

**SYNTHESIS AND PROPERTIES OF SOME  
THERMOTROPIC MESOGENS**

**A thesis submitted to the  
Bangalore University for  
the degree of  
DOCTOR OF PHILOSOPHY**

**by  
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## **DECLARATION**

*I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship or any other similar title.*

  
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## CERTIFICATE

*I certify that this thesis has been composed by Ms. Archana Ghode based on the investigations carried out by her at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or other similar title.*



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*TO MY PARENTS*

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## ABBREVIATIONS

c	crystal
S	smectic
N	nematic
I	isotropic
O	<i>ortho</i>
P	<i>para</i>
n	normal
ppm	parts per million
s	singlet
d	doublet
t	triplet
q	quartet
in	multiplet
tlc	thin layer chromatography
DSC	differential scanning calorimeter
DMS	dimethyl sulphate
DMSO	dimethyl sulphoxide
DES	diethyl sulphate
TMS	tetramethyl silane
THF	tetrahydrofuran

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## Preface

Liquid crystals represent states of matter intermediate between the crystalline solid and the isotropic liquid. A liquid crystalline system could be either lyotropic or thermotropic. The former refers to a two or more components system in which the mesomorphic behaviour is brought about by the influence of solvents. Thermotropic liquid crystals are obtained by purely thermal process, i.e., by heating certain crystalline solids or their mixtures (enantiotropic) or by cooling of isotropic liquid (monotropic).

As the work described in this thesis is concerned with the study of thermotropic systems, all further discussions will be limited to this type of liquid crystals.

Thermotropic liquid crystals may be obtained predominantly from organic compounds, but some organometallic compounds also exhibit the same. The compounds exhibiting thermotropic liquid crystalline behaviour are generally composed of molecules which are either lath-like (calamitic liquid crystals) or disc-like (discotic liquid crystals). Calamitic liquid crystals may be conveniently classified into three groups.

- 1 Nematic phase
- 2 Cholesteric phase
- 3 Smectic phase.

Similarly discotic liquid crystals may be broadly divided into

- 1 Columnar phase
- 2 Discotic nematic phase
- 3 Discotic lamellar phase.

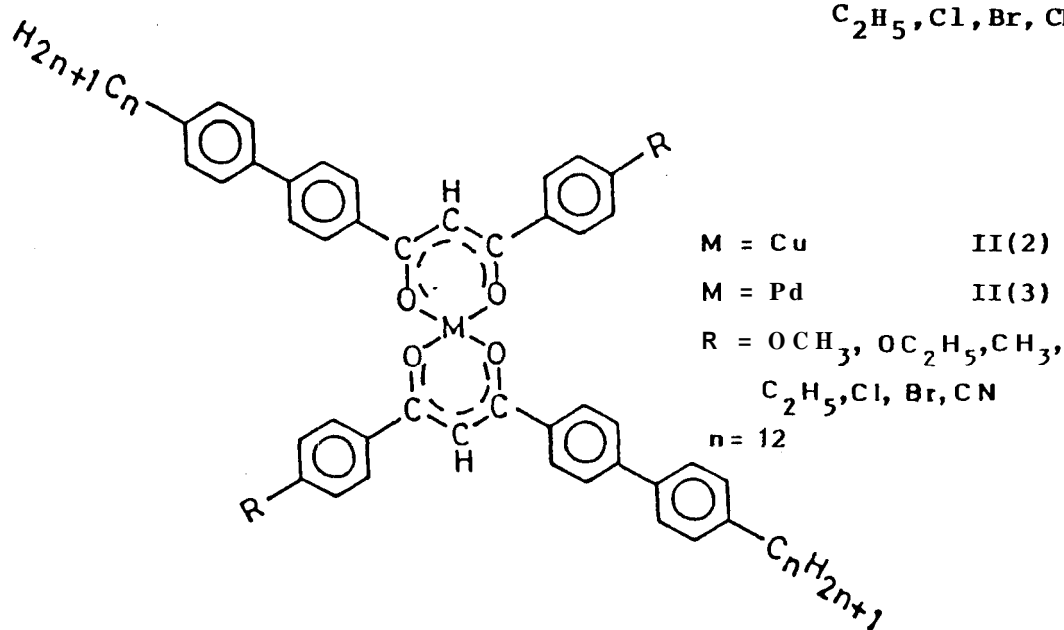
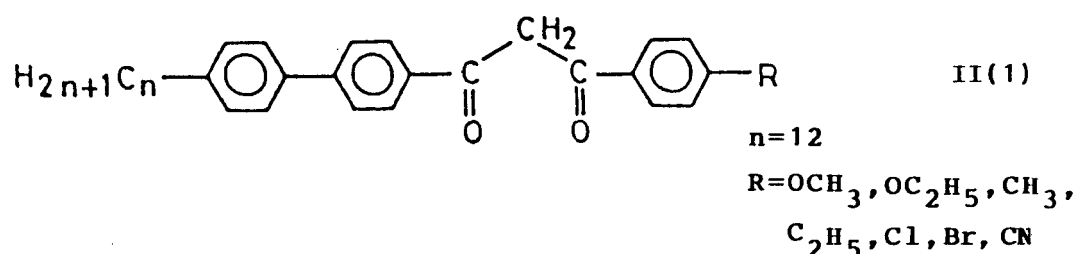
The investigations carried out in this thesis are concerned mainly with the synthesis and properties of mesogenic metal complexes. In particular, copper(II) and palladium(II) complexes of substituted  $\beta$ -diketones, platinum(II) and oxovanadium(IV) complexes of N-salicylideneaniline derivatives and the mesogenic behaviour exhibited by them.



