# Synthesis, Characterization and Mesomorphic Properties of Oxovanadium (IV) Complexes of N-(4-n-alkyloxy salicylidene)4'-n-Alkoxyanilines.

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#### Abstract

A metal oxovanadium (IV) complexes with bidentate Schiff's bases viz. N(4-n-alkyloxy salicylidene)4'-n – alkyloxyanilines obtained by the 1:1 condensation of 4-n-alkyloxy salicylaldehydes and 4-n – alkyloxyanilines have been prepared and characterized. The synthesis of the ligand N-(4-n - hexyloxysalicylidene)-4'-n-heptyloxyaniline as well as the complexes characterized by thermal microscopy for mesomorphic properties. The ligands are found to exibit interesting smectic phases and polymorphism, while the complexes showed orthogonal smectic A and smectic E phases.

Keywords: Schiff"s Bases, Mesomorphic properties, Polymorphism, phases, thermal microscopy, ligand.

# **INTRODUCTION / SURVEY OF LITERATURE**

The complexation of Schiff base with different metal ion is well documented in literature [1-8]. Metal-containing liquid crystals, popularly known as metallomesogens, are derived either from rod-like molecules or disc-like molecules, which may or may not exhibit liquid crystalline behaviour, incorporated with a metal atom [9-17]. These metallomesogens exhibit various liquid crystalline phases that are also formed by pure organic materials viz., nematic, smectic, columnar and cubic liquid crystalline phases. Since the introduction of a metal into liquid crystalline compounds possessing coordinating atom may induce novel properties, interest is growing rapidly in the field of metallomesogens [18-25]. The metal viz. copper, nickel, oxovanadium, palladium, platinum, rhodium and iridium complexes of salicylidene aniline exhibiting liquid crystalline properties are reported by different research groups [26-30]. The first report on metallomesogens of salicy lidene anilines was reported by Ovchinnikov and coworkers [32-33]. Several review articles have been published in recent years describing the characteristics of metallomesogens [34-40].

The X-ray and optical investigations carried out by Ghedini and coworkers [41-47] revealed some interesting phenomena.

The aliphatic alkyl chains located in the same side are partially folded in order to effectively fill the place between the molecules. Investigations revealed that smectic A phase is uniaxial (48-53). The evidence for the existence of the short range correlation between the metal centers reflecting the molecular packing with side-by-side arrangement of the molecular pairs. Localised biaxil ordering in smectic B phase as expecting by the metal complexation (54-58).

The work describes here the synthesis of N (4-n-hexyloxy salicylidene) 4-n-heptyloxyaniline [6O(OH).O7]and its copper (II) complex. Characterization of the compounds by different spectroscopic

methods, followed by the determination of phase transition temperatures and characterization of the phases by differential scanning calorimetry and polarizing microscopy attached with a hot stage (59-62).

#### MATERIALS AND METHODS

#### **Synthetic Procedures**

Materials: All the required chemical reagents viz (1-bromohexane, 1-bromoheptane, 4-hydroxy acetanilide and 2,4~dihydroxybenzaldehyde) were procured from M/S Tokyo Kasei (TCI), Japan, and used as such without further purification. Potassium carbonate (KC0<sub>3</sub>) and potassium iodide (Kl) were procured from E. Merck Germany and Qualigens, Bombay. All solvents used for the synthesis of compounds were procured from E. Merck. Ethanol was procured from A. K. Sales agency, Guwahati. The synthesis of the materials carried out following the procedures well documented in literature and is presented in scheme

#### **Purification of solvents:**

## Purification of absolute ethanol.

The rectified spirit (1.0 I) into a 2 L round bottom flask and 200 g of calcium oxide, which had been freshly ignited in a muffle furnace. Fit the flask with a double surface condenser carrying a CaCh guard-tube, refluxed the mixture gently for 6 h and allowed to stand overnight. The condenser was reassembled for downward distillation via a splash head adapter to prevent carryover of the calcium oxide in the vapor stream. A receiver flask was attached with a side-arm receiver adapter, which was protected by means of a calcium chloride guard tube. The ethanol was distilled gently discarding the first 20 ml of distillate. The absolute ethanol (99.5%) was preserved in a bottle.

#### Preparation of dry acetone.

In a I L round bottom flask, about 800 ml acetone was taken and it was distilled by normal distillation. Then this acetone was heated under reflux with successive addition of KMn0<sub>4</sub> until the violet color persists. It was then dried with anhydrous caso<sub>4</sub> in hot condition and again by distillation, pure acetone was obtained.

