Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Liquid Crystal Derivatives of Transition Metals (I): Tetracoordinated Copper (II) Complexes Derived From Schiffs Bases

M. Marcos [a], P. Romero [a], J. L. Serrano [a], C. Bueno [b], J. A. Cabeza [b] & L. A. Oro [b]

[a] Quimica Orgánica, Faculätad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., 50009, Zaragoza, Spain

[b] Quimica Inorgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., 50009, Zaragoza, Spain

Version of record first published: 22 Sep 2006.

To cite this article: M. Marcos , P. Romero , J. L. Serrano , C. Bueno , J. A. Cabeza & L. A. Oro (1989): Liquid Crystal Derivatives of Transition Metals (I): Tetracoordinated Copper (II) Complexes Derived From Schiffs Bases, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 167:1, 123-134

To link to this article: http://dx.doi.org/10.1080/00268948908037168

Mol. Cryst. Liq. Cryst., 1989, Vol. 167, pp. 123–134
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Liquid Crystal Derivatives of Transition Metals (I): Tetracoordinated Copper (II) Complexes Derived From Schiffs Bases

M. MARCOS, P. ROMERO and J. L. SERRANO

Química Orgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza (Spain)

and

C. BUENO, J. A. CABEZA and L. A. ORO

Química Inorgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza (Spain)

(*Received March 16, 1988*)

The synthesis, characterization and thermal behavior of several new series of Copper (II) complexes derived from Schiffs bases are reported. The complexes are of the type: $[Cu\{C_6H_3O(OR)—C(Z)=N—R'\}_2]$ (R=*n*—C_nH_{2n+1}, R'=*p*-*n*-alkoxy-(C_6H_4)—, *p*-*n*-alkyl—(C_6H_4)—, *n*-alkyl; Z=H, CH_3).

Schiffs base complexes of Copper (II) derived from an aldehyde show thermotropic mesophases (smectic discotic polymorphism), whereas complexes derived from a ketone do not. When the amine forming the imine ligand is an aromatic amine the complexes form liquid crystals, whereas if the amine is aliphatic the complexes do not give liquid crystals.

The relationship between the molecular structure and the mesomorphic behavior is discussed.

Keywords: transition metal complexes, copper, Schiffs bases, liquid crystals, smectic–discotic polymorphism

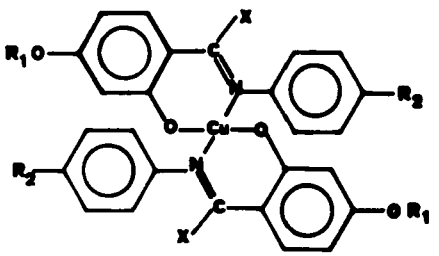
INTRODUCTION

The synthesis of mesomorphic transition metal complexes is at present arousing great interest because of the special combination of liquid crystal properties with the presence of a transition metal in the structures of the molecules. Only a few of these organic transition metal complexes exhibit discotic mesomorphism.

In 1984, Galyametdinov, Ovchimnikov *et al.*[1,2] described the synthesis and ESR spectra of some bis[salicylaldiminato]Copper(II) complexes and found that they showed crystal–smectic discotic, smectic–nematic and nematic–isotropic transitions and that the configuration of the complexes is square-planar. Recently Otha *et al.*[3] described tetrasubstituted β-diketonato Copper(II) complexes and for the

first time established from X-ray diffraction measurements that each of the discotic mesophases shown by these complexes is a discotic lamellar phase.

In this paper we present the synthesis and mesomorphic properties of several new series of disk-like tetracoordinate Copper(II) complexes of Schiffs bases derived from aldehydes or ketones with general structure:



We made a systematic study of:

A) the effect of alkyl chain length in: i) the two different phenyl groups in the imine (Series I and II), ii) the benzylidene group alone (Series III and IV), iii) the aniline group alone (Series V and VI);

Series I: X=H R_1=C_nH_{2n+1} R_2=OC_nH_{2n+1}
II: X=H R_1=R_2=C_nH_{2n+1}
III: X=H R_1=C_nH_{2n+1} R_2=$OC_{10}H_{21}$
IV: X=H R_1=C_nH_{2n+1} R_2=$C_{10}H_{21}$
V: X=H R_1=$C_{10}H_{21}$ R_2=OC_nH_{2n+1}
VI: X=H R_1=$C_{10}H_{21}$ R_2=C_nH_{2n+1}