In all, nearly 175 new compounds have been synthesised and an examination for their mesomorphic behaviour showed that 140 of them are mesogenic. The platinum(II) complexes described here represent the first examples of liquid crystalline platinum containing materials derived from salicylideneamine derivatives.

The first chapter begins with a brief description of the molecular arrangements in various classical thermotropic liquid crystals and a brief survey of mesogenic metal complexes with special emphasis on d block elements. The influence of different metal atoms on mesogenic properties has been summarised. The effect of different substituents on the mesomorphic properties, the variation of the mesomorphic behaviour in a homologous series and the relationship between chemical constitution and liquid crystallinity have also been discussed. A few important applications of liquid crystals have also been mentioned.

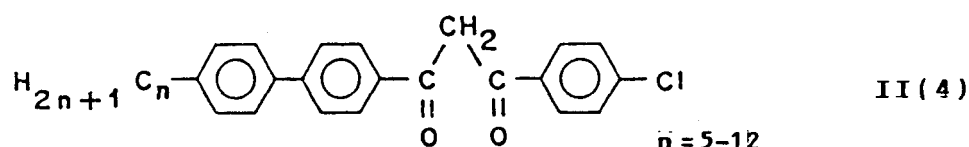
Chapter II deals with the investigations on the synthesis and mesogenic properties of [1-(4''-n-dodecylbiphenyl)-3-(4-substitutedphenyl)propane]-1,3-diones, [II(1)] and their copper(II), [II(2)] and palladium(II), [II(3)] chelates. We used different



terminal substituents on the phenyl ring to study the influence of these on the mesophases. In series II(1), except for derivatives with a terminal methoxy substituent (which is non-mesomorphic) remaining exhibit smectic mesophase. Compounds with chloro and bromo terminal substituents exhibit an enantiotropic smectic A phase and a monotropic smectic E phase. Terminal alkyl substitution seems to favour the mesophase formation as compared to the alkoxy groups in this system.

