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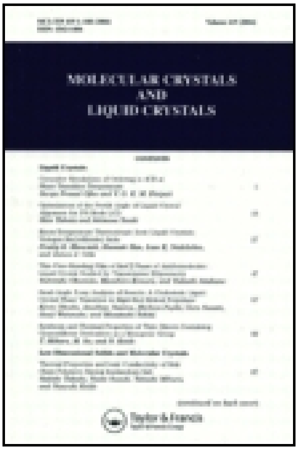

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Liquid-crystalline paramagnetic Cu(ll) complexes of enaminoketone ligands

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Liquid-crystalline paramagnetic Cu(II) complexes of enaminoketone ligands

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Studies of complexes: $[R\text{-}C_6H_4\text{-}CO(CH)_2N\text{-}Alk]_2Cu$, (I), $[Alk\text{-}CO(CH)_2N\text{-}C_6H_4\text{-}R]_2Cu$, (II), and $[R^1\text{-}C_6H_4\text{-}CO(CH)_2N\text{-}C_6H_4\text{-}R^2]_2Cu$, (III), for various terminal substituents R, R^1, R^2, are presented. For alkyl substituents R, complexes are low-melting and low-clearing nematics (group (I)) and smectics A (group (II)). Mesophases are monotropic for pure compounds, enantiotropic for mixtures. Elongation of molecular core by introduction *trans*-cyclohexyl rings into R substituents leads to enantiotropic paramagnetic mesogens. Complexes of the group (III) are high-melting and high-clearing mesogens which usually undergo decomposition in the isotropic phase. Chiral highly twisted mesophases are observed for some optically active complexes.

1. INTRODUCTION

Calamitic molecules, if form crystals having sufficiently low melting points, exhibit presence of liquid-crystalline phases. Temperature range of mesophases depends mainly on length/breadth ratio of molecular core. Within a series of compounds having a given core, isotropization temperatures are determined by terminal substituents of molecules. Anisotropy of electrical polarizability is a further factor responsible for mesophase stabilization, if compounds having substituents of similar size and shape are compared.

In contrast to classical LC molecules, a relation between molecular structure and properties for sanidic metallomesogens is not well recognized. The reasons are limited data and theoretical works in this novel research area.[14] This is an

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important limitation in designing compounds having assumed properties, e.g. those necessary for applicational purposes.

Among paramagnetic calamitic metallomesogens, a lot of copper(II) and oxovanadium(IV) complexes of salicylideneimines and β-diketones have been synthesised (see references cited in ref. 1) and their properties were studied by various methods[2-13]. Recently, complexes of enaminoketones were reported as novel promising materials for liquid crystal studies[14]. In this work we compare mesogenic properties of some new enaminoketone derivatives[14] belonging to three groups of copper(II) complexes having general formulae presented in Fig.1. As it is shown there, the compounds differ in the shape anisotropy of their rigid core. More anisotropic molecules belonging to two series, having formulae presented in Fig.2, were also examined to discuss the role of additional cyclohexyl rings as well as role of terminal alkyls in stabilization or destabilization of mesophases.

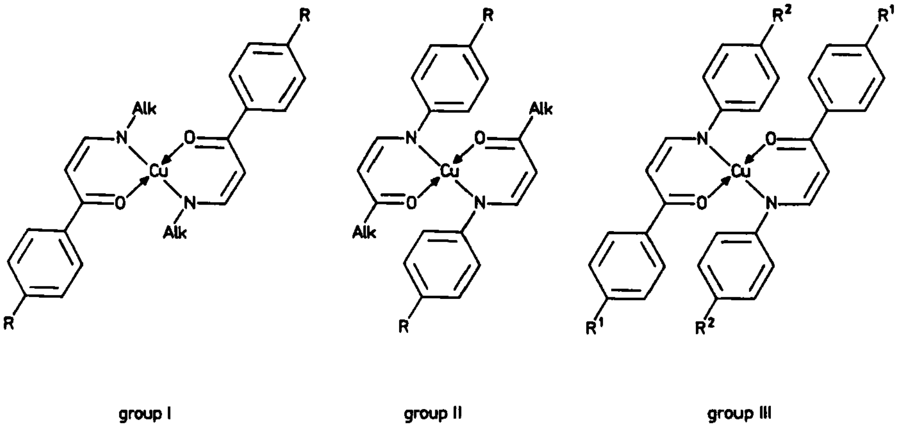

FIGURE 1 General formulae for complexes of groups I, II, III.

