂), 2867 (vs(C-H), CH₃), 2841 (vas(C-H), CH₂), 1626 (νC=N), 1276 (νC-O).

4.5.9. N-(4-octayloxysalicylidene)-4'-hexadecyloxy aniline (4-8-OR)

Yield: 0.37g, 75%. Anal. Calc. for C₃₇H₅₉NO₃: C, 78.5; H, 10.5; N, 2.4. Found: C, 78.7; H, 10.4; N, 2.2%; FAB Mass (m/e, fragment): m/z: calc. 565.4; found: 565[M+H⁺]; ¹HNMR (400MHz, CDCl₃): 0.92(t, J=6.3 Hz, 6H, -CH₃), 1.2-1.6 (m, 36H, (CH₂)₁₈), 3.7(q, J=6.2, 4H, OCH₂), 6.1(d, 8.5 Hz,²H), 6.3(s,¹H), 6.9(d, 8.7Hz, 5.6H), 7.1(d, 8.6 Hz, ²H), 7.2(d, 8.7 Hz, 4.7H), 8.5(s, 1H, CH=N), 13.4(s, 1H, OH); IR (vmax, cm⁻¹, KBr): 3431 (vOH), 2915 (vas(C-H), CH₃), 2918 (vas(C-H), CH₂), 2867 (vs(C-H), CH₃), 2841 (vas(C-H), CH₂), 1628 (νC=N), 1276 (νC-O).

4.6. Synthesis of oxovanadium (IV) complexes

The ligands, 4-18-OR (0.7 g, 1 mmol), 4-16-OR (0.6g, 1mmol), 4-14-OR (0.6g, 1mmol), 4-12-OR (0.6g, 1mmol), 4-10-OR (0.5g, 1mmol) and 4-8-OR
(0.5g, 1mmol) was dissolved in minimum volume of absolute ethanol and vanadyl sulphate, VOSO₄·5H₂O (0.08g, 0.5 mmol) dissolved in methanol was added to it followed by addition of triethylamine and refluxed for 2h. A greenish solid formed immediately was filtered, washed with diethyl ether and recrystallized from chloroform-ethanol.

4. 6.1. Complex (VO-18-OR)

Yield: 0.58g (75%)  Anal. Calc. for C₉₄H₁₅₆N₂O₇V: C, 76.4; H, 10.6; N, 1.9.
Found: C, 76.3; H, 10.6; N, 1.8%; FAB Mass (m/e, fragment): m/z: calc. 1477.1; found: 1478[M+H⁺]; IR (KBr, cm⁻¹): 1613(νC=N), 1144 (νC-O, phenolic), 981(νV=O).
4. 6. 2. Complex (VO-16-OR)

Yield: 0.51g (76%) Anal. Calc. for C$_{24}$H$_{156}$N$_2$O$_7$V: C, 76.0; H, 10.5; N, 1.9.
Found: C, 76.1; H, 10.6; N, 1.8%; FAB Mass (m/e, fragment): m/z: calc. 1420; found: 1421[M+H$^+$]; IR (KBr, cm$^{-1}$): 1610(νC=N), 1141 (νC-O, phenolic), 982(νV=O).

4. 6. 3. Complex (VO-14-OR)

Yield: 0.77g (70%) Anal. Calc. for C$_{26}$H$_{140}$N$_2$O$_7$V: C, 75.0; H, 10.3; N, 2.0.
Found: C, 75.1; H, 10.4; N, 1.9%; FAB Mass (m/e, fragment): m/z: calc. 1420; found: 1421[M+H$^+$]; IR (KBr, cm$^{-1}$): 1616(νC=N), 1141 (νC-O, phenolic), 980(νV=O).
4. 6. 4. Complex (VO-12-OR)

Yield: 0.82g (75%)  Anal. Calc. for C_{82}H_{132}N_{2}O_{7}V: C, 75.0; H, 10.1; N, 2.1.
Found: C, 75.1; H, 10.2; N, 1.8%; FAB Mass (m/e, fragment): m/z: calc. 1307.9; found: 1308[M+H^+]; IR (KBr, cm^{-1}): 1612(νC=N), 1139 (νC-O, phenolic), 982(νV=O).

