Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Pyzuk, Wieslaw , Krowczynski, Adam , Chen, Li , Gorecka, Ewa and Bickczantaev, Ildar(1995) 'Binuclear liquid crystals incorporating dia- or para-magnetic transition metals', Liquid Crystals, 19: 5, 675 — 677

To link to this Article: DOI: 10.1080/02678299508031083

URL: http://dx.doi.org/10.1080/02678299508031083

LIQUID CRYSTALS, 1995, VOL. 19, NO. 5, 675–677

Binuclear liquid crystals incorporating dia- or para-magnetic transition metals

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(*Received 3 April 1995; accepted 15 June 1995*)

Discotic binuclear Ni(II) and Cu(II) complexes of 1,2,4,5-tetrakis-(2′-alkyl-2′-homoalkylcarbonylvinylamino)benzene ligands were synthesized. These compounds exhibit columnar liquid crystal phases.

1. Introduction

Metallomesogens have attracted considerable attention in recent years owing to the possibilities of practical applications (see reviews on metallomesogens [1]). Among the reasons for initiating and continuing studies of paramagnetic liquid crystals there has been the idea of producing ferromagnetic mesophases [2]. In spite of numerous efforts, no such phases have been found among rod-like liquid crystal materials. Also columnar discotic phases, although containing chains of paramagnetic species, do not exhibit ferromagnetic properties. Actually it is well established that spontaneous spin ordering cannot occur in one-dimensional Ising systems [3]. In order to generate a macroscopic magnetic ordering a number of interacting chains is necessary. A step in a systematic approach to the design and study of such systems involves mesogenic multinuclear metal complexes. In this communication we report the synthesis and mesomorphic properties of some binuclear complexes (**6**) bearing dia- or para-magnetic metal centres.

2. Synthesis

Binuclear complexes (**6**) were synthesized according to the scheme from enaminoketone ligands (**5**). The latter compounds were obtained from freshly prepared 1,2,4,5-tetra-aminobenzene (**2**) and a symmetrical dialkyl ketone (**3**) formulated in a Claisen reaction, in a method that was used previously to obtain rod-like mesogens [4]. The crude oily product (**5**) was not mesomorphic and was used, without further purification, to obtain homometallic complexes (**6**), hereafter abbreviated as $M_2\mathrm{T}n/n+1$. Mononuclear complexes were also derived as intermediates for the synthesis of heterometallic complexes which will be described elsewhere. The complexes $\mathrm{Ni_2T}n/n+1$ and $\mathrm{Cu_2T}n/n+1$ were purified by crystallization from octane/toluene and gave red microcrystals for which elemental C, H and N analysis were satisfactory. As an example, the ^{1}H NMR spectra for $\mathrm{Ni_2T6/7}$ ($\mathrm{CDCl_3}$): $\delta = 0{\cdot}82$–$0{\cdot}98$ (m, 24 H, $\mathrm{CH_2)_3\underline{CH_3}}$ and $\mathrm{CH_2(CH_2)_4\underline{CH_3}}$), 1·2–1·75 (m, 56 H, $\mathrm{CH_2(\underline{CH_2})_3CH_3}$ and $\mathrm{CH_2(\underline{CH_2})_4CH_3}$), 2·25–2·50 (m, 16 H, $\mathrm{\underline{CH_2}(CH_2)_3CH_3}$ and $\mathrm{\underline{CH_2}(CH_2)_4CH_3}$), 7·31 (s, 4 H, $\mathrm{H^1}$), 7·39 (s, 2 H, $\mathrm{H^3}$, $\mathrm{H^6}$) is consistent with the molecular structure. The broad NMR signals observed for the Cu(II) complexes confirmed their paramagnetic nature. EPR studies performed on the Cu(II) complexes provided the averaged-factor $g_0 = 2{\cdot}087$, close to that obtained for the Cu(II) ion in a planar nitrogen–oxygen environment [5].

Besides the copper and nickel complexes, vanadoxyl complexes were also obtained, but they were found to be thermally unstable. These complexes undergo decomposition above 100–150°C, in contrast to the Ni(II) complexes which are stable even above 250°C, and the Cu(II) derivatives which have an intermediate stability.

