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## Liquid Crystals

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### Synthesis and mesomorphic properties of some platinum(II) and oxovanadium(IV) complexes

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**To cite this Article** Sadashiva, B. K. and Ghode, Archana(1994) 'Synthesis and mesomorphic properties of some platinum(II) and oxovanadium(IV) complexes', *Liquid Crystals*, 16: 1, 33 – 42

**To link to this Article:** DOI: 10.1080/02678299408036518

**URL:** <http://dx.doi.org/10.1080/02678299408036518>

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## Synthesis and mesomorphic properties of some platinum(II) and oxovanadium(IV) complexes†

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(Received 17 June 1993; accepted 17 August 1993)

The synthesis and mesomorphic properties of a homologous series of *N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-4''-*n*-decylphenylanilines and their platinum(II) and oxovanadium(IV) complexes are reported. All the ligands and their metal chelates exhibit enantiotropic mesophases, predominantly smectic A and smectic C phases. The transition temperatures and enthalpies have been determined for most of the compounds. The platinum(II) complexes have higher melting points and mesophase thermal stabilities. However, the oxovanadium(IV) complexes have a wider thermal range for the mesophase. Both platinum(II) and oxovanadium(IV) complexes containing only a chain on the biphenyl moiety exhibit a nematic phase.

### 1. Introduction

There has been extensive research on the synthesis and characterization of metallo-mesogens. Different metals have been introduced into a wide variety of systems [1]. However, the influence of the metals on the mesophase and structure property relationships for metallomesogens are still not very clear. Our interest and effort has been directed to understanding these aspects. Though a number of ligands are available for introducing metals, we have chosen substituted *N*-salicylaldimines for our investigations. Since the first report on the mesomorphic properties of bis[*N*-arylsalicylaldiminato]copper(II) [2], a number of bis-chelates of Schiff's bases have been prepared and their properties investigated [3-9].

We have reported [10] the liquid crystalline properties of bis[*N*-(4''-*n*-dodecylbiphenyl)-4-*n*-alkoxysalicylaldiminato]copper(II) compounds and their palladium(II) congeners. Recently, we have investigated the mesomorphic properties of a series of similar nickel(II) complexes [11]. Except for a very few mesomorphic systems in which platinum has been incorporated [12-14], there is no report on platinum-containing mesogenic salicylaldimines. In this paper we report our investigations on the mesomorphic behaviour of bis[*N*-(4''-*n*-decylbiphenyl)-4-*n*-alkoxysalicylaldiminato] platinum(II) and bis[4''-*n*-decylbiphenyl)-4-*n*-alkoxysalicylaldiminato] oxovanadium(IV) complexes. The former represent the first examples of liquid crystalline platinum(II) containing salicylaldimines, and only a very few series of mesogenic salicylaldiminato oxovanadium complexes are known [9, 15, 16].

### 2. Experimental

The syntheses of the ligands and their corresponding platinum(II) and oxovanadium(IV) complexes were carried out following the scheme outlined in figure 1.

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† Presented at the Fourteenth International Liquid Crystal Conference, 21-26 June 1992, University of Pisa, Italy.