2. RESULTS

2.1. Complexes of the group (I)

A homologue series with R = $H_{13}C_6O$ and Alk = C_mH_{2m+1} substituents, has been synthesized for n = 7 to 18. These compounds form crystals which melt sharply at about 70 - 80°C, to an isotropic liquid difficult to be supercooled. Liquid-crystalline state can be observed exceptionally for pure compounds, only in case of extremely rapid cooling. However, enantiotropic nematic phase is clearly seen

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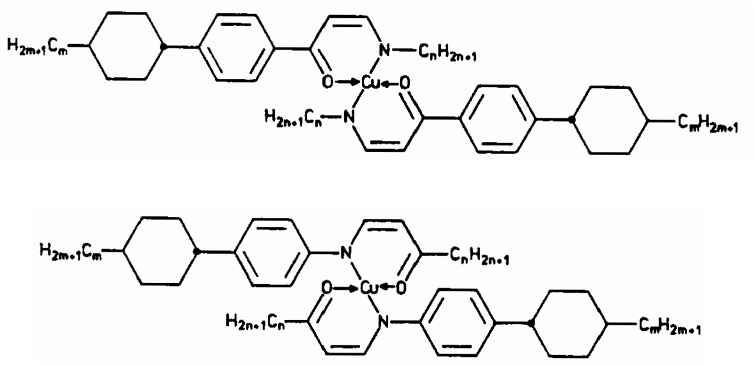

FIGURE 2 Formulae for series IV (upper) and V (lower) of *trans*-cyclohexyl complexes.

in binary systems for their near eutectic compositions. E.g., in the contact cell between homologues n = 8 (m.p. = 72.7°C (59.9 J/g)) and n = 12 (m.p. = 78.0°C (77.2 J/g)), the nematic phase appears at 58°C, ca. 3°C above eutectic temperature. Other mesophases were not observed in this mixture as well as in other binary systems. Evidently, by proper choice of mixture components, low-melting materials with stable paramagnetic nematic phase might be easily obtained.

For pure compounds, the mesophase becomes enantiotropic in case of more elongated R groups, as described below for complexes (IV). Resulting compounds usually reveal higher melting points. However, this disadvantageous effect may be limited by introduction of some branched terminal chains. E.g., the complex [R = $H_{13}C_6N(CH_3)$-C_6H_4-N=N, Alk = $C_{10}H_{21}$] melts at relatively low temperature, 81.7°C (44.7 J/g), to a viscous nematic phase having cl.p. 95.6°C (1.1 J/g).

2.2. Complexes of the group (II)

Some compounds with alkyl substituents R = OC_nH_{2n+1} and Alk = $H_{2m+1}C_m$ have been synthesized for various n and m values. Similarly to their analogues from series (I), resulting compounds are also monotropic mesogens. Some of them can be supercooled to reveal, in the range of 50 - 60°C, the presence of the smectic A phase. To enhance the mesogenic properties we synthesized compounds with R = $COOC_nH_{2n+1}$ and Alk = $H_{2m+1}C_m$ substituents. These compounds require only small, e.g. 3°C, supercooling, thus enabling measurements of the isotropization parameters, which appear typical for calamitic mesogens (see Tab.I).

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Table.I. Temperatures (in °C) and, in parentheses, entalpies (in J/g) of phase transitions for complexes $[H_{2m+1}C_m\text{-}CO(CH)_2N\text{-}C_6H_4\text{-}COOC_nH_{2n+1}]_2Cu$.

m, n	7, 6	8, 2	9, 2	11, 2	11, 4	11, 5 [a)]	11, 6
Cry-Iso	74.1	74.5	71.9	65.6	59.2	58.6	68.7
	(61.3)	(50.1)	(48.2)	(31.7)	(65.1)	(66.3)	(54.2)
SmA-Iso	47.8	59	60	62.8	55.4	38.5	58.1
	(12.3)	(11.7)	(11.8)	(12.7)	(12.6)	(8.5)	(13.8)

[a)] ester of optically active S(-)-2-methyl-1-butanol.