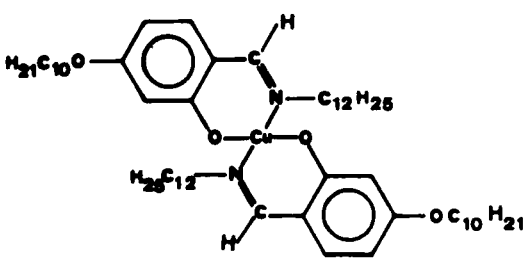
wherein n = 2, 6, 10, 14

B) differences between complexes from Schiffs bases derived from an aldehyde or a ketone

Compound 7: X=CH_3 R_1=$C_{10}H_{21}$ R_2=$C_{10}H_{21}$
Compound 8: X=CH_3 R_1=$C_{10}H_{21}$ R_2=$OC_{14}H_{29}$

C) differences between complexes from Schiffs bases derived from aromatic or aliphatic amines

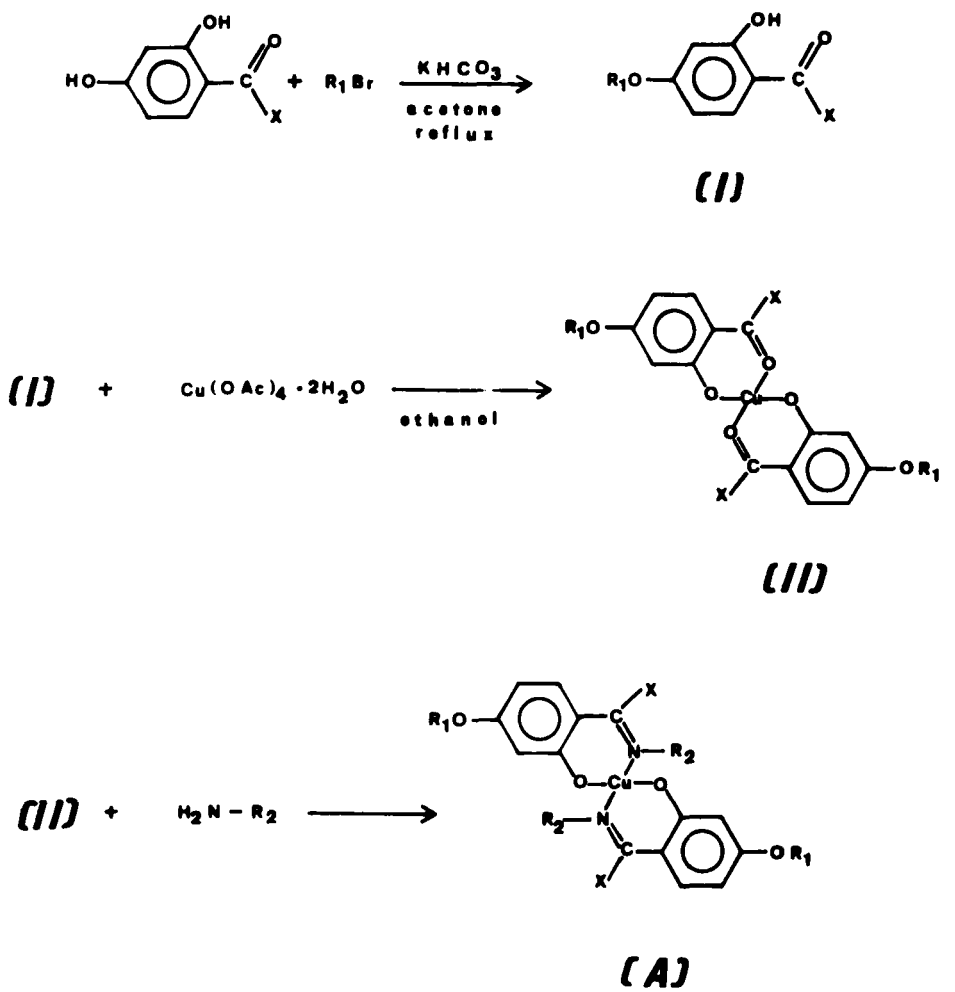
Compound 9:



EXPERIMENTAL

Synthesis

The synthetic route used to prepare the Copper(II) complexes is shown in Scheme 1.



