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Calamitic or columnar mesomorphism determined by number and position of substituents in enaminoketone Cu(II), Ni(II) and Co(II) complexes

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New enaminoketone metalomesogens with an almost equilateral triangular shape of the mesogenic core have been synthesized. They form either calamitic or columnar mesophases depending on the number and position of the substituted chains. The stability of the columnar as well as of the calamitic phases depends substantially on the central metallic ion.

1. Introduction

There is a common idea in liquid crystal chemistry that mesophase type—calamitic or columnar—is closely related to a particular molecular core shape. However, there have already been found some examples where this rule is not fulfilled. There are molecules with elongated structure which give columnar mesomphases [1, 2], or rod-like calamitic phases are formed by disc shaped molecules [3]. Moreover for polycatenar [4] liquid crystals with elongated mesogenic cores, both phases—columnar and calamitic—can occur within one homologous series even for the same substance. In this work we describe compounds with a triangular mesogenic core that exhibit either calamitic (from rods) or columnar (from discs) phases by appropriately substituting alkoxy chains. Enaminoketone Cu(II), Co(II) and Ni(II) complexes were chosen due to the relatively easy synthetic route. Their mononuclear mesogenic core with both oxygen and both nitrogen atoms in the *cis*-configuration has an almost equilateral triangular shape structure.

2. Experimental

2.1. *Synthesis*

The synthetic procedure for the designed complexes **1** with identical or different aroyl moieties is shown in scheme 1. A reaction between 4,5-dialkoxy-1,2-phenylenediamine **2** and a formyl ketone derivative **3** at room temperature proceeds selectively at only one amino group to give a crystalline compound **4** (yield 70–80%). The product **4**, using its remaining amino group, reacts further with a formyl ketone derivative **5** at higher temperatures. The reactant **5** contains in the aroyl group, an Ar_2 moiety, which can be either the same as or different from Ar_1 in component **3**.

The synthesis of **4** has been described previously [5]. To obtain ligand **6**, the semi-product **4** (1 mmol) and the sodium salt of an appropriate formyl ketone **5** (1·1 mmol) were suspended in EtOH (50 cm^3), neutralized with AcOH in EtOH and boiled for 10 min. For the symmetrical ligand **6**, the 4,5-dialkoxy-1,2-phenylenediamine **2** (1 mmol) and the formyl ketone sodium salt **4** (2·2 mmol) were used.

The solution of ligand **6** was heated under reflux for 5 min with the metal acetate, $M(OAc)_2.xH_2O$ (1·1 mmol), in EtOH (20 cm^3) when a precipitate of the complex **1** was formed on cooling. Generally the complexes **1** were recrystallized from octane and remelted under reduced pressure to remove traces of the solvent. Complexes with both aroyl groups trisubstituted were recrystallized from isopropanol. These materials exhibit liquid crystalline phases at room temperature and form colloidal suspensions in octane. The yields of the compounds **1** were in all cases similar, 50–60%. The elemental C, H and N analyses for the compounds **1** were satisfactory.

2.2. *NMR spectra*

The NMR spectra (in $CDCl_3$) of the ligand semi-products **4** and the Ni(II) complexes **1** were obtained (Varian UNITY plus 500 MHz). They are consistent with the assumed structure without any sign of additives