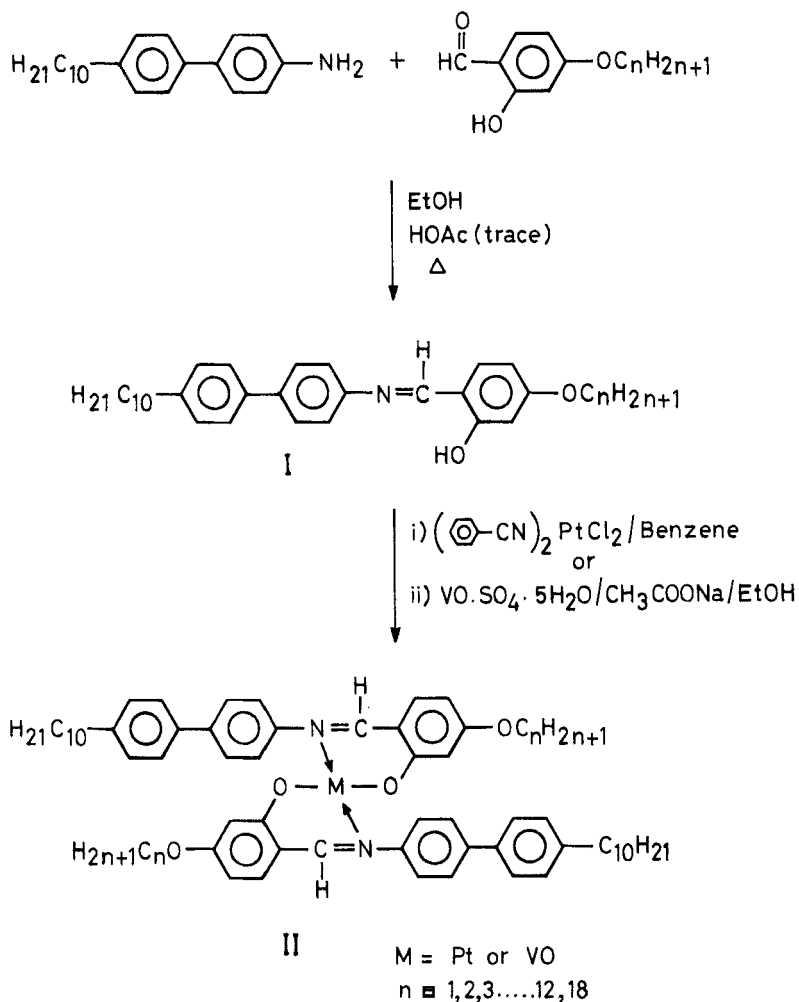


Figure 1. Synthetic scheme for the preparation of the Schiff's bases and their platinum(II) and oxovanadium(IV) complexes.

4-*n*-Decyl-4'-aminobiphenyl was prepared following a procedure described previously [10]. 2-Hydroxy-4-*n*-alkoxybenzaldehydes were prepared by monoalkylation of 2,4-dihydroxybenzaldehyde using an appropriate 1-bromoalkane in butan-2-one. *trans*-Bis(benzonitrile) dichloroplatinum(II) was prepared according to the procedure described elsewhere [17]. A detailed procedure in each case for the preparation of a ligand and its platinum(II) and oxovanadium(IV) complexes is given below. All the platinum(II) complexes are orange in colour, while the oxovanadium(IV) complexes are greenish yellow in colour.

*N*-(2-Hydroxy-4-*n*-octyloxybenzylidene)-4'-*n*-decylphenylaniline, I (n = 8)

A mixture of 4-*n*-decyl-4'-aminobiphenyl (2.0 g, 6.4 mmol), 2-hydroxy-4-*n*-octyloxybenzaldehyde (1.6 g, 6.4 mmol), ethyl alcohol (25 ml) and a drop of acetic acid was boiled for 2 hours. It was then cooled to room temperature and the precipitate

filtered off, washed with cold ethyl alcohol, dried and crystallized repeatedly from butan-2-one. Yield 1.36 g (38.8 per cent); transition temperatures ( $^{\circ}\text{C}$ )  $\text{C}_{80.0}$   $\text{S}_{144.0}$   $\text{S}_{\text{C}}$  214.5  $\text{S}_{\text{A}}$  216.5  $\text{I}$ ; IR (Nujol)  $\nu_{\text{max}}$  1629 and 1599  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}^{\text{CHCl}_3}$  ( $\epsilon$ ) 352 (37 500), 288 (16 500), 250.5 (17 000);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.8 (t, 6 H,  $2 \times -\text{CH}_3$ ), 1.2–2 (m, 28 H,  $14 \times -\text{CH}_2$ ), 2.6 (t, 2 H,  $\text{ArCH}_2$ ), 4 (t, 2 H,  $-\text{OCH}_2$ ), 6.2–7.8 (m, 11 H,  $\text{ArH}$ ), 8.7 (s, 1 H,  $-\text{N}-\text{CH}$ ), 13.7 (s, 1 H,  $-\text{OH}$ ); Elemental analysis, calculated for  $\text{C}_{37}\text{H}_{51}\text{O}_2\text{N}$ : C, 82.07; H, 9.42; N, 2.55 per cent; found: C, 81.88; H, 9.67; N, 2.42 per cent.

