LIQUID CRYSTALLINE PROPERTIES OF COMPOUNDS CONTAINING SOME TRANSITION METALS

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Doctor of philosophy

in the Faculty of Science

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, Fellowship or any other similar title.

Veena Prasad.

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" CERTIFIED "

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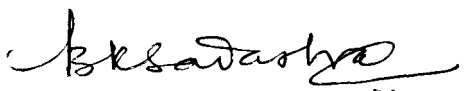
CERTIFICATE

I certify that this thesis has been composed by Ms. Veena Prasad 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.



Professor B.K. SADASHIVA
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Dedicated
to
My Teachers

कर्मण्येवाधिकारस्ते मा फलेषु कदाचन ।
मा कर्मफलहेतुर्भूर्मा ते सङ्गोऽस्त्वकर्मणि ॥ ४७ ॥

Your right is to work only, but never to the fruit thereof.
Be not you the producer of the fruits of karma;
neither shall you lean towards inaction.
– BHAGAVADGITA: 11 (47)

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In my opinion, it is very difficult to express in words certain kinds of feelings. Also, by doing so, these feelings will be diluted. However, it is always better to dilute some kinds of feelings, but, nay belief is that the feeling of gratitude should not be. Despite that, in order to avoid myself deviating too much from customary practice, I would like to record my deep sense of gratitude to several people.

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CONTENTS

Cover page: CPK molecular model of bis[N-(4″-n-dodecylbiphenyl)-4-n-hexyloxysalicylaldiminato]M(II) complex; M = Cu, Pd or Ni.

List of abbreviations

C	**crystal**
M	mesophase
S	**smectic**
D_L	discotic **lamellar**
S_A	**smectic A**
S_C	**smectic C**
S_E	**smectic E**
N	**nematic**
I	**isotropic**
	phase **exists**
	phase **does not exist**
o	ortho
m	meta
p	**para**
n	normal
IR	infrared
UV-Vis	**ultraviolet-visible**
NMR	nuclear **magnetic resonance**
ppm	**parts per million**
s	**singlet**
d	doublet
t	triplet
q	quartet
m	multiplet
dsc	**differential scanning calorimeter**

Preface

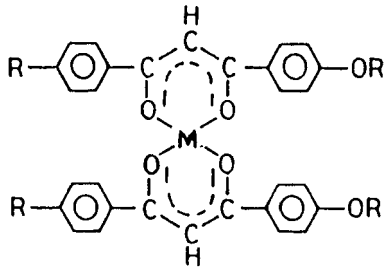
Liquid crystals as the name implies are condensed phases in which the constituent molecules are neither randomly oriented nor packed with a high degree of three - dimensional order as in crystals; they have some properties of liquids but retain some of the characteristics of crystals as well. The liquid crystalline phases are also called mesophases, and a compound which exhibits a mesophase is referred to as a mesogen. Transitions to these intermediate states may be brought about by purely thermal processes (thermotropic liquid crystals) or by the influence of solvents (lyotropic liquid crystals). Thermotropic liquid crystals can be further classified into two major classes: (a) calamitic liquid crystals, formed by the rod - like molecules and (b) discotic liquid crystals, formed by the disc - like molecules.

This thesis deals with investigations carried out on thermotropic liquid crystals. It describes mainly the synthesis and mesomorphic properties of compounds containing some transition metals. During these investigations it was found that some of the complexes were non-mesogenic. However, many of the ligands used to make these complexes were mesomorphic and these have been examined in greater detail. The relationships between the nature of the mesophase exhibited and the molecular structure of compounds of different homologous series have also been studied.

Chapter 1 begins with a brief general introduction to the subject "liquid crystals" and the molecular organisation of the compounds in different mesophases. It also throws light on the background work of the topics discussed in later chapters. Since the main object of this thesis has been to synthesise metallomesogens and to study their mesomorphic properties, these have been surveyed and discussed in greater detail. Mention is also made of some of the applications of liquid crystals.

The rest of the thesis deals with new results obtained in the present investigations, *viz.*, the synthesis and characterisation of *144* new liquid crystalline compounds belonging to different homologous series. These include both discotic lamellar as well as calamitic liquid crystals.

In Chapter 2, synthesis and mesomorphic properties of some compounds composed of disc - like molecules have been described. They belong to a series of bis[1-(4-n-alkylpheny1)-3-(4'-n-alkyloxyphenyl) propane -1,3-dionato]copper(II) and some of their palladium(II) congeners.