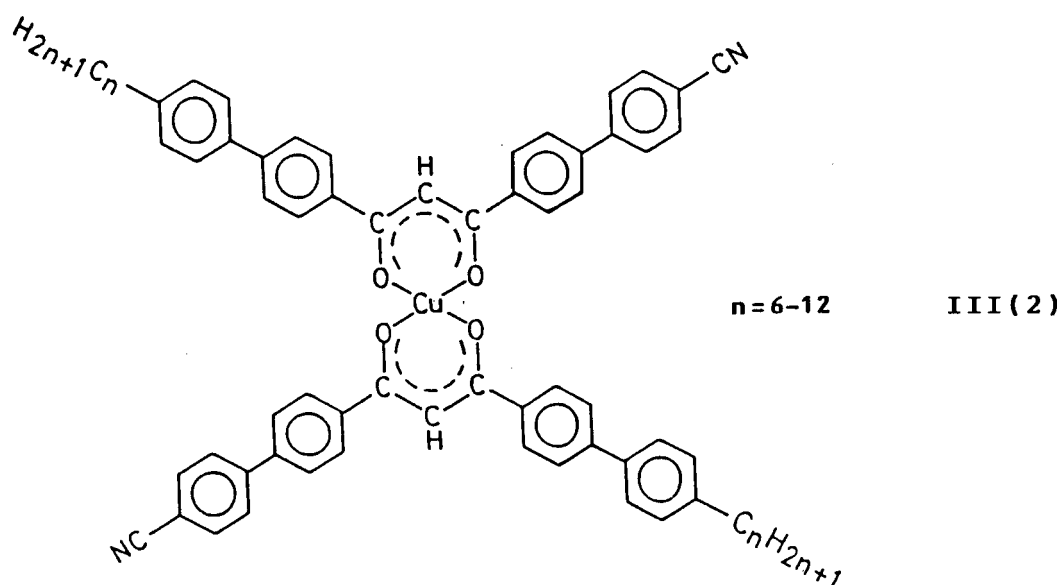
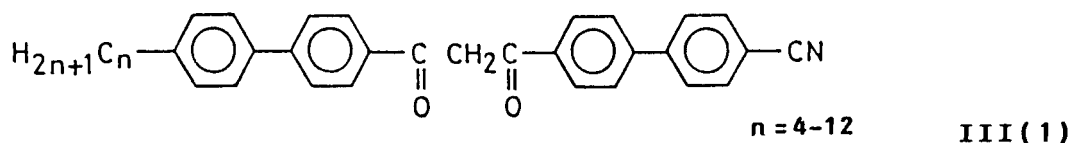
Copper(II) complexes [II(2)] show monotropic smectic A phase or a monotropic nematic phase, depending on the nature of substituents. A terminal cyano substituent which lies high in nematic group efficiency order' and low in smectic order promotes a smectic A phase.

From earlier investigations<sup>2</sup> we had found that the electron withdrawing chloro terminal group favours mesophase formation as compared to the electron donating methoxy group in the same  $\beta$ -diketone parent system. We synthesised a homologous series of  $\beta$ -diketones, [II(4)] with a chloro terminal substituent. All the homologues



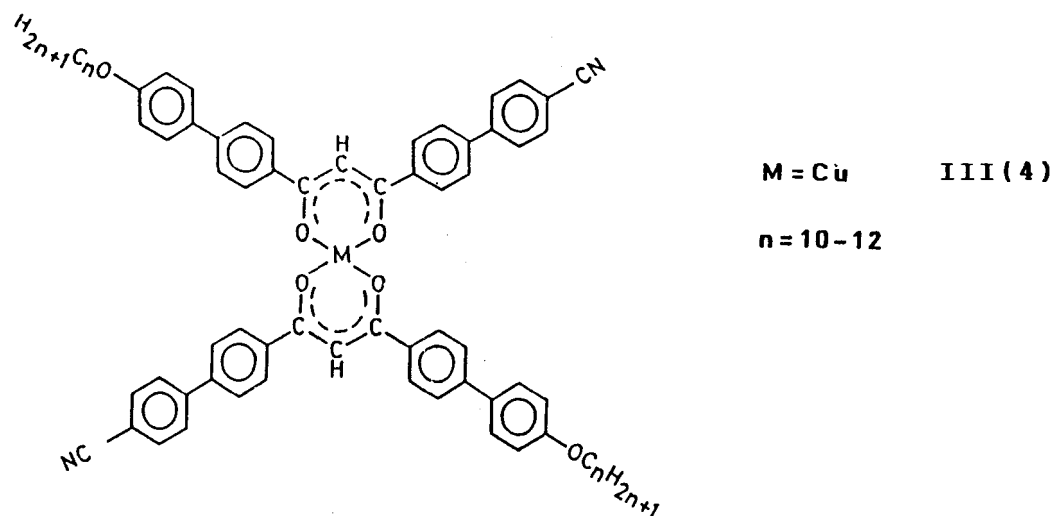
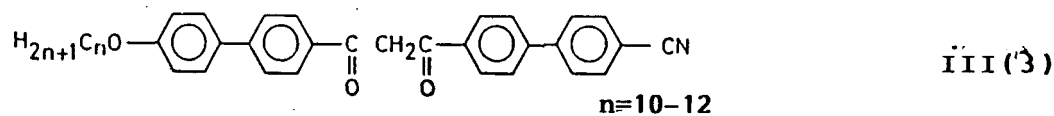
of this series show smectic A phase and the higher homologues also exhibit a monotropic smectic E phase. A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain shows a smooth curve relationship.