*Bis*[*N*-(4''-*n*-decylbiphenyl)-4-*n*-octyloxysalicylaldiminato] platinum(II), **II**,  $M = \text{Pt}$

A mixture of *N*-(2-hydroxy-4-*n*-octyloxybenzylidene-4''-*n*-decylphenyl)aniline (0.11 g, 0.2 mmol), *trans*-bis(benzonitrile) dichloroplatinum(II) (0.042 g, 0.1 mmol) and anhydrous benzene (25 ml) was boiled for twenty hours. The reaction mixture was then cooled and the orange precipitate filtered off, washed with cold benzene and recrystallized several times from benzene. Yield 38 mg (30 per cent); transition temperatures ( $^{\circ}\text{C}$ )  $\text{C}$  224.0  $\text{S}_{\text{C}}$  272.0  $\text{S}_{\text{A}}$  >290.0  $\text{I}$ ; IR (Nujol)  $\nu_{\text{max}}$  1610 and 1585  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}^{\text{CHCl}_3}$  ( $\epsilon$ ) 344 (38 500), 265.5 (76 200);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.8 (t, 6 H,  $2 \times -\text{CH}_3$ ), 1.1–2.0 (m, 56 H,  $28 \times -\text{CH}_2$ ), 2.6 [t, 2 H, ( $\text{ArCH}_2$ ) $_2$ ], 3.6 [t, 4 H, ( $\text{OCH}_2$ ) $_2$ ], 5.5 (s, 2 H,  $\text{ArH}$ ), 6.12–6.17 (d, 2 H,  $\text{ArH}$ ), 7.0–7.6 (m, 18 H,  $\text{ArH}$ ), 7.9 (s, 2 H,  $2 \times \text{N}=\text{CH}$ ); Elemental analysis calculated for  $\text{C}_{74}\text{H}_{100}\text{O}_4\text{N}_2\text{Pt}$ : C, 69.64; H, 7.84; N, 2.19 per cent; found: C, 69.26; H, 7.94; N, 2.04 per cent.

*Bis*[*N*-(4''-*n*-decylbiphenyl)-4'-*n*-octyloxysalicylaldiminato]oxovanadium (IV), **II**,  $M = \text{VO}$

To a stirred warm solution of *N*-(2-hydroxy-4-*n*-octyloxybenzylidene)-4''-*n*-decylphenyl)aniline (0.216 g, 0.39 mmol) in ethyl alcohol (25 ml) was added a solution of vanadyl sulphate pentahydrate (0.051 g, 0.19 mmol) in water (5 ml). To this greenish solution was added sodium acetate (0.068 g, 0.82 mmol) in water (7 ml). The resulting mixture was stirred and boiled for 20 min and allowed to stand at room temperature for 2 hours. The green precipitate so obtained was filtered off, washed with water, ethyl alcohol and ether, and recrystallized several times from a mixture of chloroform–ethyl alcohol. Yield 0.14 g (60.3 per cent); transition temperatures ( $^{\circ}\text{C}$ )  $\text{C}$  181.0  $\text{S}_{\text{C}}$  226.5  $\text{S}_{\text{A}}$  272.5  $\text{I}$ ; IR (Nujol)  $\nu_{\text{max}}$  1610, 1580 and 990  $\text{cm}^{-1}$ ; UV-vis  $\lambda_{\text{max}}^{\text{CHCl}_3}$  ( $\epsilon$ ) 361 (60 600), 262 (63 600); Elemental analysis calculated for  $\text{C}_{74}\text{H}_{100}\text{O}_5\text{N}_2\text{V}$ : C, 77.42; H, 8.71; N, 2.44 per cent; found: C, 76.98; H, 8.92; N, 2.01 per cent.

