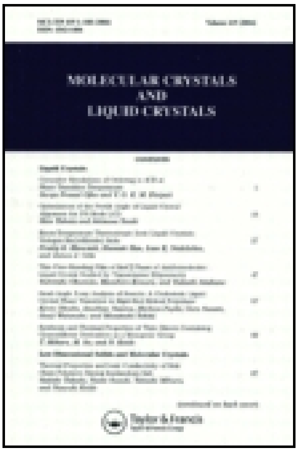

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Paramagnetic Liquid Crystal Copper (II) Complexes with Polar Groups

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Version of record first published: 24 Sep 2006.

To cite this article: Eduardo Campillos , Mercedes Marcos , Luis T. Oriol & Jose Luis Serrano (1992): Paramagnetic Liquid Crystal Copper (II) Complexes with Polar Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 215:1, 127-135

To link to this article: http://dx.doi.org/10.1080/10587259208038517

Mol. Cryst. Liq. Cryst. 1992, Vol. 215, pp. 127–135
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Printed in the United States of America

PARAMAGNETIC LIQUID CRYSTAL COPPER (II) COMPLEXES WITH POLAR GROUPS

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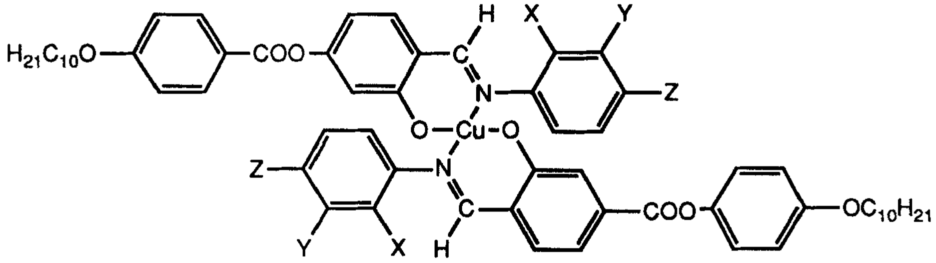
(Received April 5, 1991)

Abstract The synthesis and mesogenic behaviour of Copper (II) complexes derived from polar Schiff bases and of their corresponding ligands are reported. The ligands exhibited smectic C, smectic A and nematic phases, whereas the complexes only showed smectic A and nematic phases. Optical investigations carried out with one of the complexes showed that the nematic phase was uniaxial.

Keywords: metallo-organic, liquid crystals, NMR, IR

INTRODUCTION

The first mesogenic copper (II) complexes derived from Schiff bases were reported by Galyametdinov, Ovchinnikov et al. in 1984[1,2]. Since several papers presenting liquid crystal properties of similar complexes have appeared in the literature[3-13]. We ourselves described the mesomorphic properties of several series of copper (II) complexes derived from N-alkyl and N-aryl salicylaldimines[4,13] and made a study of the relation between the mesogenic behaviour and the molecular structure[5,12]. In these studies we found that the best liquid crystal properties are obtained with systems derived from 2,4-dihydroxybenzaldehyde. In this paper we continue this line of research in order to study in the relation between molecular structure and mesogenic activity in depth, and also, to obtain new materials suitables for practical applications. We report the mesogenic properties of a new family of complexes of copper (II) derived from imines with lateral or/and terminal polar groups in the amine part with the general structure A.