4. 6. 5. Complex (VO-10-OR)

Yield: 0.74g (74%)  Anal. Calc. for C_{78}H_{124}N_{2}O_{7}V: C, 74.7; H, 9.9; N, 2.2.
Found: C, 74.6; H, 9.8; N, 2.1%; FAB Mass (m/e, fragment): m/z: calc. 1251.8; found: 1252[M+H^+]; IR (KBr, cm^{-1}): 1611(νC=N), 1139 (νC-O, phenolic), 980(νV=O).
4.6.6. Complex (VO-8-OR)

Yield: 0.73g (73%)  Anal. Calc. for C_{74}H_{116}N_{2}O_{7}V: C, 74.2; H, 9.7; N, 2.3.
Found: C, 74.1; H, 9.6; N, 12.2%; FAB Mass (m/e, fragment): m/z: calc. 1195.8; found: 1196[M+H⁺]. IR (KBr, cm⁻¹): 1614(νC=N), 1142 (νC-O, phenolic), 982(νV=O).

4.6.7. Result and discussion

The synthetic strategy for the ligands N-[(4-n-alkoxysalicylaldimine)-4'-hexadecyloxyaniline] [abbreviated as 4-n-OR, n=8, 10, 12, 14, 16, 18 and R = -OC_{16}H_{33}] as well as mononuclear oxovanadium(IV) complexes (VO-n-OR) are presented in scheme 2.

The Schiff base ligands were synthesized by condensation of the appropriate aldehyde with the C16 -alkoxylaniline following astandard procedures. Oxovanadium complexes were obtained from the reaction of ligands with vanadyl sulfate in hot ethanol and recrystallised from methanol/CH₂Cl₂. The complexes were isolated as greenish solids in good yields. The characterization of the compounds was made by elemental analyses, FT-IR, UV-vis, ¹H-NMR and mass spectrometry. The analytical data are in good agreement with the
proposed formulae of the compounds. The ligands exhibited \( \nu \text{CN} \) stretching vibration in the region 1633-1623 cm\(^{-1} \) which shifted to lower wave number (1606-1610 cm\(^{-1} \)) upon chelation, reflecting the coordination of azomethine N atom to the metal. The \(^1\)H NMR spectra of ligands show signal at \( \delta \) 13.4-13.8 ppm, corresponding to the proton of the OH group. The signal of the imine group appeared at \( \delta \) 8.5 ppm. The FAB-mass spectra of the vanadyl(IV) complexes are concordant with their formula weights. The UV-visible spectra in chloroform (Fig. 4.15.) for the ligand (18-OR) and its complex (VO-18-OR) are found to be different showing a consistent change in the \( \pi-\pi^* \) region. A distinct change in low-energy bands with an approximate increment of 13-27 nm red shifted from ligand (286 nm, \( \varepsilon = 9000 \text{ lmol}^{-1}\text{cm}^{-1} \) and \( \varepsilon = 340 \text{ nm, } \varepsilon = 17000 \text{ lmol}^{-1}\text{cm}^{-1} \)) to complexes (313nm, \( \varepsilon = 15000 \text{ lmol}^{-1}\text{cm}^{-1} \) and 353nm, \( \varepsilon = 16000 \text{ lmol}^{-1}\text{cm}^{-1} \)) were observed. A similar type of observation was for all other homologues.