Scheme 1. Synthetic route to tetracoordinate Copper (II) complexes derived from Schiffs bases.

Preparation of the ligands (I) The 4-alkoxy-2-hydroxybenzaldehyde or 4-alkoxy-2-hydroxyacetophenone ligands (I) were synthesised as described previously.[4,5]

Preparation of the complexes (II) The Copper(II) complexes of type II were synthesized by the following procedure:

To an ethanolic solution (20 ml) containing $Cu(OAc)_4.2H_2O$ (0.017 mmole) was

TABLE I

Elemental analysis data (calculated values in parentheses) and yields for type II complexes

X	R_1	C (%)	H (%)	Yield (%)
H	C_2H_5	54.1 (54.9)	5.5(4.4)	92
H	C_6H_{13}	62.0 (61.7)	6.9(6.9)	72
H	$C_{10}H_{21}$	66.1 (66.0)	8.2(8.1)	66
H	$C_{14}H_{29}$	70.9 (72.2)	10.2(9.5)	58
Ch_3	$C_{10}H_{21}$	65.8 (66.8)	7.9(8.4)	80

added the appropriate carbonyl compound [4-alkoxy-2-hydroxybenzaldehyde or 4-alkoxy-2-hydroxyacetophenone] (0.68 mmole).

The solution was boiled for 2.5–3 h. After cooling and concentrating the solution, the crystalline complexes were filtered off, washed with ethanol and ether to remove uncomplexed ligand, and dried under vacuum.

Table I lists elemental analysis data and yields for type II complexes.

Preparation of the complexes (A) The Copper(II) chelates of the Schiffs bases were prepared by the addition of an excess of the appropriate amine to a 20 ml solution (20 ml) of the bis(carbonyl)Copper(II) complexes (0.09 mmole) in ethanol. The mixture was heated under reflux for about 30 h. After cooling, the complexes were filtered off, washed with cold ethanol and dried under vacuum.

The crystals were recrystallized from a mixture of chloroform and alcohol.

Table II lists elemental analysis data and yields for the complexes (A).

Preparation of the alkoxyanilines The alkoxyanilines were prepared following methods described in the literature[6]

Techniques

C, H and N analyses were performed using a Perkin-Elmer 240B microanalyzer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene plates.

The transition temperatures and enthalpies were measured by differential scanning calorimetry using a Perkin-Elmer DSC-2 operated at a scanning rate of 5 $Kmin^{-1}$ on heating. The apparatus was calibrated with indium (429.6 K; 28.4 J/g) and tin (505.06 K; 60.5 J/g) as standards.

The textures of the mesophases were studied by optical microscopy using a polarizing microscope (Meiji) fitted with a Mettler FP82 heating stage and FP80 control unit.

RESULTS AND DISCUSSION

None of the Copper(II) complexes of type II (Sketch 1) showed mesomorphic properties. The transition temperatures and enthalpies are given in Table III.

Phase transition temperatures and enthalpy change of the complexes of series I, II, III, IV, V and VI are gathered in Table IV.

TABLE II

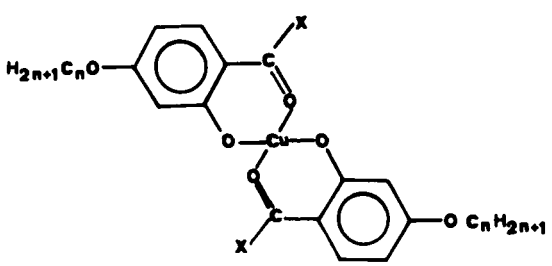
Elemental analysis data (calculated values in parentheses) and yields for complexes (A)