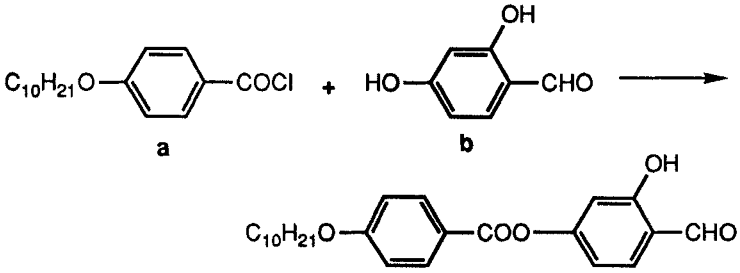
A

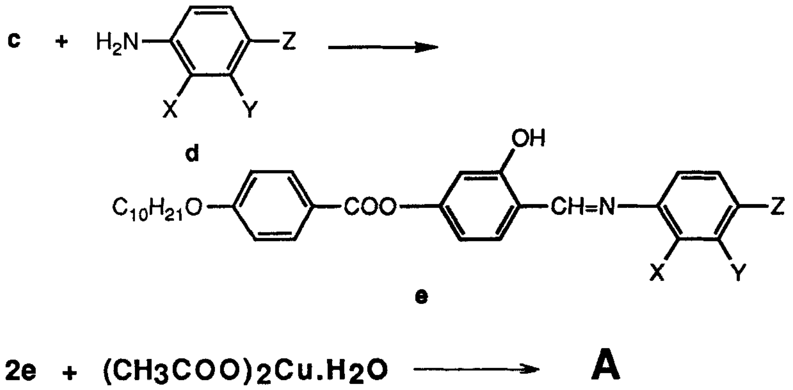
X	Y	Z	Ligand	Complex
F	H	F	1	1-Cu
H	F	H	2	2-Cu
H	CF_3	H	3	3-Cu
H	CN	H	4	4-Cu
H	H	CN	5	5-Cu
H	H	CH_2CN	6	6-Cu

EXPERIMENTAL

Synthesis

The synthetic procedure followed to prepared the copper (II) complexes is outlined in Scheme 1.





Scheme 1. Synthetic route in preparation of copper (II) complexes.

Preparation of the ligands

The free ligands were synthesized using a well known method[14] by mixing an ethanolic solution of the 4-(4′-n-alkoxybenzoyloxy)-2-hydroxybenzaldehyde with the appropriate amine.

Preparation of the complexes

The copper (II) complexes were prepared by the addition of an ethanolic solution (20 ml) containing copper (II) acetate ($Cu(OAc)_2.H_2O$) 1mmol to a hot solution of the appropriate imine (2 mmol) in ethanol (100 ml). The solution was collected by filtration and recrystallized from ethyl acetate.

Elemental analysis and yields are collected in Table I

Techniques

Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. Infrared spectra for all the complexes were obtained using a Perkin-Elmer 1600 (series FTIR) spectrometer in the 400-4000 cm^{-1} spectral range. The visible absortion spectra for the metal complexes were recorded in chloroform using a Hitachi V-3400 spectrophotometer in the 400-1000 nm spectral range. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz for ^1H, in deuteriochloroform solutions.

The textures of the mesophases were studied with an optical microscope (Nikon) equipped with a polarizing light, a Mettler FP82 hot

TABLE I Elemental analysis of Bis(N-aryl-substituted-4-[((decyloxy)-benzoyl)oxy]salicylaldimine Copper (II) complexes.

Complex	Molecular Formula	Elemental analysis (Calc.)			Yield
		C	H	N	(%)
1-Cu	$C_{60}H_{64}F_4N_2O_8Cu$	67.2(66.7)	6.2(6.0)	2.4(2.6)	64
2-Cu	$C_{60}H_{66}F_2N_2O_8Cu$	68.3(69.0)	6.2(6.4)	2.6(2.7)	54
3-Cu	$C_{62}H_{66}F_6N_2O_8Cu$	65.2(65.1)	6.1(5.8)	2.3(2.3)	49
4-Cu	$C_{62}H_{66}N_4O_8Cu$	69.8(70.3)	6.4(6.3)	5.4(5.3)	56
5-Cu	$C_{62}H_{66}N_4O_8Cu$	70.1(70.3)	6.5(6.3)	4.9(5.3)	59
6-Cu	$C_{64}H_{70}N_4O_8Cu$	70.6(70.7)	6.9(6.5)	5.1(5.2)	53

stage, and a Mettler central processor.

Measurements of temperatures of transition were made using a Perkin-Elmer DSC-2 differential scanning calorimeter with a heating or cooling rate of 10 K/min (the apparatus was calibrated with indium (156.6 ^{o}C, 28..44 J/g) and tin (232.1 ^{o}C, 60.5 J/g).