Chapter III deals with the synthesis and mesomorphic behaviour of a homologous series of [1-(4-n-alkylbiphenyl)-3-(4'''-cyanobiphenyl)propane]-1,3-diones, [III(1)] and their Cu(II) complexes, [III(2)].



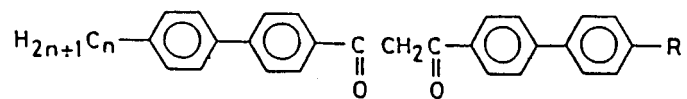
It was observed that the first four homologues of the above series [III(1)] ( $n=4$  to 7) exhibited only nematic phase. The intermediate homologue ( $n=8$ ) shows nematic and smectic A phases. The remaining higher homologues exhibit smectic polymorphism. This behaviour is in accordance with what has been observed<sup>3</sup> in a number of different homologous series. A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain shows a smooth curve relationship.

All the complexes of series III(2) show enantiotropic nematic phase. All derivatives melt above  $240^{\circ}\text{C}$  and have clearing points in the range of  $260^{\circ}$  to  $290^{\circ}\text{C}$ . Replacing Cu(II) with Pd(II) in two of the above complexes, show that the latter have higher melting points and become non-mesogenic. In order to study the effect of the alkoxy substituent on the type of mesophases and their transition temperatures in this system, we synthesised a few representative compounds belonging to the following series of compounds.

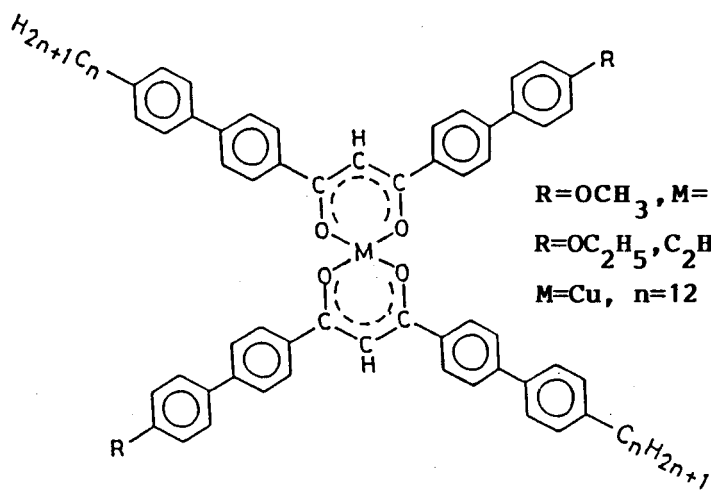


It was observed that the melting points were raised and the thermal stability of smectic A phase was increased in the compounds of series III(3) as compared to the corresponding derivatives of series III(1). We prepared copper(II) complexes [III(4)] using the ligands discussed above. These complexes exhibited enantiotropic nematic phase with high thermal stability. On complexation the melting points were raised by about  $18^\circ$  to  $87^\circ C$ , while the clearing points were raised by  $50^\circ$  to  $95^\circ C$ . The mesomorphic behaviour of these complexes have been compared with the n-alkyl substituted analogues.

