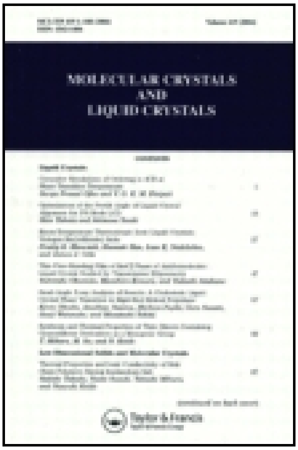

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Synthesis and Mesogenic Properties of Some β-Diketones and Their Copper (II) and Palladium (II) Chelates

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Synthesis and Mesogenic Properties of Some β-Diketones and Their Copper (II) and Palladium (II) Chelates†

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The paper deals with the synthesis and mesomorphic properties of some new copper (II) and palladium (II) complexes. Some of the ligands which are used to form these complexes also exhibit mesophases. The different mesophase types have been characterised. While none of the ligands shows a nematic phase, some of the copper and palladium chelates do exhibit a metastable nematic phase. A homologous series of eight bis[1-(p-n-alkylbiphenyl)3-(phenyl) propane 1,3-dionato] copper (II) has been prepared and all the homologues show a metastable nematic phase. A plot of the nematic → isotropic transition temperatures versus the number of carbon atoms in the alkyl chain shows smooth curve relationship.

Keywords: *β-diketone, ligand, chelate, smectic*

INTRODUCTION

In the last few years, we have reported[1–3] several copper β-diketonates exhibiting the nematic phase with paramagnetic properties, for example, bis[1-(p-n-decylbiphenyl)3-(p-substituted phenyl) propane 1,3-dionato]copper (II) complexes. Recently, Muhlberger and Haase[4] have also observed a monotropic nematic phase in some bis{1-[4-trans-(4-alkylcyclohexyl) phenyl]-alkyl propane-1,3-dionato}copper II) complexes. Apart from these there is no other report of a nematic phase in metal β-diketonates. However, the nematic phase has been observed in several copper (II) complexes of N-salicylideneaniline derivatives and in some palladium (II) azo complexes.[5–9] In this paper we wish to report the synthesis of many more such copper (II) and palladium (II) β-diketonates which exhibit the nematic phase. A homologous series of copper (II) chelates has been synthesised to examine the

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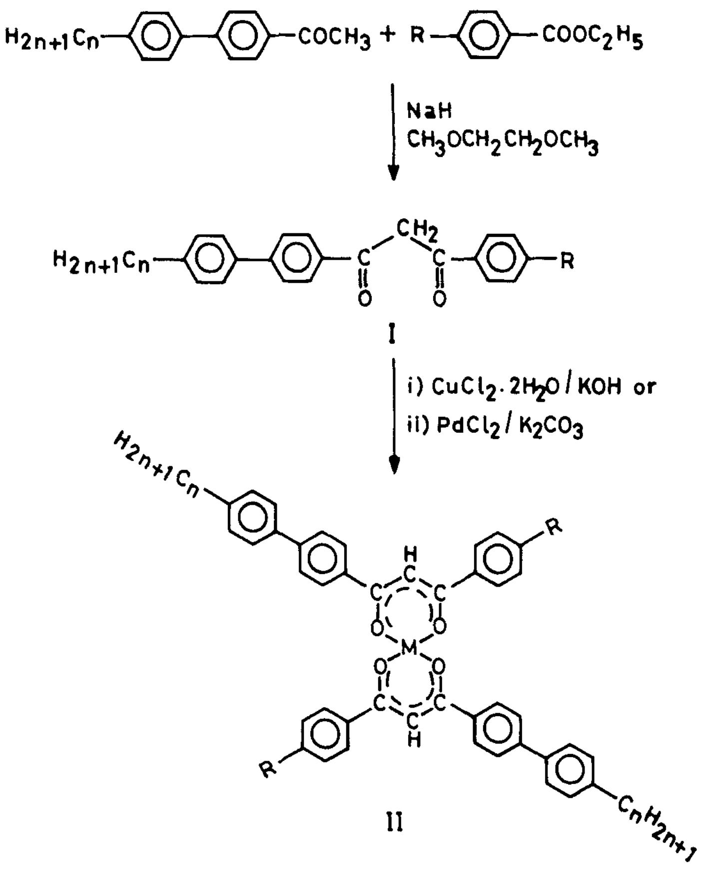
† Part of a paper presented at the Post-IUPAC International Symposium on the Synthesis of Natural Products, Bangalore, February 12 and 13, 1990, Abstracts Page 35.