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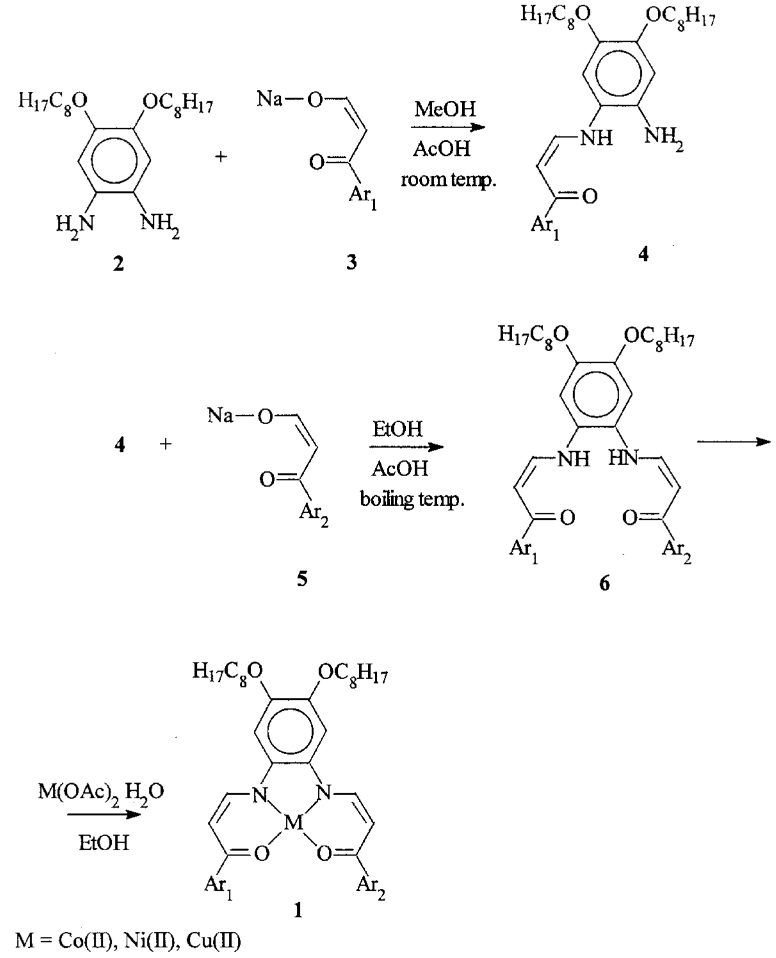


Scheme 1. Synthetic route to the *cis*-enaminoketone complexes.

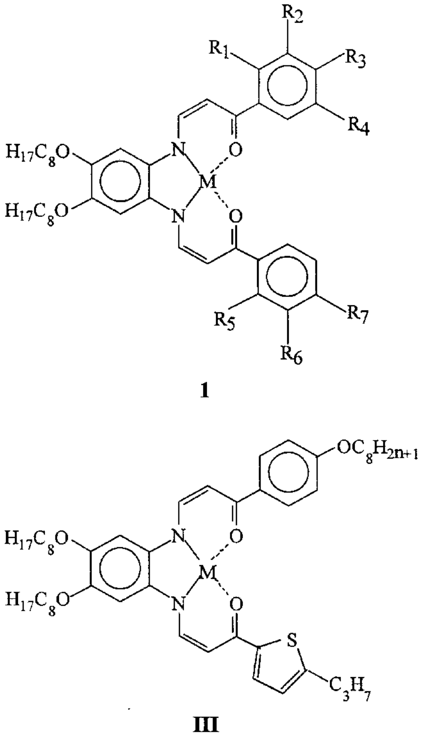
or impurities. ^{1}H NMR (CDCl$_3$) for: **4** (Ar$_1$ = 4-octyloxyphenyl) δ 0·85–1·84 [m, 45 H, OCH$_2$(CH_2)$_7$$H$], 3·49 [s, 2 H, NH$_2$], 3·90–4·04 [m, 6 H OCH$_2$], 5·97 (d, J = 7·8 Hz, H, H^2), 6·40 (s, H, H^3), 6·68 (s, H, H^6), 6·92 (d, J = 6·8 Hz, 2 H, H$^{3',5'}$), 7·31 (dd, J = 7·8, 12·2 Hz, H, H^3), 7·93 (d, J = 6·8 Hz, 2 H, H$^{2'6'}$), 11·95 (d, J = 12·2 Hz, H, NH); **1** (Ar$_1$ = Ar$_2$ = 4-octyloxyphenyl) δ 0·86–1·86 [m, 60 H, OCH$_2$(CH_2)$_7$$H$], 3·94–4·06 [m, 8 H, OCH_2(CH$_2$)$_7$H], 6·13 (d, J = 6·3 Hz, 2 H, H$^{2'}$), 6·91 (d, J = 8·8 Hz, 4 H, H$^{3\ ,5}$), 6·98 (s, 2 H, H^{3,6}), 7·43 (d, J = 6·3 Hz, 2 H, H$^{1'}$), 7·89 (d, J = 8·8 Hz, 2 H, H$^{2\ ,6}$); **4** (Ar$_1$ = 2,3,4-trioctyloxyphenyl) δ 0·84–1·88 [m, 75 H, OCH$_2$(CH_2)$_7$$H$], 3·50 [s, 2 H, NH$_2$], 3·90–4·04 [m, 10 H, OCH$_2$], 6·20 (d, J = 7·8 Hz, H, H^2), 6·40 (s, H, H^3), 6·69 (s, H, H^6), 6·70 (d, J = 8·8 Hz, H, H$^{5'}$), 7·24 (dd, J = 7·8, 12·2 Hz, H, H^3), 7·51 (d, J = 8·8 Hz, 2 H, H$^{6'}$), 11·92 (dd, J = 12·2 Hz, H, NH); **1** (Ar$_1$ = Ar$_2$ = 2,3,4-trioctyloxyphenyl) δ 0·70–1·90 [m, 120 H, OCH$_2$(CH_2)$_7$$H$], 3·90–4·03 [m, 16 H, OCH_2], 6·47 (d, J = 6·3 Hz, 2 H, H$^{2'}$), 6·66 (d, J = 8·88 Hz, 2 H, H^5), 7·01 (s, 2 H, H^{3,6}), 7·42 (d, J = 6·3 Hz, 2 H, H$^{1'}$), 7·54 (d, J = 8·8 Hz, 2 H, H^6).