In chapter IV, a brief account of the thermal behaviour of [1-(4-n-alkylbiphenyl)-3-(4'''-substitutedbiphenyl)propane]-1,3-diones, [IV(1)] and [1-(4-n-alkoxybiphenyl)-3-(4'''-methoxybiphenyl)propane]-1,3-diones, [IV(2)] and their metal chelates have been discussed. It was observed that in series IV(1) all the ligands were non-mesogenic. However, on complexation with Cu and Pd metal atoms, mesogenic behaviour was induced. In series IV(3) except for complex where  $n=12$ ,  $R=Br$  (which exhibit a smectic A phase) all the other derivatives show nematogenic behaviour. For chelates where  $R=OCH_3$  or  $C_2H_5$  and  $n=12$  the copper(II) complexes were enan-

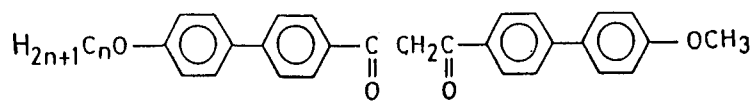


$\text{R} = \text{OCH}_3, \text{OC}_2\text{H}_5, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$  or  $\text{Br}$ .  $n = 10-12$ . **IV(1)**



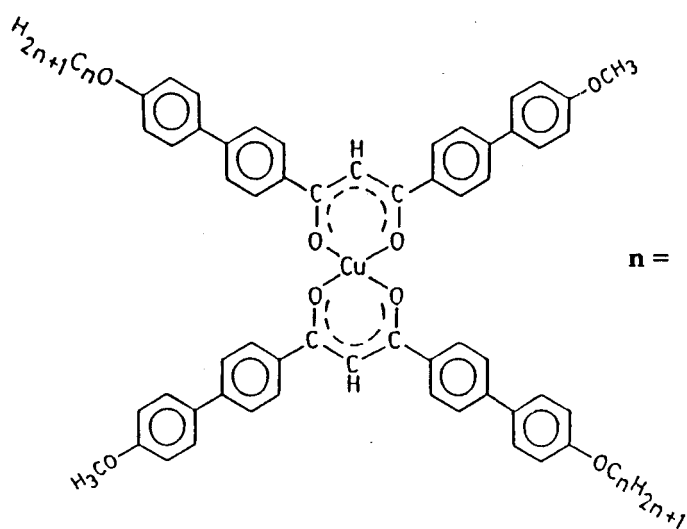
$\text{R} = \text{OCH}_3, \text{M} = \text{Cu or Pd}, n = 10-12$   
 $\text{R} = \text{OC}_2\text{H}_5, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$  or  $\text{Br}$ ,  
 $\text{M} = \text{Cu}, n = 12$

**IV(3)**



$n = 10-12$

**IV(2)**



$n = 10-12$

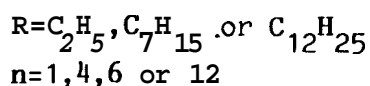
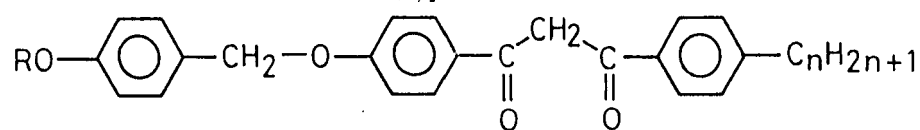
**IV(4)**

tiotropic nematic and when  $R = OC_2H_5$ ,  $n-C_3H_7$  or  $n-C_4H_9$  and  $n=12$ , the complexes exhibited a monotropic nematic phase. We know that bis[1-(4''-methoxyphenyl)-3-(4-n-dodecylbiphenyl)propane-1,3-dionato]copper(II) complex exhibits a monotropic nematic phase<sup>2</sup> whereas bis[1-(4'''-methoxybiphenyl)-3-(4-n-dodecylbiphenyl)propane-1,3-dionato]copper(II) complex exhibited an enantiotropic nematic phase. This suggests that presence of a biphenyl moiety enhances the nematogenicity in the complex. The mesogenic behaviour of these complexes have been discussed with respect to the way in which their molecular geometry affects the type of mesophase formed.