In general, the yields of the pure platinum(II) complexes were about 35 per cent, while those for the pure oxovanadium(IV) complexes were around 50 per cent. The purity of the compounds was checked by standard methods. Satisfactory elemental analysis data (Carlo-Erba Model 1106 elemental analyser) were obtained for all the compounds. Infrared spectra were recorded as nujol mulls using a Shimadzu IR-435 spectrophotometer, and electronic absorption spectra were taken in chloroform solutions on a Hitachi U-3200 UV-Vis spectrophotometer.  $^1\text{H}$  NMR spectra were recorded using deuteriochloroform with tetramethylsilane as an internal standard on a Bruker WP80SY or a AC200F NMR spectrometer. The phase behaviour of all compounds was examined with a Leitz Laborlux 12 POL polarizing microscope equipped with a Mettler FP 52 temperature controller and a FP 5 microfurnace. Calorimetric measurements were made using a Perkin-Elmer DSC-4 differential scanning calorimeter. The calorimeter was calibrated using pure indium as a standard and a heating or cooling rate of  $5^{\circ}\text{C min}^{-1}$  was employed.

Table 1. Phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ ) for *N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-4''-*n*-decylphenylanilines, I.

Compound number	<i>n</i>	C†	S <sub>1</sub> †	S <sub>2</sub> †	S <sub>C</sub> †	S <sub>A</sub> †	N†	I
1	1	•	115.0	•	•	144.5	•	•
			30.84	(103.5)	—	1.33	218.5	231.0
				1.75			1.17	0.87
2	2	•	104.5	•	—	150.5	•	•
			17.22	(102.0)		1.67	235.5	238.0
				1.88			2.75	1.00
3	3	•	94.0	•	•	151.0	•	•
			17.55	(91.5)	•	1.46	172.5‡	
				1.67			7.06	
4	4	•	85.0	—	•	151.0	•	•
			19.47		•	1.21	193.0‡	
							7.69	
5	5	•	78.0	—	•	147.0	•	•
			26.58		•	0.83	204.5‡	
							7.77	
6	6	•	83.0	—	•	146.5	•	•
			16.17		•	1.0	212.0‡	
							8.36	
7	7	•	80.0	—	•	145.0	•	•
			44.89		•	0.83	214.5	
							8.48	
8	8	•	80.0	—	•	144.0	•	•
			34.94		•	0.87	214.5	
							8.48	
9	9	•	84.5	—	•	142.0	•	•
			51.87		•	0.91	213.0	
							9.53	
10	10	•	78.0	—	•	141.0	•	•
			31.97		•	0.66	210.0	
							7.27	
11	11	•	85.5	—	•	138.0	•	•
			54.84		•	0.87	207.0	
							10.24	
12	12	•	80.0	—	•	137.0	•	•
			55.17		•	1.17	204.0	
							10.32	
13	18	•	90.0	—	•	132.6	•	•
			70.22		•	1.46	187.9	
							10.61	

† C, crystalline phase; S<sub>1</sub> and S<sub>1</sub>, unidentified smectic phases; S<sub>C</sub>, smectic C phase; S<sub>A</sub>, smectic A phase; N, nematic phase; I, isotropic phase.

‡ Enthalpies could not be determined.

•, Phase present; —, phase absent.

### 3. Results and discussion

The mesomorphic phase transition behaviour of all the compounds synthesized was examined by polarizing microscopic observation and the associated enthalpy changes were determined by differential scanning calorimetry. The mesomorphic transition temperatures and the enthalpies for the Schiff's base ligands, **I**, are summarized in table 1. The first two homologues exhibit an enantiotropic nematic phase, while the remainder predominantly show smectic A ( $S_A$ ) and smectic C ( $S_C$ ) phases. All the homologues show an enantiotropic smectic phase below the smectic C phase and this has been designated as  $S_7$  in table 1. This exhibits a schlieren texture, but the phase type has not yet been established. In addition to these, the first three homologues show a monotropic smectic phase  $S_1$ , which has not been characterized. The magnitude of the enthalpies of the various phase transitions is similar to that determined for such transitions in other series of compounds and no unusual behaviour was observed.