nature of the plot of the nematic isotropic transition temperatures versus the number of carbon atoms in the alkyl chain in such chelates. Many of the ligands used to prepare these complexes also exhibit mesophases. These mesophases have been characterised as smectic E and smectic A based on optical observations.

EXPERIMENTAL

4-n-Alkyl-4′-acetylbiphenyls were prepared as described previously.[10] Commercial ethylbenzoate was freshly distilled prior to use. The other p-substituted ethylben-



M = Cu or Pd

a) R = H, n = 5, 6. . . .12

b) R = Cl, Br, CN, CH_3, C_2H_5, OCH_3 or OC_2H_5, n = 12

FIGURE 1 General method for the preparation of the β-diketones and their copper (II) and palladium (II) chelates.

TABLE I

Transition temperatures (°C) and enthalpies of transitions (Kcals/mole) of β-diketones I, b[$]

Compound number	R	K		S_E		S_A		I
1	CH_3	.	101.5 5.25	–		.	111.0 0.95	.
2	C_2H_5	.	73.5 5.0	–		.	100.5 1.01	.
3	OCH_3	.	108.5 7.59	–		–		.
4	OC_2H_5	.	112.5 5.6	–		(.	102.0) 0.73	.
5	Cl[a]	.	127.5 11.54	(.	116.0)* –	.	143.0 1.05	.
6	Br[b]	.	139.0 7.88	(.	131.4)* –	.	143.5 0.59	.
7	CN	.	126.0 12.19	–		.	145.0 0.75	.

[$] See Table III for abbreviations.

[a] This compound has an additional smectic phase below S_E phase.

[b] There is a smectic phase above the S_E phase at 131.8°C. Both of these smectic phases have not been identified.

* The enthalpies could not be measured.

zoates were obtained by the esterification of their respective carboxylic acids using ethanol. All the β-diketones and their corresponding copper (II) and palladium (II) chelates were synthesised according to the general scheme shown in Figure 1. A typical procedure for the preparation of these is given below.

1-(p-n-dodecylbiphenyl)3-(p-methylphenyl)propane 1,3-dione, I b, R = CH_3

A mixture of p-n-dodecyl-p′-acetylbiphenyl (5.46 g, 15 mmol), ethyl p-methylbenzoate (2.46 g, 15 mmol) and anhydrous 1,2-dimethoxyethane (100 ml) was placed in a 250-ml round bottom flask fitted with a reflux condenser, a calcium chloride protective tube and an inlet tube for dry nitrogen. The mixture was stirred, sodium hydride (0.9 g, 30 mmol) dispersed in paraffin oil was added, the mixture refluxed for four hours and stirred at room temperature overnight. The reaction mixture was decomposed with water (5 ml) followed by dilute hydrochloric acid until it was acidic. The pale yellow stew so obtained was extracted with ether (3 × 100 ml) the combined ethereal solution washed with water (3 × 100 ml) and dried (Na_2SO_4). Removal of solvent afforded a pale yellow material, which was chromatographed

