Novel Discotic Liquid Crystals obtained from Substituted Bis(dithiolene)nickel Complexes

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The bis[1,2-di(*p*-n-alkoxyphenyl)ethane-1,2-dithione]nickel complexes (**4a**) and (**4b**), novel disc-like complexes with four n-alkoxy side chains, exhibit a discotic mesophase.

Only a few organic transition metal complexes exhibit discotic mesomorphism. The only complexes known to date are tetrasubstituted¹⁻³ or octasubstituted β -diketonato copper(II) complexes,⁴ and an octasubstituted copper phthalocyanine.⁵ In focusing our interest on preparation of a novel complex exhibiting discotic mesomorphism, two new disc-like complexes, bis[1,2-di(*p*-n-nonyloxyphenyl)ethane-1,2-dithione]-nickel (**4a**) and bis[1,2-di(*p*-n-undecyloxyphenyl)ethane-1,2-

dithione]nickel (4b), have been synthesized by a new method. It was found that the complexes exhibit discotic mesomorphism. These are the first nickel complexes which are discotic liquid crystals, as far as we are aware.

Syntheses of the present nickel complexes were carried out using the method illustrated in Scheme 1. The unsubstituted complex, bis(1,2-diphenylethane-1,2-dithione)nickel, has been prepared from benzoin in 35% yield by the method



ö ÓН (5)

 $THF = tetrahydrofuran, dpe = Ph_2PCH_2CH_2PPh_2$

a;
$$\mathbf{R} = C_9 H_{19}$$

b; $\mathbf{R} = C_{11} H_{23}$

Scheme 1. Synthesis of the bis(dithiolene)nickel complexes (4a,b).

reported by Schrauzer et al.⁶ We found that the substituted benzoins (5a,b) cannot be synthesized from p-nalkoxybenzaldehyde by condensation, but that the substituted benzils (3a,b) can be transformed into the desired target complexes (4a,b) in 56.8% (4a) and 58.6% yield (4b), respectively. † The substituted benzils (3a,b) were synthesized from the substituted stilbenes (2a,b) in 32.9% (3a) and 28.4% yield (3b) respectively, t by a modification of Sonoda's method.7 Unsubstituted benzil was obtained from transstilbene in 86% yield, although Sonoda et al. reported that benzil can be selectively synthesized from diphenylacetylene in 84% yield.⁷ The substituted stilbenes (**2a**,**b**), could be easily **Table 1.** Transition temperatures (T_t) and enthalpy changes (ΔH_t) of the nickel complexes, (4a) and (4b).

MgBr



* Phase nomenclatures: K = crystal, D = discotic liquid crystal, I.L. = isotropic liquid. b 1 kcal = 4.184 kJ.

prepared from the corresponding p-n-alkoxybromobenzenes (1a,b) in relatively good yield; 49% for *cis*- and *trans*-isomers of (2a) and 61% for cis- and trans-isomers of (2b), using the method reported by Tamao et al.8 Although the Wittig reaction is conventionally used for the preparation of stilbenes,^{9,10} this method was very tedious and the yield of the substituted stilbenes was low (24%, 9 27%¹⁰).

It was found that the complexes (4) exhibit discotic mesomorphism. The phase transitions for the complex (4a,b) are summarized in Table 1. The K_2 crystals of (4a) could be obtained as black needle-like crystals only by recrystallization from ethyl acetate. The K2 crystal could be not obtained by any thermal treatment. When the isotropic liquid of (4a), which has a clearing point at 189 °C, was cooled down to room temperature, it turned into another crystalline phase K_1 (plate-like) via the D phase. The same behaviour was observed for (4b). However, recrystallization of (4b) from ethyl acetate always gave a mixture of K_2 (needle-like) crystals and K_1 (plate-like) crystals (small amount). So, we were unable to determine the enthalpy change (ΔH_1) of the phase transition at 118 °C.

The phase between 109 and 189 °C of (4a) and the phase between 88 and 177 °C of (4b) were established as being the same type by miscibility tests using differential scanning calorimetry and by observation of the phase using a polarizing microscope. It was found that the D phase of (4a) is totally miscible in the D phase of (4b), and that a eutectic point exists at 52% of (4a) at 40 °C. Both of the discotic phases gave a clear zone surrounded by a lustrous ring which resembled the appearance of the discotic mesophase D1 in C8-CuII reported previously.3 Therefore it was concluded that the D phases of (4a) and (4b) are both discotic mesophases. These are the first nickel complexes exhibiting discotic mesomorphism in transition metal complexes.

Discotic liquid crystals have potential as one-dimensional organic conductors, because they readily form a columnar structure essential to organic conductors.¹¹ There have been reports of charge transfer complexes formed between π -donor discotic liquid crystals and tetracyanoquinodimethane etc.5.12 The nickel complexes (4a,b) are the first examples of π -acceptor discotic liquid crystals. The half-wave potentials for the reduction of the nickel complexes (4a,b) determined by cyclic voltammetry are -0.06 V for (4a) and -0.07 V for (4b) (vs. a saturated calomel electrode in methylene chloride solution).

[†] These complexes gave satisfactory C and H analyses, and the structures were confirmed by 1H n.m.r., i.r., and electronic spectroscopy

[‡] Both of the substituted benzils (3a,b) exhibit 'double melting behaviour': (3a) m.p. 60 and 68 °C, (3b) m.p. 66 and 71 °C. The multiple melting behaviour of glycerides is well known: D. Chapman, Chem. Rev., 1962, 62, 433.

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