Some of above compounds, e.g. that for m,n = 11,2, form directly the smectic phase when melted. Unstable crystals, which are obtained in the synthetic procedure, melt at 59.4°C. Thus, for this compound we were able to measure magnetic susceptibility in the crystal and smectic phases. In room temperature susceptibility of the complex is 1.22×10^{-6} emu/g, whereas that of the parent ligand is -6.25×10^{-7} emu/g. Thus, corresponding magnetic moment $\mu^{eff} = 1.86\ \mu_B$. In the temperature range from -170 to 80°C μ^{eff} remains almost constant and no distinct long-range magnetic interactions were found. Similar Curie-law type behavior was observed both for rod-like salicylidenimine and discogenic diketonate complexes.[15] For some crystalline diketonate copper(II) complexes, however, the presence of one-dimensional antiferromagnetic order was also reported.[16]

Properties of compounds having alkyl substituents $R = C_nH_{2n+1}$ are similar. Although clearing temperatures are lower than for ester derivatives, the SmA mesophase can be usually observed. E.g., the complex [$R = C_{14}H_{29}$, $Alk = H_{15}C_7$] has m.p. = 56.7°C (62.8 J/g) and cl.p. = 30°C. Obviously, stable low melting smectogenic substances are easily derivable among eutectic mixtures of the complexes from the group (II).

2.3. Complexes of the group (III)

Complexes having fixed $R^1 = H_{13}C_6O$ and various R^2 terminal substituents were synthesized. As it is presented in Tab.II, they are high-melting mesogens, with the only exception of that having R^2 = SCN group. This particular compound undergoes an unrecognized irreversible exothermic reaction when melted. Some of remaining compounds undergo decomposition at high temperatures, ca. 200°C, especially in the isotropic phase. Only halogen derivatives are pure smectics A, other compounds are nematics or both these phases are observed. For longer or more complex R^2 substituents, more ordered phases, including the SmC phase also exist.

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All described compounds (III) are of rather limited applicability because their mesophases are not very stable as they exist in high temperatures only. However, some depression of the melting temperature seems possible for both alkyl and alkoxy derivatives, by optimization the chain length of both terminal groups. Actually for the complex [R^1 = $H_{15}C_7O$, R^2 = OC_8H_{17}] m.p. drops to 170°C,[17] as compared to the complex [R^1=$H_{13}C_6O$, R^2=OC_6H_{13}] having m.p. = 192°C. As our tentative results indicate, a more effective way to lower the melting temperature of pure complexes is the introduction of lateral substituents into mesogenic core. For example, in comparison to the p-toluidine derivative (data presented in Tab.II, R^2=CH_3), a 2,4-xylidine analog reveals distinctly lowered m.p. = 139.5°C (45.5 J/g) but unchanged cl.p. = 189°C (1.6 J/g).

Table.II. Temperatures (in °C) and, in parentheses, enthalpies (in J/g) of phase transitions for complexes [$H_{13}C_6O$-C_6H_4-CO(CH)$_2$N-C_6H_4-R^2]$_2$Cu.

R^2	Cry		SmC		SmA		N		Iso
F		177.7 (58.6)		–		197.8 (10.0)		–	
CN		191.3 (37.4)		–		–		210[b]	
SCN		161[a]							
NO_2		200.4 (59.8)		–		–		217[b]	
CH_3		173.3 (52.5)		–		–		189.6 (1.0)	
C_2H_5		157.5 (48.0)		–		–		181.7 (1.4)	
C_4H_9		140.9 (49.8)		–		181.7 (2.4)		188	
SC_2H_5		175.7 (45.6)		–		188[b]		–	
OC_6H_{13}		191.5 (49.6)		206 (1.5)		215 (8.2)		–	
$COOC_6H_{13}$		166.5 (40.4)		171.2 (0.16)[c]		179 (9.8)		–	

[a] melting followed by an irreversible chemical reaction; its entalpy is -83 J/g;

[b] thermal decomposition in isotropic phase;

[c] a second order phase transition, data in parentheses is the specific heat change (in J/(K·g)).