![Absorption spectra of 18-OR and VO-18-OR](image)
4.6.8. Mesomorphic properties

The mesomorphic behavior of the ligands and their complexes have been investigated by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). The ligands were found to exhibit enantiotropic smectic mesomorphism. The isotropic liquid, on slow cooling, produced a schlieren texture of SmC phase with four brass defect at 81-118°C (Fig. 4.16). On further cooling an unidentified smectic phase (SmX), was observed for the compounds 4-18-OR, 4-12-OR, 4-10-OR and 4-8-OR at 72-89°C, which then transformed into crystalline phase at 54-84°C. However, the compounds 4-14-OR and 4-16-OR directly solidifies from the SmC phase at 84-91°C. The enthalpy change associated with the phase transitions were obtained from the DSC study (Table 4.4.). The enthalpy changes for the I-SmC transition and vice versa for all the ligands are found to be quite higher (ΔH= ~11-14kJmol⁻¹) for higher homologue (n=12-18), while for the lower homologues (n=8 and 10) the enthalpies were found to be ~2-4 kJmol⁻¹ only. DSC thermal traces for one representative compound for both higher and lower homologues are shown in (Fig. 4.17, Fig. 4.18). The SmC-I and I-SmC transition temperature decreases with increase in carbon chain length for higher homologue, while a rather abnormal behavior was noticed for lower homologues. The mesophase to isotropic transition temperature is found to decrease with carbon chain length. The melting temperature for the ligands 4-18-OR and 4-16-OR are quite similar but decreases abruptly with decrease in chain length for rest of the compounds. The variation of carbon chain length with temperature is shown in the Fig. 4.19. For the complexes a very interesting result were found, the higher homologues (VO-
n-OR, n=12, 14, 16, 18) exhibited focal conic texture of SmC mesophase (Fig. 4.20), where as the lower homologue (VO-n-OR, n=8, 10) showed SmA mesomorphism. Upon cooling from isotropic liquid, typical batonnets are formed which coalesce to give rise to a highly birefringent fanlike texture, characteristic of the smectic A phase (Fig. 4.21) at ~122-158°C. The DSC profiles for the complexes, (Fig. 4.22, Fig. 4.23) showed two enantiotropic transitions in the heating and two in the cooling cycle, these transitions are highly thermally stable. Quite surprisingly no transition could be detected for VO-8-OR in cooling cycle both in first and second run. A plot of transition temperature versus the number of carbon atoms in the alkoxy chain (Fig. 4.23.) show that the mesophase to isotropic transition temperature and vice versa for the complexes did not show any definite trend. The transition temperatures decreases with increasing chain length for VO-n-OR, n=14, 16 and 18, however, for the remaining analogues no systematic trend was evident. Quite unusual thermal behaviour including pronounced hysteresis for enthalpy values is believed to be due to the highly viscous nature of the compounds. This imposes severe restriction on the molecular mobility. On pressing the sample with a needle on glass cover slips, fluidity could be observed.

Fig. 4.16. SmC phase.
Fig. 4.17. DSC thermogram of 16-OR.

Fig. 4.18. DSC thermogram of 10-OR.
Fig. 4.19. Variation of carbon chain length with temperature.

Fig. 4.20. Focal conic SmC phase.

Fig. 4.21. SmA phase.
Fig. 4.22. DSC thermogram of VO-16OR.

Fig. 4.23. DSC thermogram of VO-10OR.
Fig. 4.24. Variation of carbon chain length with temperature.

Table 4.4. DSC and POM data.