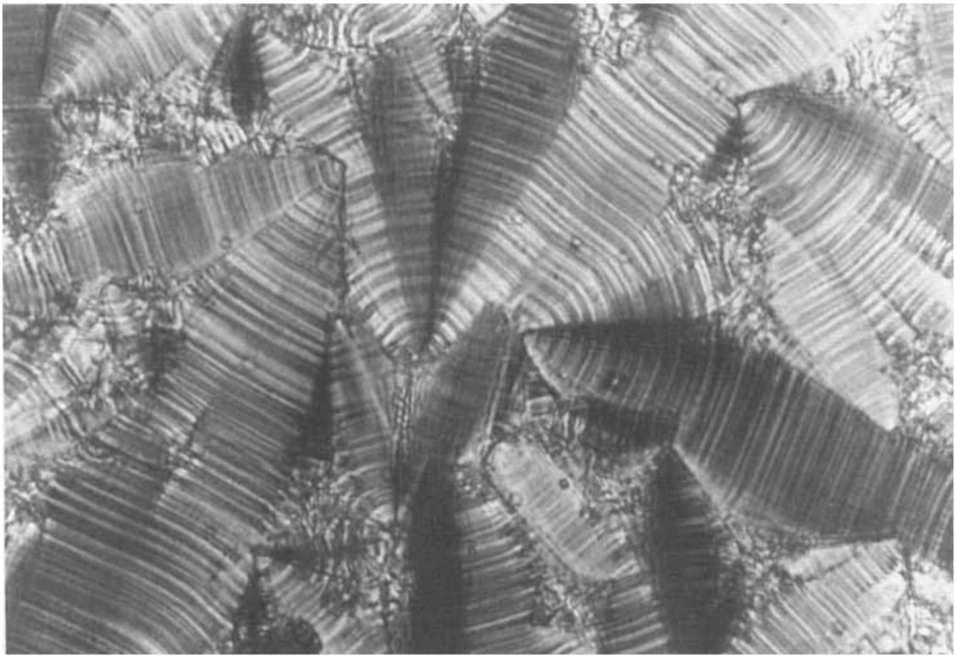


FIGURE 2 Photomicrograph of the smectic E phase of β-diketone I, $n = 12$, R = Cl at 116°C, magnification ×250. See Color Plate VI.

on silicagel and eluted with chloroform-petroleum ether (7:3) mixture. The solid material so obtained was crystallised from n-hexane several times until the melting point was constant. m.p. 111°C; IR $\nu_{\max}^{\mathrm{Nujol}}$ (cm^{-1}) 1608 and 1585; PMR δ 0.85 (*t*, $3 - C\underline{H}_3$) 1.0 − 1.8 (*m*, 20H, $10 \times -C\underline{H}_2$), 2.5 (S, 3H, ar $C\underline{H}_3$), 2.65 (*t*, 2H, ar $C\underline{H}_2$) 6.9 (S, 1H, $-C = C\underline{H}-$) 7.2 − 8.2 (*m*, 12H, ar $\underline{H}$) 16.9 (S, 1H, enol $-O\underline{H}$); UV − VIS $\lambda_{\max}^{\mathrm{CHCl_3}}$ (ε) 386 (47,800) 364 (81,300) 300 (23,700) 264 (19,700) 262 (19,800) 233 (33,700); Anal. Calcd. for $C_{34}H_{42}O_2$:C, 84.64% H, 8.71%. Found: C, 84.54%; H, 9.58%.

Bis[1-(p-n-dodecylbiphenyl)3-(p-methylphenyl)propane 1,3-dionato] copper (II), II b, R = CH$_3$, M = Cu

To a stirred solution of the above diketone (0.24 g, 0.5 mmol) in ethanol (10 ml) was added potassium hydroxide (0.028 g, 0.5 mmol) and then an ethanolic solution of cupric chloride dihydrate (0.042 g, 0.25 mmol). The mixture was stirred for three hours and left overnight. The green precipitate was collected, taken up in chloroform (75 ml), washed with water (3 × 30 ml) and dried (Na_2SO_4). Removal of solvent afforded a green residue which was crystallised from butan-2-one several times. m.p. 201°C; IR $\nu_{\max}^{\mathrm{Nujol}}$ (cm^{-1}) 1610 and 1590; UV − VIS $\lambda_{\max}^{\mathrm{CHCl_3}}$ (ε) 363 (75,300) 313 (47,700) 272 (31,500) and 233 (41,000); Anal. Calcd. for $C_{68}H_{82}O_4Cu$: C, 79.58% H, 8.0%. Found: C, 79.52%; H, 8.14%.