2.3. *Measurements*

The mesophase identification was based on microscopic observation and X-ray studies (DRON system). A Zeiss Jenapol-U polarizing microscope, equipped with a Mettler FP82HT hot stage was used. Phase transition temperatures were determined by calorimetric measurements performed with a DSC-7 Perkin-Elmer set-up. EPR studies at high temperature were performed in the X-band on a Radiopan spectrometer equipped with a nitrogen flow atmosphere heater.

3. Results and discussion

The variety of molecular structures studied was obtained by substituting alkoxy (or alkyl) chains at *ortho*-, *meta*- and/or *para*-positions of the benzoyl (or the 5-position of the thienoyl) rings (scheme 2). The phase sequence and phase transition temperatures for the compounds of the series **I–IX** are summarized in table 1. The compounds reveal enantiotropic as well as monotropic liquid crystalline phases. The results of X-ray studies for disc-like Ni(II), Cu(II), and Co(II) complexes of group **IX** are collected in table 2.



I $R_3 = OC_nH_{2n+1}$, $R_7 = OC_mH_{2m+1}$
$R_1 = R_2 = R_4 = R_5 = R_6 = H$

II $R_3 = OC_8H_{17}$, $R_7 = C_3H_7$
$R_1 = R_2 = R_4 = R_5 = R_6 = H$

IV $R_1 = R_3 = R_7 = OC_8H_{17}$
$R_2 = R_4 = R_5 = R_6 = H$

V $R_1 = R_4 = R_7 = OC_8H_{17}$
$R_2 = R_3 = R_5 = R_6 = H$

VI $R_1 = R_3 = R_5 = R_7 = OC_8H_{17}$
$R_2 = R_4 = R_6 = H$

VII $R_1 = R_2 = R_3 = R_5 = R_7 = OC_8H_{17}$
$R_4 = R_6 = H$

VIII $R_1 = R_2 = R_3 = R_6 = R_7 = OC_8H_{17}$
$R_4 = R_5 = H$

IX $R_1 = R_2 = R_3 = OC_nH_{2n+1}$,
$R_5 = R_6 = R_7 = OC_mH_{2m+1}$
$R_4 = H$

M = Co(II), Ni(II), Cu(II)

Scheme 2. Structures of the complexes.

Table 1. Liquid crystalline phases and phase transition temperatures (°C) for the M(II) complexes.