Series	X	R_1	R_2	C (%)	H (%)	N (%)	Yield (%)
I	H	C_2H_5	OC_2H_5	63.3 (64.6)	5.4 (5.7)	4.0 (4.4)	65
I	H	C_6H_{13}	OC_6H_{13}	70.4 (70.1)	8.3 (8.0)	3.4 (3.3)	44
I, III, V	H	$C_{10}H_{21}$	$OC_{10}H_{21}$	72.0 (73.3)	9.8 (9.3)	2.7 (2.6)	32
I	H	$C_{14}H_{29}$	$OC_{14}H_{29}$	74.2 (75.4)	9.9 (10.2)	1.5 (2.1)	68
II	H	C_2H_5	C_2H_5	68.3 (68.0)	5.6 (6.0)	4.8 (4.7)	80
II	H	C_6H_{13}	C_6H_{13}	73.0 (72.7)	8.9 (8.3)	3.5 (3.4)	59
II, IV, VI	H	$C_{10}H_{21}$	$C_{10}H_{21}$	74.4 (75.6)	10.0 (9.7)	2.7 (2.7)	48
II	H	$C_{14}H_{29}$	$C_{14}H_{29}$	77.2 (77.3)	12.0 (10.4)	2.2 (2.2)	49
III	H	C_2H_5	$OC_{10}H_{21}$	68.9 (70.3)	8.8 (7.8)	3.3 (3.3)	59
III	H	C_6H_{13}	$OC_{10}H_{21}$	70.9 (71.9)	9.4 (8.8)	2.9 (2.8)	45
III	H	$C_{14}H_{29}$	$OC_{10}H_{21}$	73.2 (74.5)	9.7 (9.8)	2.3 (2.3)	63
IV	H	C_2H_5	$C_{10}H_{21}$	72.9 (73.0)	9.3 (8.1)	3.5 (3.4)	86
IV	H	C_6H_{13}	$C_{10}H_{21}$	75.4 (74.3)	9.6 (8.0)	3.1 (3.3)	73
IV	H	$C_{14}H_{29}$	$C_{10}H_{21}$	76.1 (77.6)	9.4 (8.8)	2.6 (2.5)	54
V	H	$C_{10}H_{21}$	OC_2H_5	70.4 (70.1)	8.5 (8.0)	3.3 (3.3)	87
V	H	$C_{10}H_{21}$	OC_6H_{13}	71.4 (71.9)	9.4 (8.7)	2.7 (2.9)	73
V	H	$C_{10}H_{21}$	$OC_{14}H_{29}$	73.7 (74.5)	10.5 (9.8)	1.8 (2.3)	57
VI	H	$C_{10}H_{21}$	C_2H_5	71.8 (72.8)	8.9 (8.4)	3.3 (3.4)	31
VI	H	$C_{10}H_{21}$	C_6H_{13}	73.4 (74.3)	9.7 (9.0)	3.1 (3.0)	44
VI	H	$C_{10}H_{21}$	$C_{14}H_{29}$	75.9 (76.5)	10.8 (10.1)	2.1 (2.4)	59
Compound							
7	CH_3	$C_{10}H_{21}$	$C_{10}H_{21}$	75.0 (75.5)	8.98 (9.6)	2.7 (2.7)	42
8	CH_3	$C_{10}H_{21}$	$OC_{14}H_{29}$	74.5 (74.8)	9.32 (9.8)	2.5 (2.3)	63
9	H	$C_{10}H_{21}$	$C_{12}H_{25}$[a]	72.9 (73.2)	10.61 (10.4)	3.3 (3.0)	70

[a]Aliphatic amine.

TABLE III

Phase transition temperatures and enthalpies for copper (II) complexes type



X	*n*	Transition	T (°C)	ΔH (KJ/mol)
H	2	C_1—C_2	85.6	5.0
		C_2—C_3	227.7	26.6
		C_3—I	231.5	15.1
H	6	C_1—C_2	143.9	15.0
		C_2—I	202.6	43.0
H	10	C_1—C_2	138.8	9.6
		C_2—I	183.7	56.1
H	14	C_1—C_2	145.7	14.2
		C_2—I	172.4	67.9
CH_3	10	C—I	140.2	54.9

TABLE IV

Phase transition temperatures and enthalpies for Copper (II) complexes of Series I to VI.