TABLE II

Transition temperatures (°C) of enthalpies of transition (Kcals/mole) of chelates II, M = Cu, n = 12[§]

Compound number	R	K		S_A		N		I
1	CH_3	.	201.0 9.79	–		(.	162.0) 0.04	.
2	C_2H_5	.	160.0 4.5	–		(.	146.5) 0.04	.
3	OCH_3	.	179.5 10.4	–		(.	169.5) 0.03	.
4	OC_2H_5	.	179.0 8.1	–		(.	158.0) 0.04	.
5	Cl	.	196.0 11.41	–		(.	171.0)*	.
6	Br	.	201.0 8.03	(.	170.5)*	–		.
7	CN	.	218.0 6.76	(.	212.0) 0.93	–		.

[§] See Table III for abbreviations.

* The enthalpies of transitions could not be determined because of immediate onset of crystallization.

Bis[1-(p-n-dodecylbiphenyl)3-(p-methylphenyl)propane 1,3-dionato] palladium (II), II b, R = CH_3 M = Pd

A stirred mixture of diketone I b, R = CH_3 (0.246 g, 0.5 mmol) palladium chloride (0.049 g, 0.275 mmol) dry acetonitrile (60 ml) and anhydrous potassium carbonate (0.101 g, 0.75 mmol) was heated in an oil both at 50°C for twenty hours. The cooled reaction mixture was filtered, the precipitate was taken up in chloroform (100 ml), washed with water (3 × 50 ml) and dried (Na_2SO_4). Removal of solvent afforded a bright yellow residue which was crystallised from butan-2-one several times. m.p. 195°C; IR ν_{max}^{Nujol} (cm^{-1}) 1608 and 1582; PMR δ 0.8 (*t*, 6H, 2 × $-C\underline{H}_3$), 1.2 – 1.72 [*m*, 40H, (10 × $-C\underline{H}_2)_2$] 6.7 [S, 6H, (Ar $C\underline{H}_3)_2$], 2.66 [*t*, 4H, (Ar $C\underline{H}_2)_2$] 6.7 [S, 2H, $(-C = C\underline{H}-)_2$] 7.15 – 8.15 (*m*, 24H, ar$\underline{H}$); UV – Vis $\lambda_{max}^{CHCl_3}$ (ε) 412 (23,800) 380 (43,000) 322 (68,000) 271 (37,300) and 234 (64,100. Anal. Calcd. for $C_{68}H_{82}O_4Pd$: C, 76.38%; H, 7.68% Found: C, 75.83%; H, 7.76%.

The purity of the compounds synthesised was checked by spectral and microanalytical data. The infrared and electronic absorption spectra were recorded on spectrophotometers (Shimadzu IR-435 and Hitachi U-3200 respectively). The PMR spectra were taken on a FT-NMR spectrometer (Bruker WP 80 SY) in deuterochloroform with tetramethylsilane as an internal standard. Satisfactory elemental