3. Results and discussion

The phase transitions of the $M_2\mathrm{T}n/n+1$ complexes were studied by polarizing optical microscopy and differential scanning calorimetry (DSC). The transition temperatures and enthalpies are collected in the table. All the phases, with the exception of the high temperature phase D, are solids, that is, they are true crystals or highly ordered three-dimensional crystalline smectics. In the discotic phase D, the samples are sensitive to mechanical

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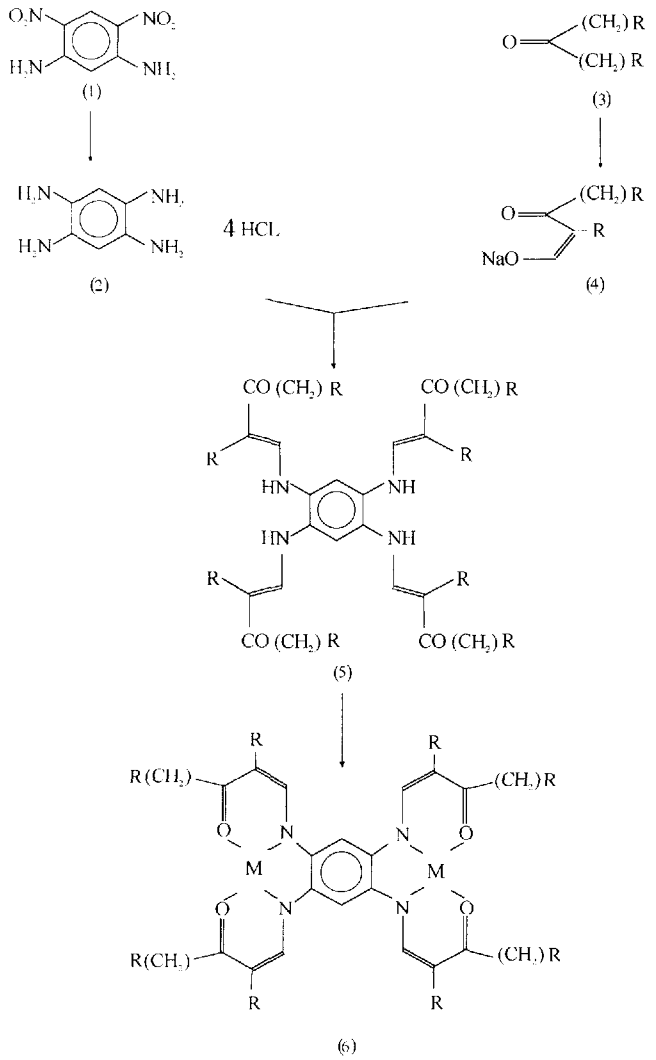
0267–8292/95 $10·00

Table. Transition temperatures (in °C) and in parentheses the enthalpy changes (in kJ mol^{-1}) for M_2T*n*/*n* + 1.

Complex	Phase behaviour			
Ni_2T5/6		P2 177·0 (11·7)	P1 197·1 (30·4)	D 231·1 (24·8) I
Cu_2T8/9	Cr 148·9 (57·5)	P2 153·0 (12·4)	P1 178·6 (47·7)	D 200·0 (24·0) I
Cu_2T10/11	Cr 143·2 (39·2)	P2 146·4 (4·6)	P1 164·0 (48·7)	D 182·6 (25·5) I
Cu_2T12/13		P2 135·0 (9·0)	P1 147·5 (56·6)	D 166·1 (23·9) I

Cr, crystal; P, unidentified phase; D, discotic phase; I, isotropic phase.