Series	R_1	R_2	Transition[a]	Temperature (°C)	ΔH (KJ/mol)
I	C_2H_5	OC_2H_5	C—I	206.0	67.1
I	C_6H_{13}	OC_6H_{13}	C—S_1	138.5	38.5
			S_1—I	165.6	6.2
I, III, V	$C_{10}H_{21}$	$OC_{10}H_{21}$	C—S_2	129.5	41.8
			S_2—S_1	151.6]	12.2
			S_1—I	155.1]	
I	$C_{14}H_{29}$	$OC_{14}H_{29}$	C—S_2	115.8	69.8
			S_2—S_1	125.8	8.7
			S_1—I	132.2	19.9
II	C_2H_5	C_2H_5	C—I	186.0	44.5
II	C_6H_{13}	C_6H_{13}	C—I	153.9	45.3
			I—S_1[b]	145.8	—
II, IV, VI	$C_{10}H_{21}$	$C_{10}H_{21}$	C_1—C_2	72.1	2.3
			C_2—C_3	98.9	9.8
			C_3—S_1	130.3	3.2
			S_1I	137.4	12.0
II	$C_{14}H_{29}$	$C_{14}H_{29}$	C_1—C_2	66.4]	28.8
			C_2—C_3	69.8]	
			C_3—C_4	89.7	10.7
			C_4—S_2	102.7	49.9
			S_2—I	113.7	12.5
III	C_2H_5	$OC_{10}H_{21}$	C_1—C_2	104.0	1.5
			C_2—S_1	117.3	28.2
			S_1—I	169.7	9.2
III	C_6H_{13}	$OC_{10}H_{21}$	C—S_1	136.6	41.1
			S_1—I	164.6	9.4
III	$C_{14}H_{29}$	$OC_{10}H_{21}$	C_1—C_2	93.7	12.9
			C_2—S_2	115.6	38.4
			S_2—S_1	135.9	0.4
			S_1—I	145.0	9.3
IV	C_2H_5	$C_{10}H_{21}$	C_1—C_2	77.0	50.8
			C_2—S_1	123.3	25.0
			S_1—I	153.9	8.7
IV	C_6H_{13}	$C_{10}H_{21}$	C_1—C_2	91.7	2.3
			C_2—S_1	138.0	27.3
			S_1—I	149.3	11.9
IV	$C_{14}H_{29}$	$C_{10}H_{21}$	C—S_2	94.9	68.5
			S_2—S_1	113.4	0.4
			S_1—I	128.1	12.9
V	$C_{10}H_{21}$	OC_2H_5	C—S_1	133.0	49.8
			S_1—I	177.7	8.9
V	$C_{10}H_{21}$	OC_6H_{13}	C—S_1	127.8	34.7
			S_1—I	161.2	9.6
V	$C_{10}H_{21}$	$OC_{14}H_{29}$	C_1—C_2	110.7	56.0
			C_2—S_2	129.4	52.5
			S_2—S_1	145.3]	12.9
			S_1—I	147.3]	
VI	$C_{10}H_{21}$	C_2H_5	C_1—C_2	109.4]	
			C_2—C_3	113.7]	6.1
			C_3—S_1	117.1]	
			S_1—I	122.7	0.7
VI	$C_{10}H_{21}$	C_6H_{13}	C—S_1	130.5	31.3
			S_1—I	145.1	10.1
VI	$C_{10}H_{21}$	$C_{14}H_{29}$	C_1—C_2	72.0	10.7
			C_2—S_2	97.9	37.3
			S_2—S_1	104.5	12.1
			S_1—I	123.8	12.2

[a]S_1 mesophase shows textures similar to S_A and S_2 is similar to S_C mesophase from optical observations.
[b]Monotropic transition.

As can be seen, all the Copper(II) complexes with Schiffs bases derived from an aldehyde and an aromatic amine show smectic phases, with the exception of the complexes whose four terminal chains each have two carbon atoms, which are not mesogenic. When the terminal chains are long, the Copper(II) complexes have two mesophases.

The transition temperatures for series I to VI are plotted against the number of carbon atoms in the terminal chains in Figures 1 to 6.

Roviello *et al.*[7] established that *bis*[*N*-*p*-(*n*-hexyloxy)phenyl, *p*-(*n*-heptyloxy)salicylaldimanato] Copper(II) shows smectic mesomorphism rather than discotic mesomorphism based on the crystal structure determined by X-ray diffraction measurements.