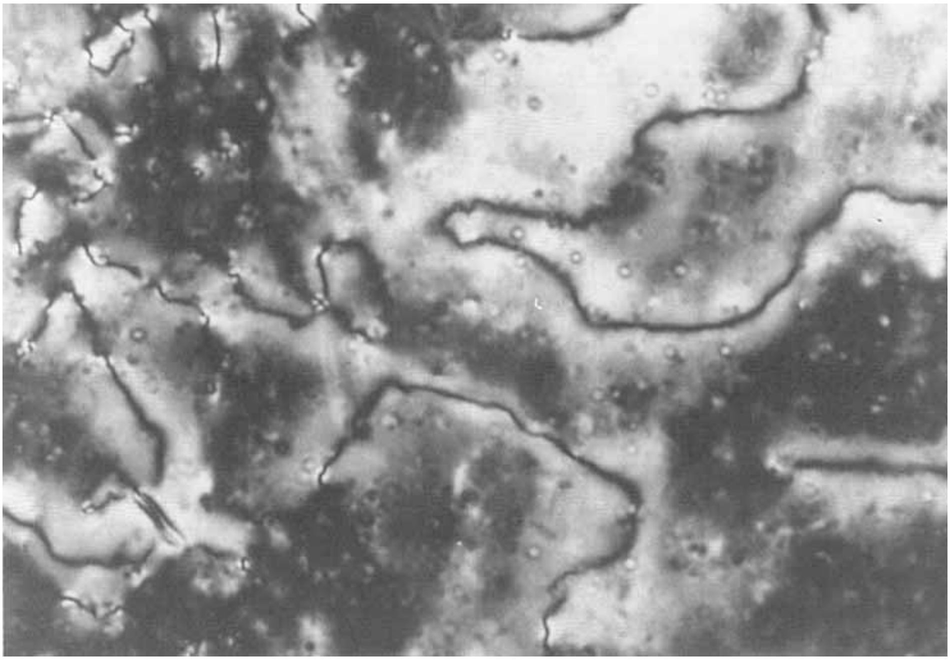


FIGURE 3 Photomicrograph of the nematic phase of complex II (b), R = OCH_3 at 168°C, magnification ×250. See Color Plate VII.

analysis were obtained for all the compounds. The transition temperatures were determined under a polarising microscope (Leitz Laborlux 12 POL) equipped with a heating stage and a controller (Mettler FP 52 and FP 5 respectively). The enthalpies of transition were determined from thermograms obtained on a differential scanning calorimeter (Perkin-Elmer, Model DSC-2). The calorimeter was calibrated using pure indium as a standard. The heating and cooling rates were 5°C/min.

RESULTS AND DISCUSSION

Table I summarises the transition temperatures and enthalpies of transitions of the β-diketones I, b. We used different terminal groups to study the substituent effect on the mesophases. Except for derivative with a terminal methoxy substituent (which is non-mesomorphic), the remaining exhibit mesophases of the smectic type. They show a focal-conic texture characteristic of the smectic A type. Compounds with chloro and bromo terminal groups, in addition to the smectic A phase, exhibit a monotropic phase which shows a striated fan-shaped texture. Further, the homeotropic regions of the smectic A phase of these compounds on cooling develop into a mosaic texture. Based on this, the monotropic phase has been identified to be smectic E. The optical texture of this phase is shown in Figure 2.

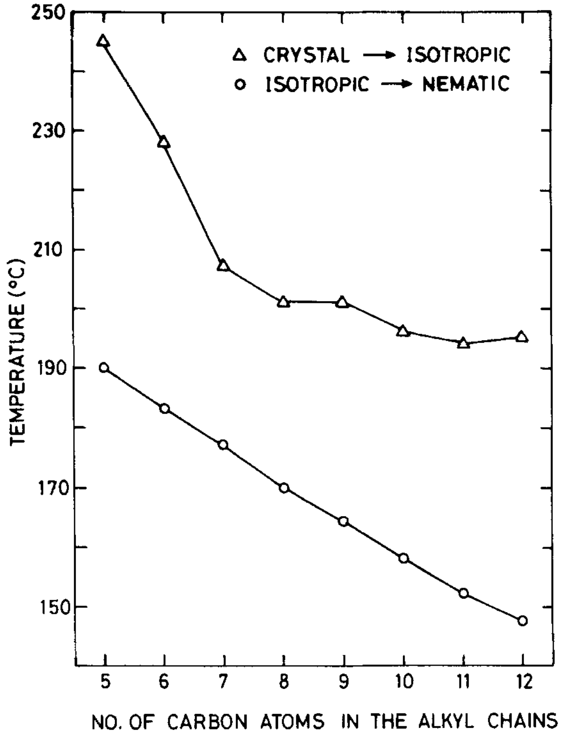


FIGURE 4 Plot of transition temperatures versus the number of carbon atoms in the alkyl chain for a series of bis[1-(p-n-alkylbiphenyl) 3-(phenyl) propane 1,3-dionato] copper (II), II (a), *M* = Cu.

We had reported [10] earlier a homologous series of β-diketones in which one of the terminal groups was hydrogen. Substitution of this hydrogen by a few other groups had varying effect on the mesophase. A similar effect is observed in the present series of compounds. The melting and clearing points are raised in every case. Alkyl substitution seems to favour the mesophase formation as compared to the alkoxy groups. The enthalpy for the smectic A → isotropic transition varies from 0.59 Kcals/mole for the cyano derivative to 1.05 kcals/mole for the chloro derivative. Though this value for compound 6 is rather low some examples are known in literature[11] with very low values.