2.4. Complexes (IV), (V) with *trans*-cyclohexyl rings

Expecting of elongation of rigid molecular core would result in an extension of mesophases temperature range we modified some complexes of groups (I) and (II) by using alkyl-*trans*-cyclohexyl R substituents instead of the alkyl ones. We synthesized some homologoues series, (IV) and (V), with Alk^1 = H_5C_2 or H_7C_3 and Alk^2 = C_nH_{2n+1}. 1,4-disubstituted-*trans*-cyclohexyl ring rather than phenyl ones were chosen to decrease melting temperatures and compounds having m.p. in the range 112 - 163°C (series (IV), m=2) or 91 - 122°C (series (V), m=2) were thus obtained. Mesophase transitions temperatures for resulting compounds are presented in Fig.3. It is seen that both groups behave in diametrically different modes. Only enantiotropic nematic phase is formed for complexes (IV). The phase is strongly destabilized by increasing length of terminal chains. In contrast, mesophases (N and SmA), being observed for complexes (V), are stabilized under the same conditions.

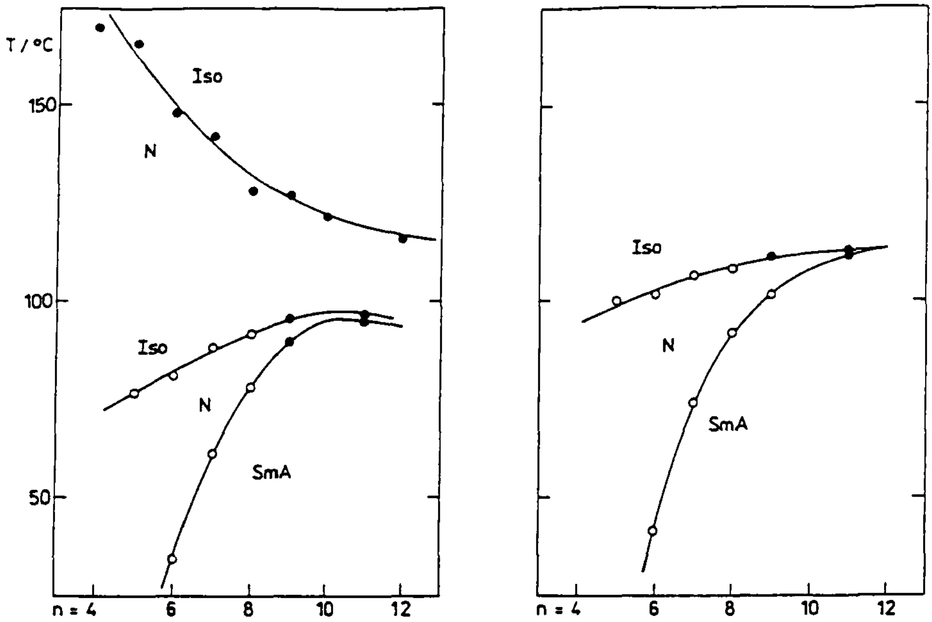

FIGURE 3 Mesomorphic phase transitions of the complexes (IV) (upper curve, left) and (V) (remaining curves) for series m = 2 (left) and m = 3 (right). Full dots denote enantiotropic transitions.