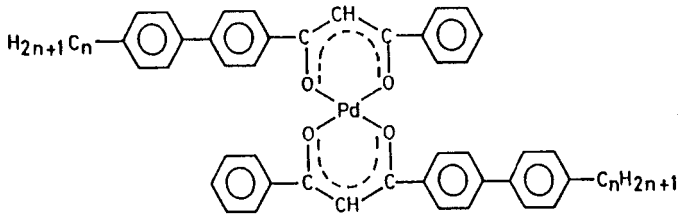
R = n - Alkyl
M = Cu or Pd

Among these copper and palladium complexes, the former exhibit mesomorphic behaviour whereas the latter do not. Though the exact nature of the mesophase shown by these compounds has not yet been resolved, optical, preliminary X-ray studies and comparison with literature data show that the mesophase is discotic lamellar. Similar compounds have been examined by Ohta ***et al.***[5]; based on X-ray studies in tlie mesophase, they have concluded that tlie mesophase is ***lamellar.*** Since the molecules have a disc-shape, they have referred to these as "discotic lamellar". The single crystal X-ray studies[6] on one of the complexes, synthesised by the author *viz.*, bis[1-(4-n-heptylphenyl)-3-(4′-n-heptyloxyphenyl)propane-1,3-dionato]copper(II), have shown that the alkyloxy chains in tlie molecule are cis to each other. Some of the β-diketones from which the above complexes have been prepared, also exhibit mesomorphic properties. A plot of the transition tempera-

tures versus the number of carbon atoms in the alkyl chain for the above series of complexes shows a smooth curve relationship.

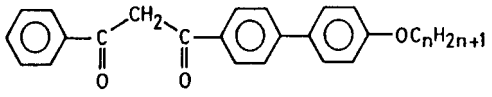
Chapter 3 deals with the synthesis and mesomorphic properties of three different homologous series. They consist of,

(i) bis[1-(4″ -n -alkylbiphenyl) -3- (phenyl)propane-1,3-dionato]palladium(II) complexes



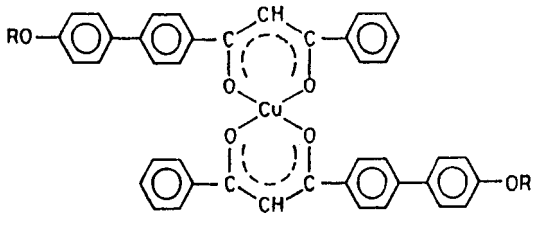
3(i)

(ii) 1-(4″ -n -alkyloxybiphenyl) -3- (phenyl)propane-1,3-diones and



3(ii)

(iii) bis[1-(4″ -n -alkyloxybiphenyl) -3- (phenyl)propane-1,3-dionato]copper(II) complexes



3(iii)

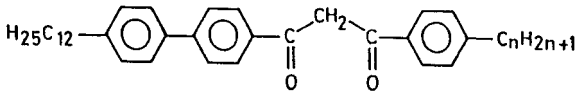
R = C_nH_{2n+1}

Palladium complexes of series 3(i), show a monotropic nematic phase. A comparison of the mesomorphic behaviour between these palladium complexes and their

corresponding copper analogues[7] have also been made. The palladium complexes have higher melting points and decompose at these temperatures. All the homologues of series 3(ii), show only a smectic A phase. The corresponding copper(II) complexes [3(iii)], have been found to be nematogenic. A comparison of tlie mesomorphic behaviour of these two series have been made with 1-(4″-n-alkylbiphenyl)-3-(phenyl)propane-1,3-diones,[8] and their copper(II) complexes, respectively. A plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain for the series 3(ii) and 3(iii) show the usual smooth curve relationships.

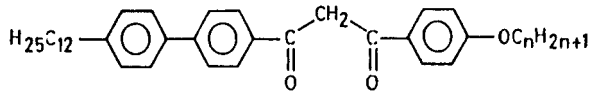
In Chapter 4, the synthesis and liquid crystalline properties of the following series of β-diketones have been discussed in greater detail as only one of the copper complexes synthesised exhibited mesomorphism.

(i) 1-(4″-n-Dodecylbiphenyl)-3-(4-n-alkylphenyl)propane-1,3-diones and



4(i)

(ii) 1-(4″-n-dodecylbiphenyl)-3-(4-n-alkyloxyphenyl)propane-1,3-diones

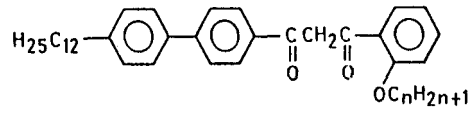


4(ii)

Both tlie series of compounds exhibit a smectic A phase. A few of the copper complexes of series 4(i), were found to be non-mesomorphic and hence were not pursued further. Among a few copper complexes synthesised in series 4(ii), 01114 tlie methyloxy derivative has been found to be mesomorphic, and hence the remaining homologues were not prepared.

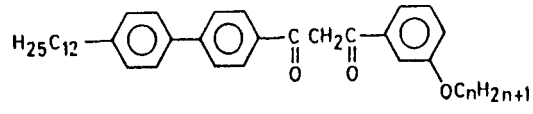
Chapter 5 begins with a survey of the mesomorphic properties of compounds containing a laterally substituted chain. It has been found that most of the mesogenic metal complexes contain flexible chains in the *para* position. In order to examine the influence of a flexible chain in the *ortho* and *meta* positions, the following two series of β-diketones (ligands) have been synthesised.