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<td>18-OR</td>
<td>Cr 96.3(83.6) SmC 114.3(13.0)</td>
<td>I 111.9 (11.9) SmC 89.0(9.0) SmX 84.4 (49.5) Cr</td>
</tr>
<tr>
<td>16-OR</td>
<td>Cr 96.5(74.4) SmC 117.8(14.6)</td>
<td>I 116.1(13.8)SmCr 91.7(74.1)Cr</td>
</tr>
<tr>
<td>14-OR</td>
<td>Cr 91.6(26.5) SmC 119.4(13.7)</td>
<td>I 118.1(12.8)SmC 84.3(63.7) Cr</td>
</tr>
<tr>
<td>12-OR</td>
<td>Cr 87 (58.7) SmC 120.2 (10.4)</td>
<td>I 118.5 (9.5) SmC 79 (4.5)SmX 70.6 (34) Cr</td>
</tr>
<tr>
<td>10-OR</td>
<td>Cr 83.8 (49.1) SmC 115.1 (4.5)</td>
<td>I 113.1 (2.9) SmC 76.3 (3.6) SmX 54.5 (18.9)Cr</td>
</tr>
<tr>
<td>8-OR</td>
<td>Cr 81.8 (50.6) SmC 116.3 (4.3)</td>
<td>I 115.2 (6.6) SmC 72.2 (4.1)SmX 58.9 (38.9)Cr</td>
</tr>
<tr>
<td>VO-18-OR</td>
<td>Cr 132.4(32.8) SmC 140.3 (5.2)</td>
<td>I 139(5.5)SmC109.8(18.9)Cr</td>
</tr>
<tr>
<td>VO-16-OR</td>
<td>Cr 133.5(25.4) SmC 144.9(6.0)</td>
<td>I 143.8(5.1)SmC 85.6(11.7)Cr</td>
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<tr>
<td>VO-14-OR</td>
<td>Cr 131.9(29.2) SmC 150.3(12.6)</td>
<td>I 149.5(11.5)SmC111.3(6.9)Cr</td>
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<tr>
<td>VO-12-OR</td>
<td>Cr 125.7(14.9)SmC 150.2(11.1)</td>
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<tr>
<td>VO-10-OR</td>
<td>Cr 131.7(24.0) SmA 158.7(10)</td>
<td>I 157.5(6.9) SmA89.9(4.6) Cr</td>
</tr>
<tr>
<td>VO-8-OR</td>
<td>Cr 82.8 (95.9)SmAl22.5(8.9)</td>
<td>-</td>
</tr>
</tbody>
</table>
4.6.9. Electrochemical study

The electrochemical behavior of the complex VO-16-OR was investigated using cyclic voltammetry study. The redox nature of the complexes were probed by cyclic voltammetry in acetonitrile solution in the potential range –1.2 to 1.0 V versus SCE electrode. The voltammogram (Fig. 4.25) displayed a quasireversible (peak-to-peak separation >100 mV) one-electron response at $E_{1/2} = 0.51V$, $(E_p^s = 0.78V, \ E_p^u = 0.24V, \ \Delta E_p = 0.54V)$. The vanadyl complex shows one electron transfer redox peak corresponding to the formation of the VO(IV)/VO(V) couple.
4.6.10. Variable temperature magnetic susceptibility study

The variable temperature magnetic susceptibility measurements were carried out for a representative complex VO-16-OR (Fig.4.26). The compound obeying Curie-Weiss law can be considered as magnetically isolated spin centres. Absence of any maximum in $\chi_M$ vs $T$ plot led us to infer nonexistence of strong exchange interactions among the spin centers. The strength of efficient super exchange path is presumably hindered by coordinating ability of metal ion.

![Graph showing variation of magnetic susceptibility with temperature](image)

**Fig.4.26.** Variation of magnetic susceptibility of with temperature.

4.6.11. DFT study

As X-ray quality crystals could not be grown, DFT studies were undertaken to ascertain the energy optimized structures. Geometry optimization of a representative complex, VO-8-OR (Fig.4.27.) has been performed without
applying any symmetry constrain within the generalized gradient approximation (GGA) level using the Becke-Lee-Yang-Parr (BLYP) [276] exchange and correlation functional implemented in the DMol3 [272]. The DNP basis set chosen in this study is a double-numerical atomic orbital augmented by polarization functions [278]. The DNP basis set is comparable to 6-31G** Gaussian basis sets with a better accuracy for a similar basis set size due to core electron inclusion. The global cutoff radius is set to be 5.0 Å. The convergence criteria for energy, force, and displacement were $1 \times 10^{-5}$ hartree, $2 \times 10^{-3}$ hartree/Å, and $5 \times 10^{-3}$ Å, respectively. The 3D isosurface plots of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the complex are shown in Fig. 4.28 and Fig. 4.29. The energies of the HOMO and LUMO of the VO(IV) complex derived from DFT are found to be -3.894 eV and -2.311 eV, respectively ($\Delta E = 1.583$ eV). The electron density of the LUMO is localized mainly on the C—N bonds while the HOMO is a predominantly C—O bond orbitals. Pertinent here is to mention that mesogenic vanadyl(IV) - tetradentate Schiffbase complexes reported earlier by us were relatively more resistant to oxidation presumably owing to greater HOMO-LUMO gap ($\Delta E = 1.9$eV). This correlates well with $E_{1/2}$ values obtained from the cyclic voltametric experiments(vide infra). Thus the complexes reported herein are anticipated to be of relevance to redox catalysis. Significant geometric parameters of the optimized VO(IV) complex evaluated at BLYP/DNP level are furnished in Table 4.5. The average V—O and V—N bond lengths are 1.95, and 2.18 Å, respectively. The bond length between oxido ligand and vanadium is evaluated to be 1.623 Å. The bond angles varied
from 86.30 to 162.70 respectively, suggesting a distorted square pyramidal geometry around the vanadyl(IV) centre.