Within group (IV) of *trans*-cyclohexyl complexes two other series with $Alk^1 = H_{13}C_6$[18a] and $H_{21}C_{10}$[18b] were synthesized in order to obtain low melting nematogens. The best compound, $Alk^1 = H_{21}C_{10}$, $Alk^2 = C_4H_9$ has cl.p. = 149.8°C (2.25 J/g), but still unsatisfactorily high m.p. = 96.4°C (31.7 J/g). Of interest are properties of compounds having branched terminal chains. Methyl group, if attached to α- or β-carbon atom of Alk^2 substituents, produces very large[18b] or small depression of isotropization temperature, respectively. Thus, optically active mesophases can be easily studied for β-substituted complexes. For example, the complex [$Alk^1 = H_{13}C_6$, Alk^2 = S(-)-$CH_2CH(CH_3)C_2H_5$] reveals strongly twisted cholesteric and blue phases without selective light reflection in the visible range.

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The phase sequence is: Cry 121.3°C (31.2 J/g) N* 152.4°C (0.11 J/g) BP 154.3°C (1.4 J/g) Iso, and the compound has no remarkable tendency to crystalize in room temperature.

3. DISCUSSION AND CONCLUSIONS

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Besides complexes described above, other enaminoketone copper(II) complexes having more developed terminal groups have been also examined by us. In result, paramagnetic mesophases were observed for about a hundred of compounds. In spite of limitation of experimental material, it is evident that there is no correlation between length/breadth ratio and mesophase stability. This is the case irrespective whether the ratio is referred to molecular rigid core only or to molecule as whole. The shortest core is present in complexes of the group (II), which form the SmA phase. In contrast, longer molecules of complexes (I) form ordered nematic, thus less ordered phase. Complexes of the groups (I), (III) have the same core length, but reveal different properties of mesophases. In the latter case molecular core cannot be planar for steric repulsions between phenyl rings. However, there is no hindrances in these intermolecular interactions which lead to an orientational ordering. The most stable mesophases are just formed by complexes of the group (III), probably in connection with higher polarizability of the core. In result, it can be concluded that mesophase stability does not depend simply on molecular elongation but is dependent on more subtle details of molecular geometry and influenced by electric charge distribution within molecules.

Within a given group of complexes, compounds behave in usual way; the longer is the molecular core, the more stable mesophases appear. Terminal substituents stabilize or destabilize mesophases, depending on the core structure. Probably, it reflects different molecular geometry of complexes (I) and (II) (or (IV) and (V)) as a result of possible slight nonplanarity of N-substituents with respect to the enaminoketone ring. Differences in electric charge distribution along molecules may be also important. Other feature discriminating both groups of complexes is the type of preferred mesophases - smectic A and nematic for group (I) and (II), respectively.

Although coloured,[14] the enaminoketone copper(II) complexes are not useful as dyes for guest-host displays because of their rather low dichroism. However, the complexes are promising as low-melting and high-soluble paramagnetic mesogens. Although there are several ways to obtain low-melting materials, as optimization

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of type and length of terminal substituents, preparation of asymmetric complexes or eutectic mixtures, introduction of lateral substituents or branched terminal chains, pure compounds having required properties have not been obtained yet. In contrast, satisfying mixtures of complexes are easy to prepare Opticaly active complexes are of interest because of duplication of their terminal chiral substituents. In result, their twist-dependent properties are more pronounced than those of parent ligands.

4. EXPERIMENTAL

All complexes are obtained in the reaction of parent ligands with copper(II) acetate in boiling alkaline solution in methanol. Products, which precipitated when cooled reaction mixtures, were recrystallized from an appropriate hydrocarbon, usually hexane. Ligands were synthesized in the manner described previously.[14] Mesophases were identified basing on their textures, conoscopic figures and DSC peaks. In some doubtful cases, identifications were confirmed by tentative phase diagrams with reference compounds. Microscopic observations were performed using a polarizing Zeiss microscope equipped with the Mettler hot stage. Phase transition temperatures and thermal effects were determined from DSC thermograms taken on Perkin-Elmer DSC-7 set-up. A scan 2.5 to 10°C/min, suited to examined compounds, depends on their thermal stability, temperature distance between phase transitions, range of supercooling necessary to observe monotropic transitions, etc.

Paramagnetic properties of complexes were confirmed in solutions, crystals, mesophases and isotropic liquids by ESR spectra. Magnetic susceptibility was determined by applying the Gouy balance method.

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