#### **Preparation of p-n-hexyloxysalicylaldehyde**

2,4-dihydroxybenzaldehyde, potassium bicarbonate (KHCO<sub>3</sub>), potassium iodide (catalytic amount) and 1-bromohexane mixed in 250 ml of dried acetone. The mixture was refluxed for 24 hrs and filtered when hot, to remove insoluble solutes. Dilute HCl was added to neutralize the warm solution, which was then extracted twice with CHCl3. the combined CHCl3 extracts were concentrated to give a pure solid. The solid was purified by column chromatography with a mixture of Hexane/CHCl3. the solvent was evaporated to give a pale yellow colour.

A solution of 1-bromoheptane was added to a suspension of 4-acetamidophenol and potassium carbonate along with a catalytic amount of potassium iodide in dry acetone The mixture was heated and reflux for 24hrs. The compound obtained is filtered. The product was crystalised from hot ethanol and a white solid was obtained.

# Synthesis of N-(4-N-hexyloxysalicylidene)-4'-n-heptyloxyaniline,6O(OH)O7.

An ethanolic solution (50ml) of 2-hydroxy-(4-n-hexyloxy) benzaldehyde (2.22g,10mmol) was added to an ethanolic solution of 4-n-heptyloxyaniline (2.07g,10mmol). The solution mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 hrs to yield the light yellow Schiffs base N-[2-hydroxy-(4-nhexyloxy)benzylidene]-4'-n-heptyloxyaniline,2.The precipitate was collected by filtration and recrystallized several times from absolute ethanol to give a pure compound.

# Synthesis of oxovanadium (IV) Complex:

To a suspension of [6O(OH)O7] LH (411 mg, 1 nmol) in ethanol (20 mL) were added potassium hydroxide (56 mg, 1 nmol) in ethanol (5 mL) and, drop wise, 4 mL of a warm ethanolic solution containing 125 mg (0.5 nmol) of vanadyl sulphate pentahydrate. The mixture was stirred at room temperature for 1 h; the resulting light green precipitate was filtered, washed with diethyl ether and recrystallized from chloroformethanol, yield 360 mg (40%).

# **RESULTS AND DISCUSSION**

#### **Elemental analysis:**

The elemental analysis of the elements Carbon, hydrogen and nitrogen experimentally found and theoretically determined was presented in Table 1. The experimental results are found to be in good agreement with theoretical values.

No.	Compound	Molecular	Found (Theoretical) &		
		formula	С	Н	Ν
1	6O(OH)O7	C <sub>26</sub> H <sub>37</sub> NO <sub>3</sub>	75.87 (75.80)	9.06 (9.21)	3.40 (3.41)
2	VO[6O(O)O7] <sub>2</sub>	$C_{52}H_{72}N_2O_7V$	70.44 (70.33)	8.10 (8.17)	3.05 (3.15)

# Table 1

#### Elemental analysis for the ligands, copper (II) complex

# **IR spectral analysis:**

# (a) 6O(OH) 07:

The FTIR spectrum of 6O(OH) O7 value/data is shown in Table 2. The alkane (CH<sub>3</sub>) C-H asymmetric stretching peak appear near 2958 cm<sup>-1</sup> and the alkane methylene (-CH<sub>2</sub>) C-H asymmetric stretching frequency is observed near 2929cm<sup>-1</sup> also, the alkane (CH<sub>3</sub>) C-H stretching frequency is observed near 2871cm<sup>-1</sup> and methylene (-CH<sub>2</sub>)C-H stretching frequency is observed near 2858 cm<sup>-1</sup>. The imine (Schiff base) CH=N stretching frequency was observed near 1628 cm<sup>-1</sup>. The frequency observed near 1566 cm<sup>-1</sup> indicates the

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presence of (C=C) aromatic group. However, IR data are of little structural values since several absorptions v(C=N) free, V(C=H) ring overlap in the range 1630-1530 cm<sup>-1</sup>. The overlap of C=N and C-C absorption precludes unequivocal assignment of these bands.