Fig. 4.27. DFT structure of VO-80R.

Fig. 4.28. LUMO diagram of VO-80R.

Fig. 4.29. HOMO diagram of VO-80R.
Table 4.5. Selected bond lengths (Å) and bond angles (°) of VO-8-OR.

<table>
<thead>
<tr>
<th>Structure parameter</th>
<th>VO-8-OR</th>
</tr>
</thead>
<tbody>
<tr>
<td>V—O1</td>
<td>1.952</td>
</tr>
<tr>
<td>V—O2</td>
<td>1.953</td>
</tr>
<tr>
<td>V—N1</td>
<td>2.181</td>
</tr>
<tr>
<td>V—N2</td>
<td>2.183</td>
</tr>
<tr>
<td>V—O</td>
<td>1.623</td>
</tr>
<tr>
<td>O1—V—O2</td>
<td>129.5</td>
</tr>
<tr>
<td>N1—V—N2</td>
<td>162.7</td>
</tr>
<tr>
<td>N1—V—O1</td>
<td>86.3</td>
</tr>
<tr>
<td>N2—V—O2</td>
<td>86.5</td>
</tr>
</tbody>
</table>

4.7. Oxovanadium(IV) complexes of the type [VO(L)_2], [L=N-(4-n-alkylsalicylaldimine)-4'-hexadecyloxyaniline.

4.7.1. Synthesis

The synthesis of the Ligands and complexes is shown in Scheme 4.

Scheme 4.

**Scheme 1.** C_{n}H_{2n+1}Br, KHCO_3, KI, dry acetone, Δ, 40h, and ii. glacial AcOH, absolute EtOH Δ, 4h iii. VOSO_4.5H_2O, MeOH, TEA, Δ, 1h.
4.7.2. Synthesis of 4-n-alkoxysalicylaldehyde

Alkoxysalicylaldehyde derivatives were prepared following the general method (4.2.2, 4.5.2).

4.7.3. Synthesis of N-(4-n-decyloxysalicylidene)-4'-n-propylaniline, 4-10-3

![Chemical structure](image)

An ethanolic solution of 2-hydroxy-(4-decyloxy)-salicylaldehyde (0.27g, 1mmol) was added to an ethanolic solution of 4-n-propylaniline (0.135g, 1mmol). The solution mixture was refluxed with a few drops of acetic acid as catalyst for 3 h to yield the yellow Schiff base N-(4-n-decyloxysalicylidene)-4'-n-propylaniline. The precipitate was collected by filtration and recrystallised several times from absolute ethanol to give a pure compound.

Yield: 0.36g, 78%. Anal. Calc. for C_{28}H_{37}NO_{2}: C, 78.9; H, 9.4; N, 3.5. Found: C, 79.1; H, 9.3; N, 3.6%; FAB Mass (m/e, fragment): m/z: calc. 395.1; found: 396[M+H^+]; ^1H NMR (400 MHz, CDCl₃): δ 0.88(t, J = 6.8Hz, 6H, CH₃), 0.93-1.8 (m, -CH₂ of methylene proton in side chain), 2.6(t, J = 7.6Hz, Ph-CH₂), 3.97(t, J = 6.8Hz, 2H, -OCH₂), 6.48(s, 1H, H-aryl), 7.2(d, J = 4.8, 2H, H-aryl), 8.5(s, 1H, CH = N), 13.9(s, 1H, OH). IR (νₚₓₓ, cm⁻¹, KBr) : 3433(νOH), 2921(ν_{as(C-H)}CH₂), 2850 (ν_{as(C-H)}CH₂), 1629(νC-N), 1287(νC-O).
**4.7.4. Synthesis of N-(4-n-tetradecyloxysalicylidene)-4′-n-propylaniline, 4-14-3**