(i) 1-(4″-n-Dodecylbiphenyl)-3-(2-n-alkyloxyphenyl)propane-1,3-diones and



5(i)

(ii) 1-(4″-n-dodecylbiphenyl)-3-(3-n-alkyloxyphenyl)propane-1,3-diones



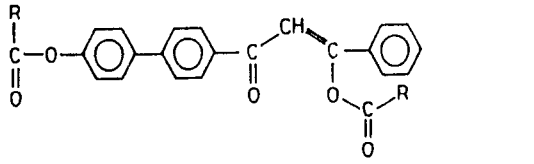
5(ii)

A few copper(II) complexes synthesised did not show any mesophase, and hence all the complexes of the two series 5(i) and 5(ii) have not been prepared. Interestingly, the ligands exhibited mesophases at fairly low temperatures and these have been examined in greater detail.

The compounds of homologous series 5(i) where the alkyloxy chain has been substituted in the *ortho* position of the phenyl ring, exhibit a nematic phase at relatively low temperatures. The homologue where n = 12, shows a monotropic smectic A phase in addition to the nematic phase. In contrast, in series 5(ii) except the first homologue which exhibits a monotropic nematic phase, all the other β-diketones in which the alkyloxy chain is in meta position of the phenyl ring, exhibit a smectic A phase. X - ray studies as a function of temperature in the mesophase of 1-(4″-n-

dodecylbiphenyl)-3-(3-n-dodecyloxyphenyl)propane-1,3-dione, have shown it to be a monolayer smectic A phase.

Apart from the above two series of β-diketones, a series of 1-(4″-n-alkanoyloxybiphenyl)-3-(n-alkanoyloxy)-3-(phenyl)-2-propene 1-ones 5(iii), wherein the lateral long-chain has been attached to the bridging group of the molecule, have also been prepared. All these compounds have been found to be mesogenic.

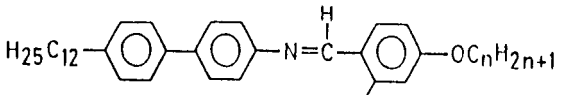


5(iii)

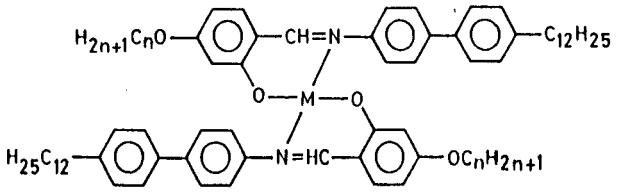
$R = C_nH_{2n+1}$

These compounds exhibit an enantiotropic smectic A phase. Some of the middle homologues exhibit a monotropic smectic E phase as well. X-ray studies as a function of temperature in tlie smectic A phase of two of the homologues where n=8 arid n=11, indicate that the lateral long-cliain substituent does riot extend along the long molecular axis, but bend inwards in contrast to the compounds of series 5(ii).

In chapters 2, **3,** and 4, the use of substituted β-diketones as ligands to obtain mesogenic complexes have been discussed. In chapter 6, a different approach to obtain metallomesogens has been undertaken. Here substituted o-hydroxy Schiff's bases have been used as ligands. These belong to a series of N-(2-hydroxy-4-n-alkyloxybenzylidene)-4″-n-dodecylphenylanilines. All the ligands are mesogenic.



Using the above ligands, thirteen each of copper(II), palladium(II) and nickel(II) complexes have been prepared.



All the thirtynine complexes have been found to be mesomorphic. Basically they show smectic A and smectic C phases. A comparison of the mesogenic properties of these palladium, copper and nickel complexes shows that the nickel complexes have tlie lowest melting as well as clearing poirits arid tlie palladiurri complexes have the highest transition temperatures. In fact, there are very few mesogenic nickel complexes which are reported in tlie literature.[9,10,11] Interestingly all tlie homologues of the above series of nickel complexes were found to be liquid crystalline.

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

1. Thermotropic mesomorphism in a series of copper β-diketonates and their ligands. (Veena Prasad and B.K. Sadashiva). Mol. *Cryst. Liq. Cryst.*, 195, 161 (1991).
2. Liquid crystalline properties of o-hydroxy substituted Schiff's bases and tlieir copper(II) and palladium(II) complexes. (Veena Prasad and B.K. Sadashiva). *Mol. Cryst. Liq. Cryst.*, 225, **303** (1993).
3. Mesogenic properties of nickel(II) complexes of N-(2-hydroxy-4-n-alkoxy benzylidene) 4″-n-dodecylphenylanilines. (Veena Prasad and B.K. Sadashiva). Mol. *Cryst. Liq. Cryt.*, (in press).
4. Thermotropic mesomorphism in some β-diketones with lateral chains. (B.K. Saclasliiva and Veena Prasad). - Paper presented at the 14^{th} International *Liquid Crystal* Conference, University of Pisa, Pisa, Italy, June 21-26, 1992 (Abstract No.A-P14).

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