In the case of our compounds, the texture of the mesophase, observed by optical microscopy, represented by S_1 is similar to the textures shown by a S_A mesophase (homeotropic and fan-shaped textures), whereas that of the mesophase represented by S_2 is similar to the broken fan-shaped texture of smectic C. However, these mesophases show a higher viscosity than the S_A and S_C phases displayed by rod-like compounds, and a peak in the DSC for the S_2—S_1 transition can be observed. Due to the disc-like molecular structure, we propose that these mesophases are discotic smectic phases. As Otha *et al.* recently[3] identified a discotic lamellar phase for *bis*[1,3-di(*p*-n-alkoxyphenyl)propane-1,3-dionato]Copper(II) complexes which they described as being similar in texture to the broken fan-shaped texture of S_C,

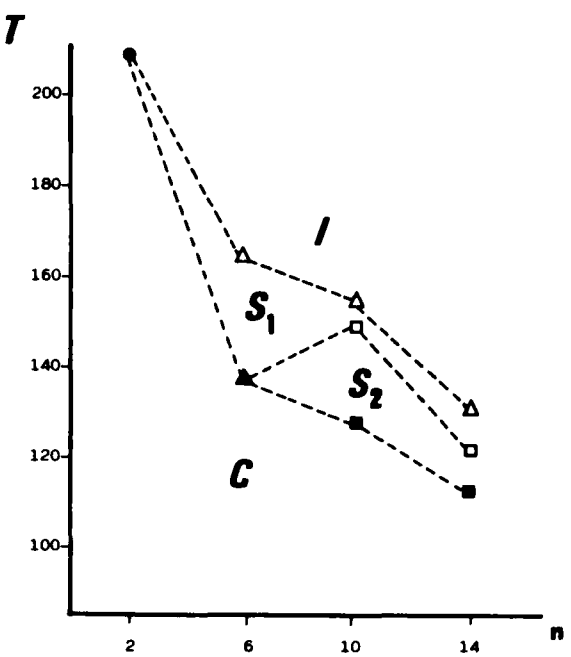


FIGURE 1 Plot of transition temperatures against number of carbon atoms (*n*) in the terminal chain for the compounds of series I.

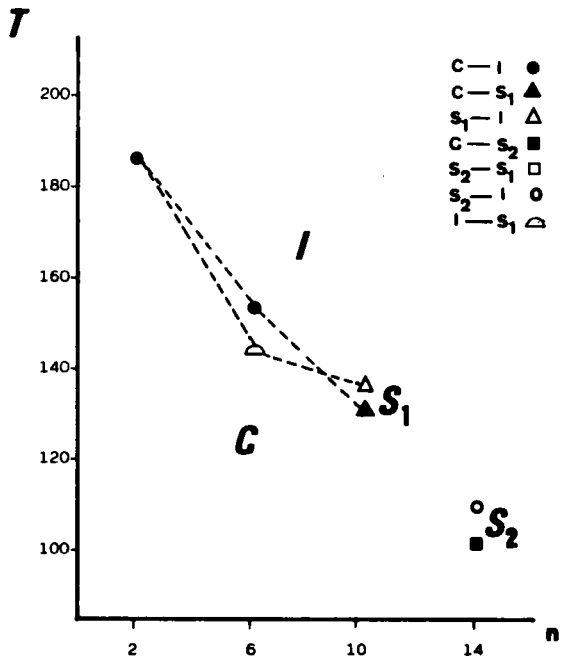


FIGURE 2 Plot of transition temperatures against number of carbon atoms (n) in the terminal chain for the compounds of series II.

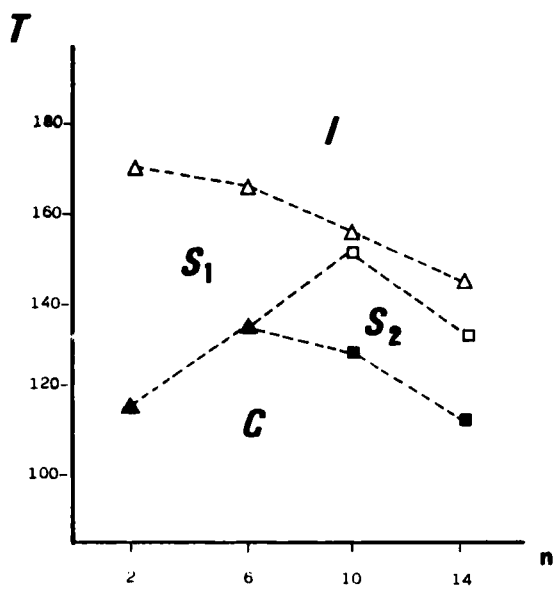


FIGURE 3 Plot of transition temperatures against number of carbon atoms (n) in the terminal chain for the compounds of series III.