![Chemical structure](image)

Yield: 0.35g, 78%. Anal. Calc. for C30H45NO2: C, 79.7; H, 10.0; N, 3.1. Found: C, 79.8; H, 10.1; N, 3.2%; FAB Mass (m/e, fragment): m/z: calc. 451.3; found: 452[M+H⁺]; 'H NMR (400 MHz, CDCl₃): δ 0.89(t, J = 6.8Hz, 6H, CH₃), 0.94-1.8 (m, -CH₂ of methylene proton in side chain), 2.7(t, J = 7.4Hz, Ph-CH₂), 3.97(t, J = 6.7Hz, 2H, -OCH₂), 6.48(s, 1H, H-aryl), 7.3(d, J = 4.9, 2H, H-aryl), 8.4(s, 1H, CH = N), 13.8(s, 1H, OH). IR (v max cm⁻¹, KBr): 3432(νOH), 2922(νas(CH₃)CH₂), 2851 (νas(C-H)CH₂), 1628(νC=N), 1286(νC-O).

**4.7.5. Synthesis of N-(4-n-tetradecyloxysalicylidene)-4′-n-propylaniline, 4-16-3**

![Chemical structure](image)

Yield: 0.42g, 80%. Anal. Calc. for C32H49NO2: C, 80.1; H, 10.3; N, 2.9. Found: C, 80.2; H, 10.4; N, 2.8%; FAB Mass (m/e, fragment): m/z: calc. 479.3; found: 480[M+H⁺]; 'H NMR (400 MHz, CDCl₃): δ 0.91(t, J = 6.7Hz, 6H, CH₃), 0.94-1.8 (m, -CH₂ of methylene proton in side chain), 2.5(t, J = 7.4Hz, Ph-CH₂), 3.98(t, J = 6.7Hz, 2H, -OCH₂), 6.48(s, 1H, H-aryl), 7.2(d, J = 4.9, 2H, H-aryl), 8.5(s, 1H, CH = N), 13.2(s, 1H, OH). IR (v max cm⁻¹, KBr): 3431(νOH), 2921(νas(CH₃)CH₂), 2850 (νas(C-H)CH₂), 1627(νC=N), 1286(νC-O).
4.8. Synthesis of complexes

4.8.1. Synthesis of oxovanadium(IV) complex, (5-10-3)

The ligand 4-10-3 (0.39g, 1mmol) was dissolve in minimum volume of absolute ethanol and equimolar amount vanadyl sulphate VOSO_4.5H_2O (0.11g, 0.5mmol) in methanol was added followed by addition of tryethylamine and refluxed for 2h. A greenish solid formed immediately and was filtered, washed with diethyl ether and recrystallised from chloroform-ethanol.

Yield: 0.35g (70%)  Anal. Calc. for C_52H_72N_2O_5V: C, 72.9; H, 8.4; N, 3.2. Found: C, 72.8; H, 8.5; N, 3.1%; FAB Mass (m/e, fragment): m/z: calc. 855.4; found: 856[M+H^+]; IR (KBr, cm⁻¹): 1610(νC=N), 1135 (νC-O, phenolic), 981(νV=O).
4.8.2. Synthesis of oxovanadium(IV) complex, (5-14-3)

\[
\begin{array}{cc}
\text{C}_{14}H_{29}O \text{V} & \text{C}_3H_7 \\
\text{C}_3H_7 & \text{O}\text{C}_{14}H_{29}
\end{array}
\]

Yield: 0.37g (75%) Anal. Calc. for \(\text{C}_{63}\text{H}_{88}\text{N}_2\text{O}_3\text{V}\): C, 74.4; H, 9.1; N, 2.8. Found: C, 74.3; H, 9.2; N, 2.7%; FAB Mass (m/e, fragment): m/z: calc. 967.6; found: 968[M+H\(^+\)]; IR (KBr, cm\(^{-1}\)): 1606(\(\nu\text{C}=\text{N}\)), 1133 (\(\nu\text{C}-\text{O, phenolic}\)), 983(\(\nu\text{V}=\text{O}\)).