Complex	M = Ni	M = Cu	M = Co
I			
n = *m*			
6	SmC 122 I; m.p. 132	SmC 101 SmA 108 I; m.p. 118	
8		SmA 109 I; m.p. 126	
10	Cr 136 I		
n *m*			
6 10	SmA 116 I; m.p. 131	Cr 138 I	
2 8	SmA 120 I; m.p. 119	Cr 116 I	
II	SmC 105 N 106 I; m.p. 121	SmC 80 SmA 88 I; m.p. 100	
III	SmC 104 N 106 I; m.p. 120	SmC 87 SmA 92 I; m.p. 106	
IV	m.p. 144, recryst. temp. 90		
V	SmA 116 I; m.p. 125		
VI	SmC 81 SmA 90 I; m.p. 104		
VII	m.p. 62, recryst. temp. 56		
VIII	m.p. 104, recryst. temp. 95		
IX			
n = *m*			
8	$\mathrm{Col_h}$ 68 I; m.p. below room temp.	$\mathrm{Col_h}$ 112 I; m.p. below room temp.	$\mathrm{Col_h}$ 85 I; m.p. below room temp.
10	$\mathrm{Col_h}$ 54 I; m.p. below room temp.	$\mathrm{Col_h}$ 103 I; m.p. below room temp.	$\mathrm{Col_h}$ 71 I; m.p. below room temp.
n *m*			
8 10	$\mathrm{Col_h}$ 62 I; m.p. below room temp.	$\mathrm{Col_h}$ 107 I; m.p. below room temp.	$\mathrm{Col_h}$ 64 I; m.p. below room temp.

Table 2. X-ray diffraction signals corresponding to crystallographic distances (in Å) obtained from diffractograms and (in parentheses) values calculated from the hexagonal crystallographic cell (complexes of group **IX**).

M	(1 1 0)	(2 2 0)	(3 3 0)	(3 1 0)	(4 2 0)	(0 0 1) *d*	distance between tails	cell dimensions
$n = 8$								
Ni	24·4	12·3	8·3	14·4	9·4	3·3	4·4	$a = 48{\cdot}8$
		(12·2)	(8·1)	(14·1)	(9·2)			$b = 28{\cdot}2$
Cu	24·2	12·6	8·2	14·7	9·5	3·3	4·3	$a = 48{\cdot}4$
		(12·1)	(8·1)	(14·0)	(9·1)			$b = 27{\cdot}9$
$n = 10$								
Ni	26·2	13·2	8·6	15·3	10·0	3·3	4·4	$a = 52{\cdot}4$
		(13·1)	(8·7)	(15·1)	(99·9)			$b = 30{\cdot}2$
Cu	26·7	13·5	8·9	15·5	10·2	3·3	4·4	$a = 53{\cdot}4$
		(13·4)	(8·9)	(15·4)	(10·1)			$b = 30{\cdot}8$
Co	26·1	13·3	8·6	15·3	10·1	3·3	4·4	$a = 52{\cdot}2$
		(13·0)	(8·7)	(15·1)	(9·9)			$b = 30{\cdot}1$

Nematic and smectic phases (SmA and SmC) were observed with the most elongated molecules in which terminal chains are substituted at the *para*-positions of both aromatic rings (**I**, **II**, **III**). The LC stability was found to be better for the nickel complexes for which the isotropization temperatures are higher than for the related copper complexes. The length of the terminal chains seems not to influence profoundly the phase stability. For one copper complex (**I**, with $n = 6$), X-ray measurements show that the ratio of the smectic A layer thickness to the length of the fully extended molecule along its core symmetry axis is about 1. This confirms the assumption that the averaged molecular core symmetry axes are along the smectic layer normal.

Broadening the molecular structure by substituting two chains in one of the benzoyl rings at the *ortho*- and *para*- or *ortho*- and *meta*-positions gives two isomeric compounds. For the nickel complex of structure **IV** mesophases are not observed, whereas the nickel complex of structure **V** exhibits a monotropic smectic A phase. Further modification of the molecular structure by substituting two chains into each of the benzoyl rings results in a nearly disc-shaped complex **VI** which unexpectedly forms calamitic smectic A and C phases.