All the palladium(II) complexes were found to have a higher melting point than their corresponding copper(II) complexes and show a nematic phase.

In series IV(2) all the three synthesised derivatives were non-mesomorphic but their Cu(II) complexes exhibited enantiotropic nematic phase. A comparison of the mesogenic properties of these complexes with their corresponding alkyl analogues showed that these alkoxy complexes had higher thermal stability of nematic phase.

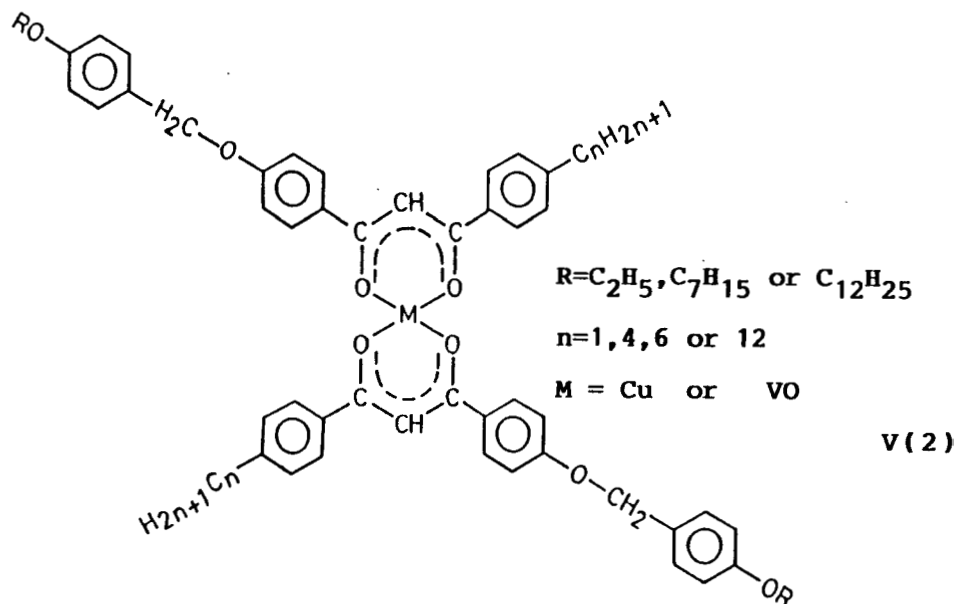
In chapter II, we had reported the synthesis of  $\beta$ -diketones in which a biphenyl moiety and a phenyl ring were employed in the 1,3-positions. With a view to examine the effect of a methyleneoxy bridging group between two phenyl rings on the mesomorphic properties of such a  $\beta$ -diketone system as well as their metal complexes, several compounds were synthesised. In chapter V, the synthesis and mesogenic properties of such  $\beta$ -diketones [V(1)] have been discussed.



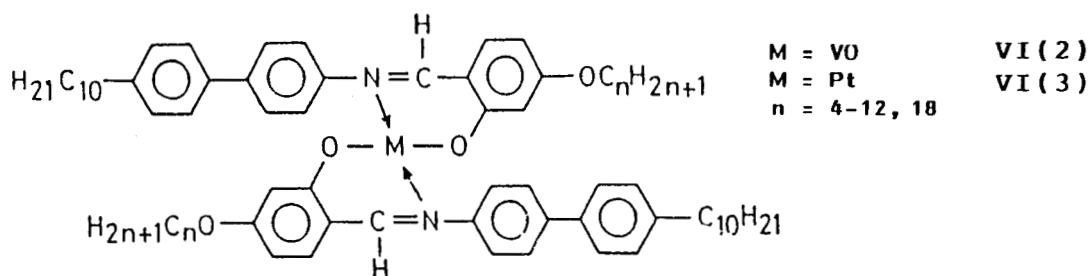
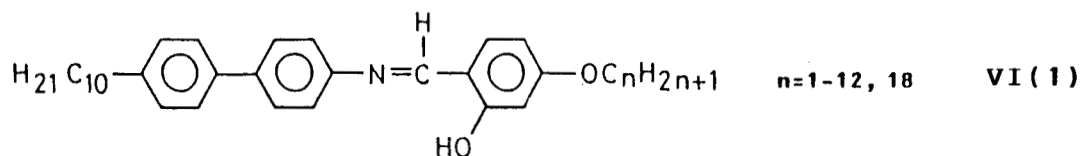
V(1)