4.8.3. Synthesis of oxovanadium(IV) complex, (5-16-3)

\[
\begin{array}{cc}
\text{C}_{16}H_{33}O \text{V} & \text{C}_3H_7 \\
\text{C}_3H_7 & \text{O}\text{C}_{16}H_{33}
\end{array}
\]

Yield: 0.39g (78%) Anal. Calc. for \(\text{C}_{64}\text{H}_{96}\text{N}_2\text{O}_5\text{V}\): C, 75; H, 9.4; N, 2.7. Found: C, 75.1; H, 9.3; N, 2.8%; FAB Mass (m/e, fragment): m/z: calc. 1023.6; found: 1024[M+H\(^+\)]; IR (KBr, cm\(^{-1}\)): 1616(\(\nu\text{C}=\text{N}\)), 1133 (\(\nu\text{C}-\text{O, phenolic}\)), 980(\(\nu\text{V}=\text{O}\)).
4.9. Results and discussion

The synthetic approach for ligands N-[(4-n-alkoxysalicylaldimine)-4/-m-alkylaniline] (hereafter abbreviated as 4-n-m, where n and m indicates the number of carbon atoms in alkyl chains, n=10, 14, 16, 18 and m=3) as well as mononuclear oxovanadium(IV) complexes (5-n-m) are presented in Scheme 4. The Schiff bases were synthesized by condensation of the appropriate aldehyde, with the corresponding aniline following standard procedures. The oxovanadium(IV) complexes,5-n-m, were prepared by the reaction of appropriate ligands with vanadyl sulphate (IV) in hot ethanol and recrystallised from methanol/CH₂Cl₂; the complexes were isolated as greenish solids in good yields. The characterization of the compounds was done by elemental analyses, FT-IR, UV-vis, ¹H-NMR and mass spectrometry. The analytical data of the compounds are good agreement with the proposed structure. The Schiff bases exhibited νCN stretching vibration in the infrared region 1633-1623 cm⁻¹. This band is shifted to a lower wave number (1606-1610 cm⁻¹) upon chelation, reflecting the coordination of azomethine N atom to the metal. ¹H NMR spectra of ligands show signal at 13.4-13.8 ppm, corresponding to the proton of the OH group. The proton NMR signal of the imine group appears at 8.5 ppm for ligands.