A plot of the phase transition temperatures versus the number of carbon atoms in the alkoxy chain for the Schiff's bases, **I**, is given in figure 2. Here, the trend observed for like transition points is normal, viz. there is a regular effect in the beginning, followed by

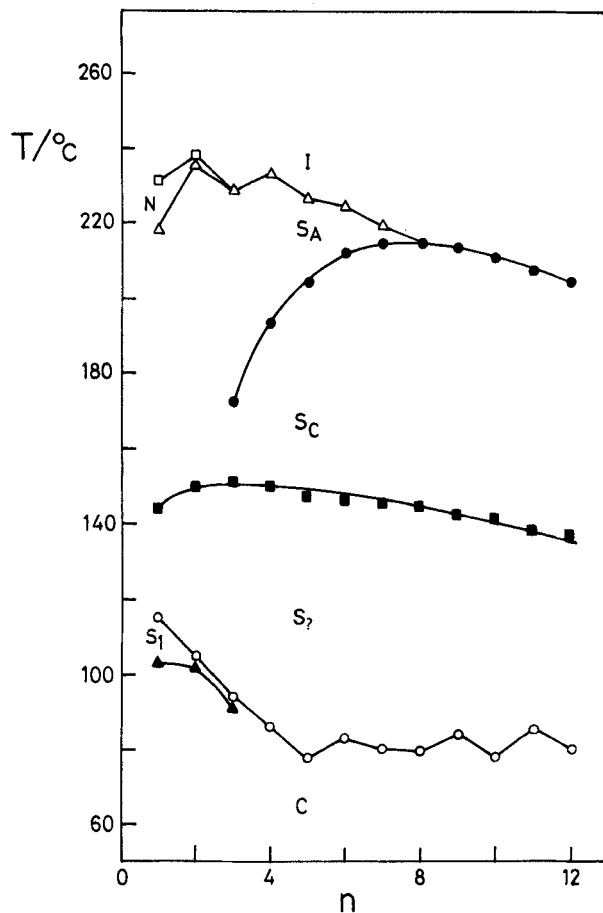
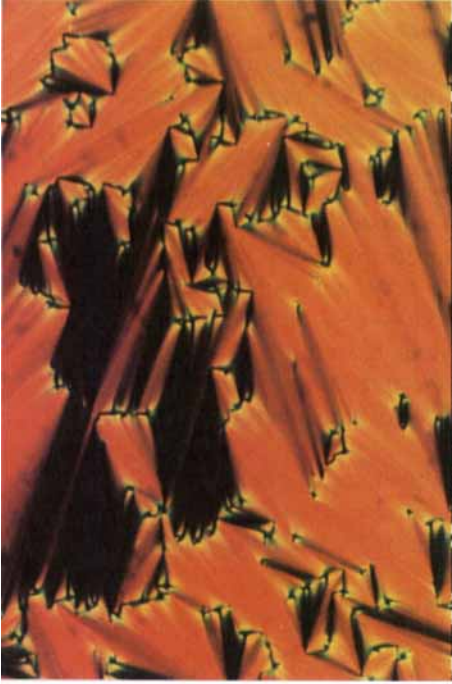
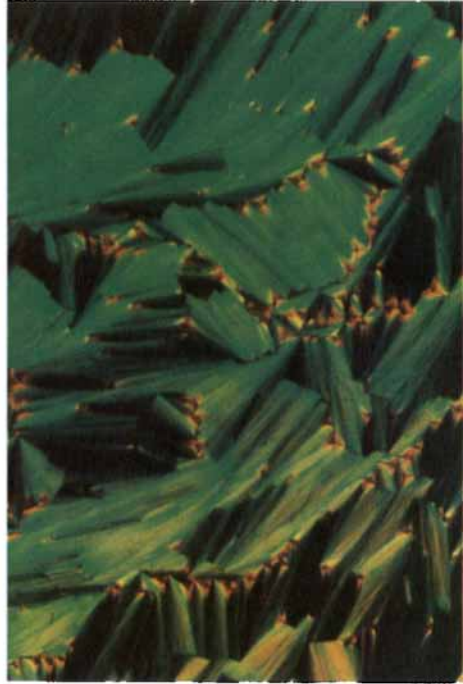


Figure 2. Plot of transition temperatures versus the number of carbon atoms ( $n$ ) in the alkoxy chain for Schiff's bases, **I**.  $\circ$ , C- $S_C$ ,  $S_A$  or  $S_7$ ;  $\bullet$ ,  $S_C$ - $S_A$  or  $I$ ;  $\triangle$ ,  $S_A$ -N or  $I$ ;  $\blacksquare$ , S- $S_C$  or  $S_A$ ;  $\square$ , N- $I$ ;  $\blacktriangle$ ,  $S_7$ - $S_1$ .