For complexes with three substituents on one of the aroyl phenyl rings and two on the other ring (**VII**, **VIII**) the melting temperatures are substantially depressed, but no liquid crystal phases were observed.

Complexes with 2,3,4-substituted phenyl rings (**IX**) reveal discotic properties. They form the columnar hexagonal ($\mathrm{Col_h}$) phase stable over a broad temperature range with melting points below room temperature. The mesophase stability depends on the central metallic ion and is better for copper complexes for which the clearing points are 40–50°C higher then for the nickel complexes.

Analysis of powder X-ray diffractograms for the copper(II), nickel(II) and cobalt(II) complexes of group **IX** confirms a highly organized hexagonal columnar phase structure. The X-ray patterns for all three complexes are very similar. A relatively sharp peak corresponding to a spacing (d) between discs indicates considerable transitional order of the mesogenic cores within a column. The diffused peak related to the alkoxy chains and reflecting their liquid-like order is slightly shifted toward larger crystallographic distances (4·4 Å). From crystallographic data an estimated density of the complexes is 1·1 and 0·97 $\mathrm{g\,cm^{-3}}$ for $n = 8$ and 10, respectively. This confirms the reliability of the interpretation of the X-ray measurements.

It is worth noticing that the oxidation state (II) of the cobalt complexes was confirmed by their paramagnetic properties. The cobalt EPR spectrum is observed at liquid nitrogen temperature [6]. In NMR studies H(1) signals within the range -10 to $+20$ ppm are broadened and shifted from their usual positions due to contact and pseudo-contact interaction between protons and the unpaired cobalt electron.

4. Conclusions

Summarizing, in the mononuclear *cis*-enaminoketone complexes, the changes in number and position of the substituted chains can substantially affect the liquid crystalline structure. These metalomesogens, without any modification of the molecular core, can form either calamitic or columnar phases. Moreover the central metallic ion profoundly influences the stability of the hexagonal columnar phase, as well as the smectic phases. A similar effect on thermal stability has already been found for calamitic copper(II) and nickel(II) complexes [7]. The observed broadening of the temperature range of the $\mathrm{Col_h}$ phase for the copper(II) complexes in comparison with the nickel(II) complexes cannot be related to any obvious differences in liquid crystalline or molecular structure. The X-ray studies of the disc-like copper, nickel and cobalt complexes give almost identical crystallographic parameters. However the lower clearing temperatures for the Ni(II) complexes could result from steric hindrance exerted by additional ligands substituted in the nickel axial position. This possibility should be excluded however. The presence of axial ligands leads to a pseudo-octahedral configuration and paramagnetic properties of nickel(II) compounds. In our case the NMR spectrum obtained shows sharp signals typical for diamagnetic compounds. Moreover in the NMR spectrum there is no evidence for any unexpected substituents, and this ensures that the nickel complexes form a flat tetragonal configuration.

A possible explanation for the unexpectedly large differences in the stabilities of the hexagonal columnar phases for the complexes described could be related to the fact that there is about a 10% wider coordination plane for the copper than for the nickel complexes [8]. In a flat discotic molecule, the wider coordination plane leads to a higher anisotropy of the molecular shape and subsequently to a higher anisotropy of the polarizability, which is the main reason for mesophase formation. For rod-like molecules, the same effect decreases the shape anisotropy and disturbs mesophase formation. In the present results, the hexagonal columnar phase is more stable for the copper complexes with a larger coordination plane than for the nickel complexes. In the case of the calamitic phases, the stability is reversed and the nickel complexes with the smaller coordination plane have the higher clearing temperatures as observed here and in other experiments [7]. Contrary to the situation for previously investigated binuclear disc-like complexes [2] which construct the hexagonal columnar phase from molecular dimers, EPR studies of the discotic complexes under investigation showed that in the mononuclear complexes there is no exceptional interaction between two molecules. The columns in the liquid crystalline phase are formed by single molecular entities.

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