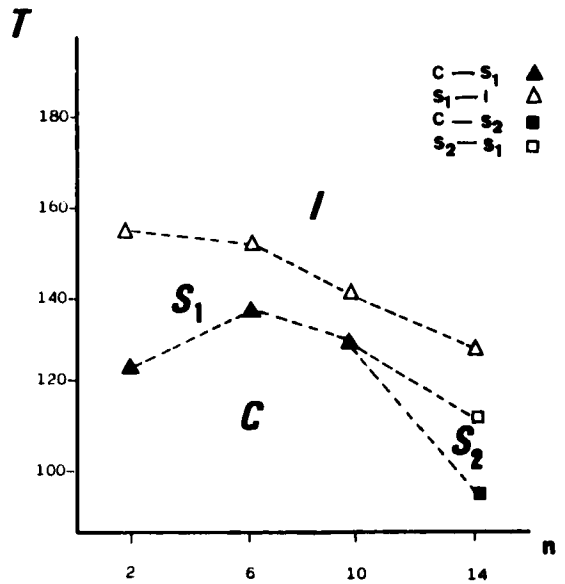


FIGURE 4 Plot of transition temperatures against number of carbon atoms (n) in the terminal chain for the compounds of series IV.

we think that the S_2 mesophase of our complexes are the same as the D_L phase described by Ohta.

The compounds prepared with Schiffs bases derived from ketones (compounds 7 and 8) and from an aliphatic amine (compound 9) did not show mesomorphic properties. Their melting points and transition enthalpies are given in Table V.

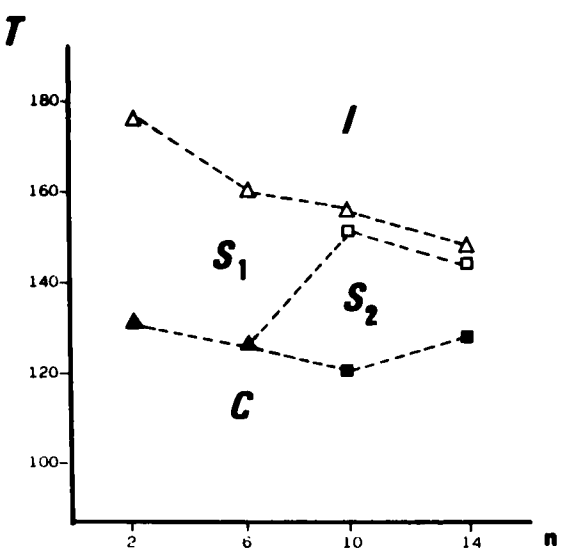


FIGURE 5 Plot of transition temperatures against number of carbon atoms (n) in the terminal chain for the compounds of series V.

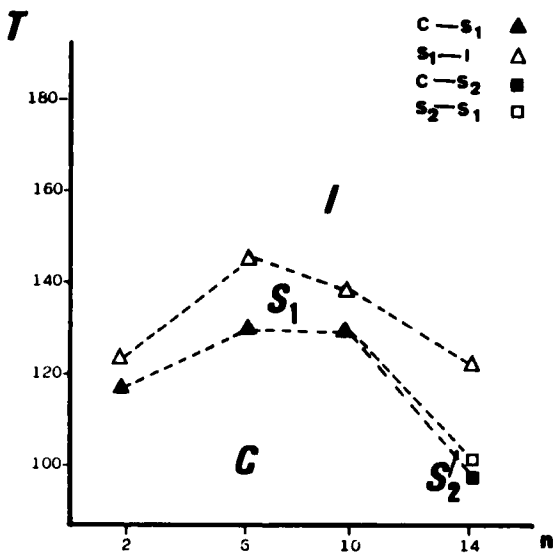


FIGURE 6 Plot of transition temperatures against number of carbon atoms (n) in the terminal chain for the compounds of series VI.

Most of the mesomorphic compounds showed crystalline polymorphism (see Table IV).