#### Table - 2

Functional group	Stretching frequency (cm <sup>-1</sup> )		
v (CH3-)	2958		
v (-CH <sub>2</sub> -)	2929		
v (-CH <sub>3</sub> ) C-H	2871		
v (-CH <sub>2</sub> -)	2858		
V <sub>CH=N</sub>	1629		

IR data of the compound **6O(OH)O7** 

# (b) [6O(O)O7]<sub>2</sub>VO :

The compound 6O(OH)O7 which shall be abbreviated as LH after losing its proton coordinates to the vanadyl moiety to give bichelated transition metal complex. The reaction between the ligand and vanadyl sulphate is a straightforward process and afforded the vanadyl complex salicylidene derivative 6O(OH)O7. The compound was characterized by elemental analysis and IR spectroscopy where v(V=O) at 980 cm<sup>-1</sup> was detected for this compound. The penta-coordinated oxovanadium (IV) complex in the solid state is found to exist either as an isolated molecule or as polymer containing hexa-coordinated vanadium atoms as they form through V=O-V=O- interactions. The V=O-V=O- interactions in such polymers leads to a lowering of the v(V=O) stretching frequency from 950-1000 to 800-860 cm<sup>-1</sup>. The absence of such a shift in the present case in v(V=O) for the complex reflects the formation of monomeric structure and the absence of formation of polymer. Further our results are in agreement with the earlier reported literature data and ESR data which also supported the formation of monomeric structured species. Even though the possible coordination geometries that can be considered for a penta-coordinated species are trigonal-bipyramidal and square-pyramidal, the bis(salicylideneiminato)- oxovanadium(IV) complexes in general adopts the square pyramidal geometry. Hence similar geometry is suggested for the present compound.

#### NMR-ANALYSIS : [6O(OH)O7]

The NMR spectrum of 60(OH)O7 value/data is given in table 3

<sup>1</sup>H NMR spectroscopy gives the information of the nature and environment of the proton located in different chemical environments. The methyl (CH<sub>3</sub>-) protons labelled as "D" gave two triplets at  $\delta = 0.88$  and 0.92 with a coupling constant J = 6.9 Hz, whereas methylene protons labelled as "C" (CH<sub>2</sub>)<sub>3</sub> and (CH<sub>2</sub>)<sub>3</sub> (type C and C') protons of the methylene group as well as CH<sub>2</sub>CH<sub>2</sub>O-Ph (type B and B') attached to the phenyl ring gave a multilet in the region  $\delta = 1.27 - 19.0$ . The protons of the methylene group attached to the phenyl ring CH<sub>2</sub>O-Ph (type A and A') gave a triplet at  $\delta = 3.95$  and 4.00 with a coupling constant J = 6.6 Hz. However the signals observed at  $\delta = 6.45$  (dd, J = 8.1 Hz and 2.1 Hz) for H(a) as a doublet of doublets because of interaction or ortho and meta protons. The proton labelled as H(b) gave a signal at  $\delta = 7.44$  with a coupling constant J = 7.5 Hz. The signal at 6.44 (d, 1H, J = 2.1 Hz) appeared for H(c). The signal of protons labelled as H(X, X') and H(A, A) appeared as doublets at  $\delta = 6.90$  and  $\delta = 7.30$  respectively are due to the interaction of the ortho

protons with a coupling constant J = 8.7 Hz and 7.5 Hz. The imine proton appeared as a singlet at  $\delta$  = 8.50. The phenolic proton appeared as broad singlet at  $\delta$  = 13.95 indicating the strong intermolecular H-bonding.

Table – 3
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Assigned	Number of	δ values in	Multiplicity	J values in		
Protons	Protons	ppm		Hz		
H <sup>D.D</sup>	6Н	0.9 - 1.05	t			
H <sup>C,C</sup>	14H	1.27 – 1.5	m			
$H^{B,B}$	4H	1.7 – 1.9	quintet			
$\mathrm{H}^{\mathrm{A},\mathrm{A}}$	4H	3.95 - 4.00	t	6.6		
$\mathrm{H}^{1}$	1H	6.44	d	2.1		
$\mathrm{H}^2$	1H	6.45	dd	8.1, 2.1		
$H^3$	1H	7.44	S	7.5		
H <sup>4,7</sup>	2H	7.30	d	8.7		
${ m H}^{5,6}$	2Н	6.90	d	7.5		
CH = N	1H	8.50	S			
OH	1H	13.95	s br			

# NMR data of the compound **6O(OH)O7**

# Differential Scanning Calorimetry and Thermal Microscopy.

# (a) 6O(OH)O7

The differential scanning calorimetry spectrum of 6O(OH)O7 value/data is given in table 4.