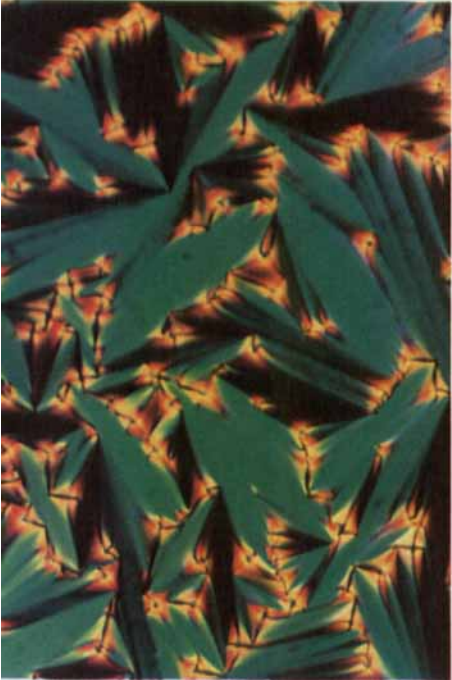


(a)



(b)

Figure 5.



(a)



(b)

Figure 3.

a gradual decrease in the  $S_A \rightarrow I$  transition temperatures. Similarly, the curve joining the  $S_C \rightarrow S_A$  transition points rises initially and merges with the falling  $S_A \rightarrow I$  curve at the octyloxy derivative.

The transition temperatures and the accompanying enthalpies for the bis[*N*-(4''-*n*-decylbiphenyl)-4'-*n*-alkoxysalicylaldehyde]oxovanadium(IV), complexes II,  $M = VO$  are given in table 2. Complexes with  $n \geq 4$  were prepared and all exhibit enantiotropic smectic phases. It is worth mentioning here that all these complexes have a pronounced  $V=O$  stretching vibration frequency around  $990\text{ cm}^{-1}$ . This conforms with observations for other oxovanadium complexes [18], and a monomeric structure is suggested for such species [19, 20]. Complexes with  $n = 4, 5$  and 6 exhibit only a  $S_A$  phase, while the remainder show both  $S_A$  and  $S_C$  phases. These have focal-conic and broken focal-conic textures respectively, and typical photomicrographs are shown in figure 3. They have fairly wide mesophase ranges with high clearing temperatures. The values of the enthalpies for the  $S_C \rightarrow S_A$  and  $S_A \rightarrow I$  transitions determined for these vanadyl complexes are similar to those obtained for such transitions for non-metallo-mesogens.