Several copper(II) and oxovanadium(IV) complexes, [V(2)] synthesised using the above ligands were found to be non-mesomorphic. This behaviour suggests that molecular linearity and rigidity cannot be altered too much for a compound to

exhibit a mesophase.



Chapter VI begins with a survey of the mesomorphic properties exhibited by *o*-hydroxy substituted Schiff's bases and their metal chelates. Synthesis and liquid crystalline properties of a homologous series of N-(2-hydroxy-4-n-alkoxybenzylidene)-4''-n-decylbiphenylanilines (ligands), [VI(1)] and two homologous series of bis[N-(4''-n-decylbiphenyl)-4-n-alkoxysalicylaldiminato] oxovanadium(IV), [VI(2)] and bis[N-(4''-n-decylbiphenyl)-4-n-alkoxysalicylaldiminato]platinum(II), [VI(3)] have been discussed.



It is believed that these series of platinum(II) complexes are the first examples of mesogenic platinum containing salicylideneamine derivatives.

The first salicylideneaminato complex containing an oxovanadium group was reported by Galyametdinov et al.<sup>4</sup> in 1984 which exhibited smectic A and smectic C phases. Since then very few series of mesogenic oxovanadium complexes of *o*-hydroxy substituted Schiff's bases have been reported.<sup>5-7</sup> We have found that the mesophases ( $S_A$  and  $S_C$ ) obtained in the oxovanadium(IV) complexes, VI(2) are also observed in the ligands from which they are derived. Replacing the *n*-decyl chain with an ethyl or *n*-pentyl group on the biphenyl moiety in series VI(2), resulted in the oxovanadium complexes showing a nematic phase in addition to smectic phases. The clearing temperatures of all Pt(II) complexes were greater than 250°C. All the homologues show a focal-conic texture and the mesophase was characterised as smectic A phase. Higher homologues show a smectic C phase with a broken focal-conic texture. It was interesting to note that in series VI(3) removal of the alkoxy substituent from the phenyl ring, gives rise to a nematic phase in addition to the smectic phases. It was found that replacement of oxovanadium(IV) with platinum(II), gives higher melting and clearing temperatures. The higher transition temperatures are due to square planar arrangement of the platinum containing chelate rings as compared to the square pyramidal arrangement of the oxovanadium complexes.<sup>8</sup>

Some of the results presented in this thesis are reported in the following publications/conference.

1. Terminally chloro substituted mesogenic  $\beta$ -diketones.  
(Archana Ghode and B.K.Sadashiva) *Mol. Cryst. Liquid Cryst. Lett.*, 8, 39 (1991).
2. Synthesis and mesogenic properties of some  $\beta$ -diketones and their copper(II) and palladium(II) chelates.  
B.K.Sadashiva, Archana Ghode and P.Rani Rao  
*Mol. Cryst. Liquid Cryst.*, 200, 187 (1991).



3. Mesogenic  $\beta$ -diketones and metallomesogens.  
B.K.Sadashiva, L.Umadevi and Archana Ghode  
Paper presented at the Thirteenth International Liquid Crystal Conference,  
Vancouver, Canada, July 22-27, 1990 - Abstract No.Syn-43-p-Tue.
4. Synthesis and mesomorphic properties of some platinum(II) and oxovanadium(IV) complexes. B.K.Sadashiva and Archana Ghode *Liquid Crystals*, 1993 (in press).

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