Thermogravimetric analyses were obtained on a Perkin-Elmer TGS-2 equipped with a system 4 microprocessor controller at a heating rate of 10 K/min under nitrogen.

RESULTS AND DISCUSSION

Synthesis and Characterization of the complexes

The complexes were prepared by reacting the appropriate imine with copper (II) acetate monohydrate in warm ethanol. The complexes were isolated as green, greenish-brown or brown solids with good yields and are soluble in toluene, chloroform, dichloromethane and insoluble in hexane, cyclohexane ether and ethanol.

Elemental analyses of the complexes are consistent with their proposed structures.

The infrared spectra of the metal complexes show a stretch band around 1611-1620 cm^{-1} which is assigned to ν (C=N). It was found that this band shift to a lower frequency by 5-9 cm^{-1} compared to that of the free ligands. There is a stretch band between 1719-1736 cm^{-1} assigned to the ester group ν(C=O).

The electronic spectra of the complexes show an absorption band centered around $\lambda = 623\text{-}671$ nm

The stability of the complexes was studied by thermogravimetric analysis and none of the complexes showed weight loss until 290 °C or higher temperatures. However, we observed by optical microscopy that some of the complexes decompose after the complex has become isotropic.

Mesogenic Behaviour

The optical and thermal data of the ligands and the complexes are summarized in Table II.

The ligands showed smectic C, smectic A and nematic mesophases whereas the complexes exhibited only smectic A and nematic phases. The nematic phase of the complexes shows textures that are typical of this type of mesophase[15], the marbled texture on heating and schlieren texture on cooling. The smectic A phase of the complexes was identified by the appearance on heating of both mielinic and homeotropic textures wihtout subjecting the sample to mechanical stress. A homeotropic texture was also observed on cooling and in some cases a focal-conic texture was observed on cooling from the isotropic liquid.

The viscosity of these mesophases was similar to that observed in the mesophases of the ligands.

A simplified form of the phase behaviour is shown in Figures 1 and 2. As can be observed, both ligands and complexes with fluor atoms in the structure (1,2,3 and 1-Cu, 2-Cu, 3-Cu compounds) exhibit nematic mesophase.

The compounds with a cyano group (4,5,6 and 4-Cu, 5-Cu, 6-Cu compounds) show smectic mesophase but the ligands also exhibit a nematic one. It is therefore evident that the fluor and cyano groups behave

TABLE II Transition temperatures(°C) for the ligands and complexes

Ligand	Transition	T°C	Complex	Transition	T°C
1	C - N	87	1-Cu	C_1-C_2	162
	N - I	184		C_2- N	171
				N - I	265
2	C_1-C_2	59	2-Cu	C_1-C_2	81
	C_2- N	81		C_2- N+C	166
	N - I	128		N+C-N	172
	N - S_C*	81		N - I	196
3	C - I	98	3-Cu	C_1-C_2	59
	I - S_A*	80		C_2- N	147
				N - I	150
4	C - I	123	4-Cu	C - S_A	165
	I - N*	115		S_A - I	205
5	C - S_A	107	5-Cu	C_1-C_2	176
	S_A- I	240		C_2-C_3	186
				C_3-S_A	194
				S_A- I(dec.)	276
6	C - S_A	137	6-Cu	C - S_A	200
	S_A-N	191		S_A- I(dec.)	231
	N - I	214			
	S_A-S_C*	136			

* Monotropic transition.

quite different. The cyano group, with a strong dipolar moment, favours intermolecuar interactions which give rise to more ordered mesophases.