The ligand 6O(OH)O7 on heating exhibited four phase transitions at 65.0<sup>o</sup>C ( $\Delta$ H = smeared with the next transition), 66.3<sup>o</sup>C ( $\Delta$ H = 33.07 kJ/mol,  $\Delta$ S = 97.4 J/mol/K), 123.9<sup>o</sup>C ( $\Delta$ H = 2.39 kJ/mol,  $\Delta$ S = 6.02 J/mol/K), and 126.7<sup>o</sup>C ( $\Delta$ H = 2.36 kJ/mol,  $\Delta$ S = 5.90 J/mol/K) in differential scanning calorimetry. However in cooling four phase transitions were recorded in DSC at 125.7<sup>o</sup>C (Isotropic – Nematic,  $\Delta$ H = 2.61 kJ/mol,  $\Delta$ S = 6.56 J/mol/K), 122.9<sup>o</sup>C (smectic A-smectic C,  $\Delta$ H = 1.96 kJ/mol,  $\Delta$ S = 4.97 J/mol/K), 57.8<sup>o</sup>C (Smectic C-Smectic I,  $\Delta$ H = 2.15 kJ/mol,  $\Delta$ S = 6.49 J/mol/K), and 44.4<sup>o</sup>C (Smectic I-smectic J,  $\Delta$ H = 16.04 kJ/mol,  $\Delta$ S = 50.45 J/mol/K).

All the phase transitions were observed by a change in the optical textures in heating cycle without any characteristic features by polarizing optical microscopy attached with a hot stage. However, the ligand on slow cooling from isotropic liquid exhibited a thread like texture with two brush defect and also schlieren texture of nematic phase at  $126.5^{\circ}$ C as shown in plate 1. On further cooling the thin film of the sample exhibited a focal conic fan texture at  $126.2^{\circ}$ C as shown in plate 2, confirming phase as Smectic A phase. The focal conic texture of smectic A phase of 60(OH)O7 at  $125.1^{\circ}$ C at a different position of the slide was shown in plate 3. On subsequent cooling focal conic texture transformed into a shlieren texture with undulation lines at  $124.1^{\circ}$ C as shown in plate 4 were characterizing the phase as Smectic C. The smectic A – smectic C phase transition could be detected by differential scanning calorimetry only in some cases but with a very low value of enthalpy indicating a weak first order transition. In the present case we observed small enthalpy change JETIR2009460 Journal of Emerging Technologies and Innovative Research (JETIR) www.jetir.org 1212

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associated with the smectic A – smectic C transition. On further cooling the schlieren texture of the smectic C phase had been transformed into a platelet texture at  $60.5^{\circ}$ C as shown in plate 5, characterizing phase as smectic 1. On further cooling the platelet texture transformed into a mosaic texture as shown in plate 6 at  $48.0^{\circ}$ C, characterizing the phase as smectic J. The mosaic texture transformed into a featureless texture of broken mosaic domains on further cooling at  $40.5^{\circ}$ C, characterizing the transition as smectic J to crystalline state.

#### Table 4

#### Transition temperatures of the compound 6O (OH)O7

DS	SC data	Microscopic data		
Phases	T <sup>0</sup> C (Enthalpy H	Phases	$T^0C$	
	in kJ/mol)			
Cr-S4	65.0 (smeared)	Cr – SmJ	59.0	
S4-S3	66.3 (33.07)	SmJ - SmI	67.2	
S3-S2		SmI – SmC	-	
S2-S1	123.9 (2.39)	SmC - SmA	124.1	
S1-N		SmA-N	126.1	
N-Iso	126.7 (2.36)	N-Iso	128.1	
Iso-N	125.7 (2.61)	Iso-N	127.2	
N-S1		N-SmA	126.2	
S1-S2	122.9 (1.96)	SmA – SmC	124.5	
S2-S3	57.8 (2.15)	SmC –SmI	60.5	
S3-S4	44.4 (16.04)	SmI – SmJ	48.1	
S4-Cr		SmJ – Cr	40.5	

#### by DSC and thermal microscopy

# (b) [6O(O)O7]<sub>2</sub>VO

#### **Textural and Calorimetric Investigations:**

The recorded spectrum of value/data of differential calorimetry of the complex is described below. The complex  $[6O(O)O7]_2VO$  on heating exhibited two phase transitions at  $197.3^{\circ}C$  ( $\Delta H = 31.34 \text{ kJ/mol}$ , S = 66.68 J/mol/K) and  $245.2^{\circ}C$  ( $\Delta H = 1.18 \text{ kJ/mol}$ ,  $\Delta S = 2.28 \text{ J/mol/K}$ ) in differential scanning calorimetry. However in cooling three phase transitions were recorded in DSC at  $249.5^{\circ}C$  (Isotropic-smectic A,  $\Delta H = 1.59 \text{ kJ/mol}$ ,  $\Delta S = 3.05 \text{ J/mol/K}$ ),  $178.2^{\circ}C$  (smectic A-smectic B,  $\Delta H = 5.34 \text{ kJ/mol}$ ,  $\Delta S = 1.85 \text{ J/mol/K}$ ) and 174.0 (Smectic B-Crystal,  $\Delta H = 14.39 \text{ kJ/mol}$ ,  $\Delta S = 32.19 \text{ J/mol/K}$ ).