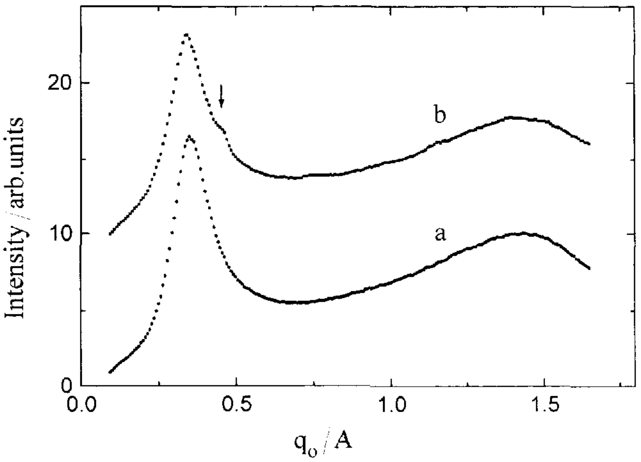


where *R* is alkyl chain

Scheme. Reagents and conditions (**1**) and (**2**): Zn, HCl_{aq}/EtOH (1 : 1); (**3**) and (**4**) Na, H.COOEt, Et_2/THF; (**2**) + (**4**) and (**5**): MeOH, AcOH room temp., 12 h; (**5**) and (**6**) BuOH, $M(OAc)_2$ H_2O in MeOH, 5 min reflux.

stress. Under stress, a viscous birefringence or formation of a weakly dichroic paste has been observed. On cooling the isotropic liquids, the dendritic texture appeared. On further cooling, no orthogonally oriented domains were found, suggesting that the discotic D phase—probably hexagonal, but see X-ray data—remains optically biaxial. The same columnar D phase was observed for both the Ni(II) and Cu(II) complexes, as proved by miscibility studies.

The structure of the discotic mesophase was also investigated by X-ray scattering measurements. The compound Ni_2T5/6 were chosen for its good thermal stability. At high temperature, the pattern obtained for powder sample revealed only two strong and relatively broad peaks (see the figure). The peak positions correspond to the intermolecular distances 18·5 and 4·4 Å. The former can be attributed to the effective column diameter, whereas the latter is probably related to the length of the melted alkyl chains. A reflection band corresponding to the intracolumnar disc separation, which is expected to be at *c*. 3·3 Å, a typical Ni–Ni length [6], was absent from the X-ray diffractograms. A comparison of molecular dimensions (from 20·3 × 28·3 Å for the fully extended alkyl chain conformations and 10 × 15 Å for the rigid core only) with the intermolecular distance of 18·5 Å suggests the



X-ray diffractograms of discotic phase (D) of Ni_2T5/6 at 212°C (*a*) and 192°C (*b*). The arrow indicates the position of the peak related to herring-bone order (see text).

occurrence of a significant interdigitation of the peripheral alkyl chains, which must be accompanied by a remarkable freezing of molecular rotation around the axis normal to the disc plane. The increasing interdigitation with longer alkyl chains agrees with the observed destabilization of mesophases for the higher homologues of the $Cu_2Tn/n + 1$ series, whilst the hindered rotation of the molecules results in the optical biaxiality of the mesophases.

Characteristics of the columnar phase D is a small correlation length of the positional order (less than 100 Å), as estimated from the analysis of the shape of the low angle X-ray scattering peak from powder samples. Moreover, there is a lack of other signs of intermolecular ordering in the high temperature range. Therefore the D phase could be built up from liquid-like or bond-oriented columns. Attempts to verify the structure by X-ray diffraction on monodomains have failed due to difficulties in obtaining well-aligned samples. However, the temperature evolution of the powder spectra suggests a rather hexatic-like structure. On cooling the mesophase below 200°C, an additional weak signal appeared in the low angle range. The relevant spacing of 13·6 Å, that is 1/1·36 of the value of the main band, might point to a local herring-bone ordering [7] which could develop within the hexatic structure as a result of the restricted molecular rotation expected for highly interdigitated alkyl chains.

So far binuclear paramagnetic mesogens have been reported among alkyl carboxylates [1] and some Schiffs base complexes [8] not forming metallic chains, and among very recently synthesized derivatives of planar bisphthalocyanines [9]. Our new discotic complexes are capable of forming columnar discotic phases with restricted molecular rotation, and in such cases, the existence of interacting transition metal chains within a single column might be expected. Magnetic studies of the spin interactions between metal centres are now in progress.

This work is a contribution to KBN Project 2P303 024 07. Synthetic work was supported in part by BST-94/95 and X-ray measurements by NSF grant no DMR 89-20147 (ALCOM) and the Characterization Facilities of the Liquid Crystal Institute, Kent State University.

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