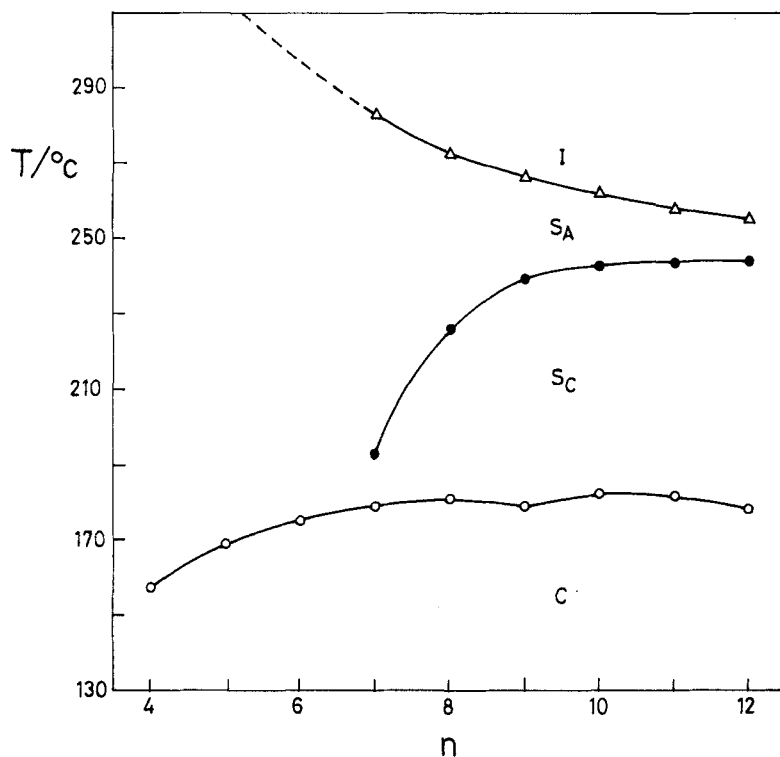


Figure 4. Plot of transition temperatures versus the number of carbon atoms ( $n$ ) in the alkoxy chain for the oxovanadium(IV) complexes, II,  $M = VO$ .  $\circ$ ,  $C-S_A$  or  $S_C$ ;  $\bullet$ ,  $S_C-S_A$ ;  $\Delta$ ,  $S_A-I$ .

Figure 3. Microscopic texture observed on cooling the isotropic liquid of complex II,  $n = 12$ ,  $M = VO$ . (a) Focal-conic texture of the smectic A phase at  $249.9^\circ\text{C}$ . (b) Broken focal-conic texture of the smectic C phase (the same region as (a) at  $236.5^\circ\text{C}$ ).

Figure 5. Microscopic texture observed on cooling the isotropic liquid of complex II,  $n = 12$ ,  $M = Pt$ . (a) Focal-conic texture of the smectic A phase at  $261.5^\circ\text{C}$ . (b) Broken focal-conic texture of the smectic C phase at  $258.0^\circ\text{C}$ .



Table 2. Phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ ) for the bis[*N*-(4'-*n*-decylbiphenyl)-4'-*n*-alkoxy-salicylal-diminato]oxovanadium(IV), **II**,  $M = \text{VO}$ .

Compound number	<i>n</i>	C $\dagger$		C <sub>1</sub>	S <sub>C</sub>	S <sub>A</sub>	I
1	4	—		● 158.0 31.64	—	● > 290*	●
2	5	—		● 169.0 41.59	—	● > 290*	●
3	6	—		● 175.0 40.50	—	● > 290*	●
4	7	● 176.0	●	● 179.5 21.27	● 193.5*	● 283.5 9.23	●
5	8	—	●	● 181.0 40.58	● 226.5*	● 272.5 7.31	●
6	9	● 76.5	●	● 179.5 37.41	● 239.0*	● 266.0 9.15	●
7	10	—	●	● 182.5 49.82	● 241.0 0.37	● 262.0 9.36	●
8	11	—	●	● 181.5 57.81	● 243.5 0.25	● 258.0 9.46	●
9	12	—	●	● 178.0 55.14	● 244.5 0.36	● 255.5 9.47	●
10	18	● 92.0	●	● 165.5 54.75	● 226.0 0.41	● 233.5 8.76	●

\* Enthalpies could not be determined.

$\dagger$  C $\rightarrow$ S<sub>C</sub> transition enthalpies given above include any enthalpies for previous C $\rightarrow$ C transitions.

●, Phase present; —, phase absent.

An examination of the transition temperatures for the oxovanadium(IV) complexes indicates that as the chain length is increased, the S<sub>C</sub> mesophase range increases, while the S<sub>A</sub> mesophase range and the combined mesophase range decrease. A plot of the phase transition temperatures against the number of carbon atoms in the alkoxy chain for this series is shown in figure 4. The S<sub>C</sub> $\rightarrow$ S<sub>A</sub> and S<sub>A</sub> $\rightarrow$ I transition points lie on smooth curves. The dotted line indicates that the clearing temperature for three homologues could not be determined due to thermal decomposition at high temperatures.

There are not many homologous series of complexes containing oxovanadium(IV) group about which to make reasonable generalizations. A comparison of the mesomorphic properties of the present oxovanadium(IV) complexes with those of bis[4-((4-*n*-alkoxybenzoyl)oxy)-*N*-*n*-propylsalicylal-diminato]oxovanadium(IV) [9] shows that the latter series is completely nematogenic. Similarly, for other complexes with *N*-alkyl chains [16], the nematic mesophases seems to dominate, though smectic phases appear for sufficiently long chains. Also, smectic phases are favoured when *p*-substituted *N*-aryl groups are present.