All the phase transitions were observed by changes in the optical textures in heating cycle with out any characteristic features by polarizing optical microscopy attached with a hot stage. However, the complex on slow cooling from isotropic liquid a thin film of the sample exhibited batonnets which coaslesced to a focal conic fan texture at 248.2°C as shown in plate 10, confirming the phase as Smectic A phase. The focal conic texture of smectic A phase of [6O(O)O7]<sub>2</sub>VO at 196.1°C at a different position of the slide was shown in plate 11. On subsequent cooling focal conic texture transformed into a texture with crossed lines across the fans at 177.8°C as shown in plate 12 characterizing the phase as Smectic E. On further cooling the texture of the

smectic E phase had been transformed at  $172.2^{\circ}$ C to a broken texture characterizing the transition as smectic E to crystalline state.

Two an ions of the mesogenic N(4-n-hexloxysalicylidene)-4'-n-heptyloxyaniline (LH) molecules are coordinated to a vanadyl group. After the incorporation of the V=O group between two L moieties the newly formed vanadyl complex not only exhibited only smectic A phase with the reduction of mesophases but also exhibited the isotropic phase at a higher temperature than the copper complex. The vanadyl complex is thermally stable and do not decompose upon melting. The smectic A phase is confirmed by the observation of focal conic fan shaped texture.

The earlier reported homologues of vanadyl complexes formed by N[4-n-(heptyloxy)salicylidene)-4'-(octyloxy)aniline] [47] and the N-(4-(4-(decyloxy)benzoyloxy)salicylidene-R (R = n-C<sub>m</sub>H<sub>2m+1</sub>: m = 1, 5, 10; R = - C<sub>6</sub>H<sub>4</sub>OC<sub>m</sub>H<sub>2m+1</sub>: m = 1, 2, 5, 10) [55] or N-[(4-R-benzoyloxy)salicylidene)-n-propylamine] (R = C<sub>m</sub>H<sub>2m+1</sub>O: m = 5-12, 14,16, 18) [62] series exhibited smectic A [47] and smectic C [55] or nematic phases [55, 62]. The comparison of the available data illustrates that the nature of phase variants i.e., mesomorphism depends mainly on the end substituents viz. the size of alky or alkyloxy chains or linking groups. The reported mesogenic vanadyl complexes are comparatively rare and the few examples reported so far involved either substituted acetylacetone or salicylideneaminato ligand. The earlier reported homologues of vanadyl complexes formed by N[4-n-(heptyloxy)salicylidene)-4'-(octyloxy)aniline] (1b : n = 7, m = 8) [47] and the N-(4-(4-decyloxy)benzoyloxy)salicylidene)-alkylamines, (1d : n= 10, m = 1, 5, 10); N-(4-(4-(decyloxy)benzoyloxy)salicylidene)-alkylamines, (1e : n=10, m = 1, 2, 5, 10) (alkylaniline = -C<sub>6</sub>H<sub>4</sub>OC<sub>m</sub>H<sub>2m+1</sub> : m = 1, 2, 5, 10) [55] or N-[(4-n-alkyloxy-benzoyloxy)salicylidene)-n-propylamine] (alkyloxy = C<sub>n</sub>H<sub>2n+1</sub>O: n = 5-12, 14, 16, 18) [62] series exhibited smectic A [47] and smectic C [55] or nematic phases [55, 62]. The comparison of the available data illustrates that the nature of phase variants i.e., mesomorphism depends mainly on the end substituents viz. the size of alky or alkyloxy chains or linking groups.

# CONCLUSION

The Schiff base [6O(OH)O7], and its oxovanadium (IV) complexes exhibiting liquid crystalline behaviour had been successfully synthesized and characterized. The nature of the liquid crystalline phases exhibited by the ligand is totally different from its oxovanadium (IV) complexes. The oxoanadium (IV) complexes exhibited orthogonal SmA and SmE phases. The clearing temperature increases by -120<sup>o</sup>C in the case of oxovanadium (IV) complex on coordination inferring the thermal stability.

# Data Availability-

The data used to support the findings of the study are included within the article.

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Conflict of Interest- The author declares no conflict of interest.

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