The complexes melt at higher temperatures than the ligands and the clearing temperatures are also higher. However, the mesophase ranges are wider in the ligands than in the complexes. As happened with the ligands the highest temperatures and widest mesophase ranges were observed for complexes where the substituents are in position 4 of the

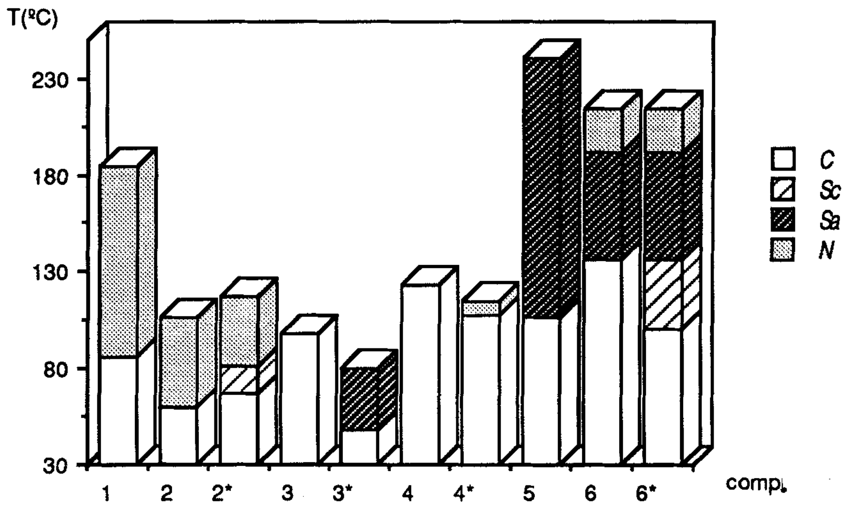


FIGURE 1 Transition temperatures of ligands (n* cooling process)

anilinic ring. The steric effect of the lateral groups decreases the stability of the mesophase, and the sequence of melting temperatures and clearing temperatures for the complexes are respectively:

$4\text{-CH}_2\text{CN} > 4\text{-CN} > 2,4\text{-di F} > 3\text{-F} > 3\text{-CN} > 3\text{-CF}_3$
$4\text{-CN} > 2,4\text{-di F} > 4\text{-CH}_2\text{CN} > 3\text{-CN} > 3\text{-F} > 3\text{-CF}_3$

The negative influence of the lateral substituents is similar to that observed with the ligands but less marked, thus, while some 3-substituted ligands (compounds 3 and 4) are monotropic all the complexes show enantiotropic mesophases. This effect of lateral groups has also been observed recently for another research group[10].

Studies carried out with the complex 1-Cu, to determine the biaxiality of the nematic mesophase showed that it was uniaxial. And X ray studies in the mesophase of this complex showed an interdigitated disposition of the molecules with smectic A cybotactic domains.

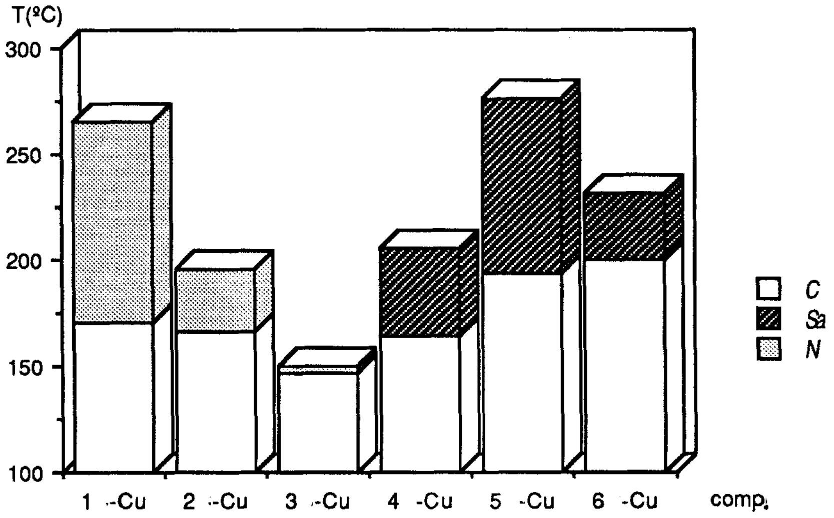


FIGURE 2 Transition temperatures of copper (II) complexes

ACKNOWWLEDGEMENTS

This work is supported by the CICYT (Comisión Interministerial de Ciencia y Tecnología)(Spain) project no. MAT 90-0813.

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