4.9.1. Thermal Study and Phase Behavior

The phase transitions of the compounds were monitored using differential scanning calorimetry (DSC) at 5°C min⁻¹ heating rate. The transition temperatures along with associated enthalpies and entropies are shown in Table-4.6. The ligands and their complexes exhibit liquid crystalline behavior and studied by thermal analysis and polarizing optical microscopy(POM) with a hot stage. From the DSC study revealed that the compound 4-10-3 showed three transitions on heating cycle and two transitions on cooling cycle(Fig.4.30). The transitions at 90.8°C(ΔH = 1.1 kJmol⁻¹) is due to the isotropic N phase, at 67.6°C(ΔH = 1.1 kJmol⁻¹) is due to the N-SmC phase. No
transitions from mesophase to crystalline phase was observed in DSC. POM study showed that on slow cooling the samples a schlieren texture of N phase was observed at 90° C, Fig.4.31 which on further cooling a schlieren texture of SmC phase with four brass defect at 67° C is produced Fig.4.32. The compound solidified at 37° C. A similar type of observation was noted for 4-14-3. The compound 4-16-3 also showed three transitions on heating as well as in cooling cycles Fig.4.33. The transition at 85.3° C (ΔH = 2.1 kJmol⁻¹) is due to the isotropic to N phase and at 83.9° C (ΔH = 1.4 kJmol⁻¹) is due to the N to SmA phase. On cooling the isotropic a schlieren texture of N phase appeared at 85° C (Fig.4.34.) and a fan like texture (Fig.4.35) of SmA phase at 83° C was observed under POM study. On further cooling the sample solidifies at 76° C. In DSC study the complex 5-10-3, showed three transitions in heating and two in the cooling cycle Fig.4.36. The transition at 167.6° C (ΔH = 37.5 kJmol⁻¹) is due to the I-SmA and at 128.8° C (ΔH = 40.7 kJmol⁻¹) is due to the SmA-SmE transition. No SmE-Cr transition was detected in DSC. The POM study revealed that on slow cooling the sample showed a high birifringent fan like texture of SmA phase at 167° C,(Fig.4.37) which on further cooling showed a arced fan like textures of SmE phase at 128° C, (Fig.4.38) solidifies at 116° C. The compound (5-14-3) showed two transitions each in heating and in cooling cycle. The transitions at 150° C(ΔH = 3.7 kJmol⁻¹) is due to the I-SmA phase and at 76.6° C(ΔH = 78.9 kJmol⁻¹) is due to SmA-Cr phase. A high birefringent broken focal conic texture of SmA phase observed in the case of VO-14-R at 150° C, the compound also showed arced texture of SmE phase at 120° C, the compound solidifies at 76° C. The SmA-SmE phase transition cannot be detected in DSC. The compound 5-
16-3 showed three transitions both in heating and cooling cycle (Fig.4.39). The transition at 154°C (ΔH = 7.7 kJmol⁻¹) is due to the I-SmA phase and at 116°C (ΔH = 8.1 kJmol⁻¹) is due to the SmA-SmE phase. The POM study also showed focal conic texture of SmA phase at 154°C (Fig.4.40), and at 116°C, the compound showed arced textures of SmE phase at 116°C (Fig. 4. 41).

Table-4.6. DSC and POM data

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-10-3</td>
<td>Cr 43.5 (28.9) SmC 68.4 (0.2) N 91.7 (1.0) I</td>
<td>190.8 (1.1) N 67.6 (0.2) SmC</td>
</tr>
<tr>
<td>4-14-3</td>
<td>Cr 59.5 (45.1) SmC 83.6 (0.3) N 88.1 (1.8) I</td>
<td>187.1 (1.8) N 82.8 (0.2) SmC</td>
</tr>
<tr>
<td>5-10-3</td>
<td>Cr 83.6 (39.5) SmA 97.6 (34.8)</td>
<td>1167.6 (37.5) SmA 128.8</td>
</tr>
<tr>
<td></td>
<td>SmE 171.3 (126.2) I</td>
<td>(40.7) SmE</td>
</tr>
<tr>
<td>5-14-3</td>
<td>Cr 97.7 (26.4) SmA 150.0 (4.8) I</td>
<td>1150.0 (3.7) SmA 76.6 (8.9) Cr</td>
</tr>
<tr>
<td>5-16-3</td>
<td>Cr 101.8 (78.9) SmA 145.4 (7.1)</td>
<td>1154.3 (7.7) SmA 116.1 (8.1)</td>
</tr>
<tr>
<td></td>
<td>SmE 155.9 (8.4) I</td>
<td>SmE 87.8 (16.1) Cr</td>
</tr>
</tbody>
</table>

![Fig.4.30. DSC thremogram of 4-10-3.](image-url)
Fig. 4.31. Nematic phase

Fig. 4.32. SmC phase

Fig. 4.33. DSC thermogram of 4-10-3

Fig. 4.34. Nematic phase

Fig. 4.35. SmA phase.
Fig. 4.36. DSC thremogram of 5-10-3.

Fig. 4.37. SmA phase.

Fig. 4.38. SmE phase.

Fig. 4.39. DSC thremogram of 5-16-3.
Fig. 4.40. SmA phase.

Fig. 4.41. SmE phase.