—Six of the complexes have two solid polymorphs

C_1—C_2–Mesophase

Series III:	R_1=C_2H_5	R_2=$OC_{10}H_{21}$
	R_1=$C_{14}H_{29}$	R_2=$OC_{10}H_{21}$
Series IV:	R_1=C_2H_5	R_2=$C_{10}H_{21}$
	R_1=C_6H_{13}	R_2=$C_{10}H_{21}$
Series V:	R_1=$C_{10}H_{21}$	R_2=$OC_{14}H_{29}$
Series VI:	R_1=$C_{10}H_{21}$	R_2=$C_{14}H_{29}$

—Two complexes have three solid polymorphs

C_1–C_2–C_3–Mesophase

Series II:	R_1=$C_{10}H_{21}$	R_2=$C_{10}H_{21}$
Series VI:	R_1=$C_{10}H_{21}$	R_2=C_2H_5

—And one complex has four solid polymorphs

C_1–C_2–C_3–C_4–Mesophase

Series II: R_1=$C_{14}H_{29}$ R_2=$C_{14}H_{29}$

Some of these solid state transitions could be observed by optical microscopy.

TABLE V

Phase transition temperatures and enthalpies for complexes 7, 8 and 9

Compound	Transition	Temperature (°C)	ΔH (KJ/mol)
7	C—I	212.9	20.1
8	C_1—C_2	72.0	
	C_2—I	140.2	18.6
9	C_1—C_2	92.2	5.5
	C_2—I	96.8	12.1

None of the low temperature solid polymorphs occur during the second heating in the DSC and only the highest temperature solid polymorphs remain.

Comparative study of the mesomorphic properties in series I to VI.

As said before, the smectic polymorphism detected in the complexes of series I to VI was S_1 mesophase (similar to S_A) and S_2 mesophase (similar to S_C).

As can be seen in Figures 1 to 6, the latter phase only appears when the total number of carbon atoms in the terminal chains in the imine is high ($\geq$ 20 in series I, III and V; $\geq$ 24 in series IV and VI, and $\geq$ 28 in series II). The S_2 mesophase appears for a lower total number of carbon atoms in complexes whose imine has alkoxy terminal chains in both aromatic groups than when the aniline part has an alkyl group as terminal chain.

It can also be seen that the mesophase ranges are greater in the case of the tetra-alkoxy homologues. Since the melting temperatures are similar and the clearing points are higher, this indicates that alkoxy groups enhance liquid crystal thermal stability in Copper(II) complexes (as in rod-like compounds) due to the increased molecular polarizability.

In these compounds, the effect of reversal of the terminal chains (series III and V and Series IV and VI) is not significant; the melting and clearing temperatures are similar, with the exception of the compound in which one of the two terminal chains of the imine is an ethyl group. This compound has a lower clearing point when the ethyl group is in the aniline part (compound of series VI) ($\simeq$ 31°) and a much shorter mesophase range.

Comparative study of the mesomorphic properties in complexes whose imine is derived from a ketone or an aldehyde

The effect of replacing the hydrogen in the imine group by a methyl group has been examined (compounds 7 and 8).

In both cases the broadening effect of the methyl group reduces the liquid crystal properties to such an extent that compounds 7 and 8 are not mesomorphic—see Table V. However, the interactions in the solid state must be relatively stronger in the ketone derived complexes as can be deduced from their melting points (Tables IV and V).

Comparative study of the mesomorphic properties in complexes whose imine ligand is derived from an aromatic or an aliphatic amine

The effect of replacing the aromatic amine in the imine ligand by an aliphatic amine was also examined. As can be seen in Table V, the compound whose amine is aliphatic (compound 9) did not show liquid crystal properties, which may be due to a loss of anisotropy of the polarizability in the molecule.

References

1. I. V. Ovchinnikov, Y. Galyametinov, G. I. Ivanova and L. M. Yagforava, *Dokl. Akad. Nauk. SSSR*, **276**, 126 (1984).
2. Y. Galyametdinov, I. V. Orchinnikov, M. B. Bolotin, N. B. Etigen, G. I. Ivanova and L. M. Yagfarova, *Izu. Akad. Nauk. SSSR, Ser Khim*, 2379 (1984).
3. K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **140**, 131 (1986).
4. M. Artigas, M. Marcos, E. Meléndez and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **130**, 337 (1985).
5. M. Marcos, E. Meléndez and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **91**, 157 (1983).
6. P. Keller and L. Liebert, *Solid St. Phys., Suppl.*, **14**, 19 (1978).
7. A. Roviello, A. Sirigu, P. Iammelli and A. Immirzi., *Liquid Crystals*, **3**, 115 (1988).