The thermal behaviour and the calorimetric data for the bis[*N*-(4'-*n*-decylbiphenyl)-4'-*n*-alkoxy-salicylal-diminato]platinum(II) complexes, **II**,  $M = \text{Pt}$  are reported in table 3. These are perhaps the first examples of liquid crystalline platinum containing materials derived from salicylal-dimines. All the complexes show crystal-crystal transitions. Like their oxovanadium(IV) congeners, these platinum(II) complexes are also smectogenic, except that all the transition temperatures are higher. In fact, the clearing temperatures for the homologues up to  $n = 9$  are  $> 290^{\circ}\text{C}$ . The higher transition temperatures are due to the square planar arrangement of the chelate rings

Table 3. Phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ ) for the bis[*N*-(4''-*n*-decylbiphenyl)-4''-*n*-alkyloxysalicylaldiminato]platinum(II), II,  $M = \text{Pt}$ .

Compound number	<i>n</i>	$C_1$	$C^{\dagger}$	$S_C$	$S_A$	I				
1	4	●	142.0	●	239.0 57.64	—	●	> 290.0*	●	
2	5	●	153.5	●	234.5 53.29	—	●	> 290.0*	●	
3	6	●	168.0	●	235.0 50.32	—	●	> 290.0*	●	
4	7	●	170.0	●	227.5 41.38	●	257.0*	●	> 290.0*	●
5	8	●	167.0	●	224.0 33.81	●	272.0*	●	> 290.0*	●
6	9	●	162.0	●	221.5 52.70	●	271.0*	●	> 290.0*	●
7	10	●	168.5	●	218.0 54.21	●	272.5 0.62	●	284.5 7.06	●
8	11	●	165.5	●	211.0 43.97	●	267.5 0.62	●	278.0 8.86	●
9	12	●	170.0	●	211.0 42.76	●	264.0 0.58	●	272.0 4.51	●
10	18	●	169.0	●	190.0 71.56	●	243.0 1.08	●	249.0 1.92	●

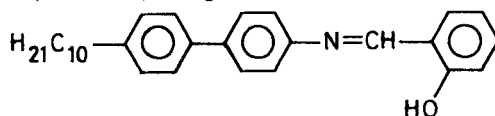
\* Enthalpies could not be determined.

†  $C \rightarrow S_C$  transition enthalpies given above include those for any previous  $C \rightarrow C$  transitions.

●, Phase present; —, phase absent.

as compared to the square pyramidal geometry at the centre of the oxovanadium complexes [21]. All the homologues show a focal-conic texture while complexes from  $n=7$  onwards exhibit a broken focal-conic texture at a lower temperatures. These have been characterized as smectic A and smectic C phases and the textures exhibited by these are shown in figure 5. For the Pt(II) complexes also, the  $S_C$  mesophase range increases while that for the  $S_A$  phase decreases with increase in chain length. However, the total range of the mesophase remains almost the same ( $62 \pm 6^{\circ}\text{C}$ ) irrespective of the chain length.

In order to examine the influence of the chain on the mesophase, *N*-(2-hydroxybenzylidene)-4''-*n*-decylphenylaniline and its oxovanadium(IV) and platinum(II) complexes were prepared, and their transition temperatures ( $^{\circ}\text{C}$ ) with the associated enthalpies ( $\text{kJ mol}^{-1}$ ) are given below:



C 90.5  $S_7$  108.5  $S_C$  128.0  $S_A$  174.0 I  
27.58 2.17 0.54 8.48

Oxovanadium(IV) complex:

C 155.5  $S_C$  184.0 N 196.8 I  
23.53 0.16 0.50

Platinum(II) complex:

C 228.8  $S_C$  240.0  $S_A$  250.5 N 255.0 I  
64.16 0.96 0.62

It is seen that both the complexes exhibit a nematic phase, while the ligand from which they are derived does not. We have seen earlier that even a short chain such as butoxy in the 4-position on the salicylaldehyde destroys this nematic phase. It is also clear that non-planarity of the chelate ring is responsible for lower transition temperatures, as well as for a longer range of the nematic phase. In addition, the nature of the metal atom is important for the thermal stability of the mesophase. In all the above complexes the order of mesophase thermal stability is platinum > oxovanadium.

We wish to acknowledge the help of Mr P. N. Ramachandra in the preparation of some of the intermediates and Mr K. Subramanya for the microanalyses.

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