The transition temperatures and enthalpies of transition of the green coloured copper chelates are given in Table II. As compared to ligands, the melting points are raised by about 60 to 100°C upon complex formation while the clearing points are raised by 28 to 67°C. Five of the seven complexes exhibit a metastable nematic phase while the remaining two show a metastable smectic phase. While the ligand with a methoxy group is non-mesogenic, the corresponding copper chelate exhibits a nematic phase. It is interesting to note that a chloro substituent (compound 5) induces a nematic phase while a bromo group (compound 6) induces a smectic phase. This behaviour is in accordance with what has been observed,[12] viz., a chloro terminal group has a higher nematic group efficiency order while a bromo substituent has a higher smectic group efficiency order. However, in compound 7 the

TABLE III

Transition temperatures (°C) of chelates II, M = Pd, n = 12[§]

Compound number	R	K		S_A		N		I
1	CH_3*	.	195.0	–		(.	162.0)	.
2	C_2H_5*	.	177.0	–		(.	149.0)	.
3	OCH_3	.	177.0	–		(.	164.5)	.
4	OC_2H_5	.	183.0	–		(.	151.0)	.
5	Cl*	.	201.0	(.	178.0)	–		.
6	Br*	.	196.0	(.	177.0)	–		.
7	CN	.	212.0	(.	197.5)	–		.

[§] Enthalpies of these chelates could not be determined because of thermal decomposition.

* Chelates 1, 2, 5 and 6 have crystal-crystal transitions at 134.0, 138.0, 167.5 and 169.0°C respectively.

Key: K: Crystal, S_E: Smectic E phase, S_A: Smectic A phase, N: Nematic phase, I: Isotropic phase. Temperatures in parentheses indicate monotropic transitions.

terminal cyano substituent which lies high in the nematic group efficiency order and low in the smectic order promotes a smectic A phase. The optical texture of the nematic phase of complex II (b), R = OCH_3 is shown in Figure 3.

Probably a comment about the enthalpies of the nematic-isotropic transition (T_{NI}) seems to be in order. It is seen in Table II that the values for this transition is of the order of 0.03 to 0.04 Kcals/mole. These values are certainly low as compared with those of the normal low molecular weight calamitic mesogens.[13] We had obtained similar results in all our earlier investigations of copper β-diketonates for this transition. This is perhaps due to the persistence of a high degree of nematic-like short range order in the isotropic phase. In fact, low enthalpies for T_{NI} have been obtained by Caruso *et al.*,[9] Marcos *et al.*[14] and Ovchinnikov *et al.*[15] in various salicylideneamino metal complexes.

Very few homologous series of compounds containing transition metals have been prepared so far and those exhibiting nematic phase is negligibly small for making any reasonable generalizations. In order to examine the type of curve one would get for the N → I transition in metal chelates, a homologous series of eight bis[1-(p-n-alkylbipheny)3-(phenyl) propane 1,3-dionato]copper (II) has been synthesised. Some of the ligands used to prepare these chelates also exhibit the nematic phase.[10,16] All the homologous chelates show a metastable nematic phase. The transition temperatures plotted against the number of carbon atoms in the alkyl chain is shown in Figure 4. It is seen that there is a decrease of T_{NI} as the chain is lengthened and these points lie on a smooth curve.

Binary mixtures were prepared with a view to obtaining an enantiotropic nematic phase, but none of the mixtures within the homologous series appeared to show enantiotropic behaviour. However, a mixture of the homologue $n = 8$ and complex bis[1-(p-n-decylbiphenyl)3-(p-methoxyphenyl) propane 1,3-dionato]copper (II)[2] (39.6: 60.4 weight %) did exhibit an enantiotropic nematic phase, but only over a narrow range (< 0.5°C). Attempts were made to synthesise variants of these structures as well as other paramagnetic complexes to produce nematics that are enantiotropic over a wider temperature range. The results of these will be published elsewhere.[17]

The transition temperatures of palladium chelates II (M = Pd, $n = 12$) which were obtained in a highly crystalline form are given in Table III. The first four complexes in this table are all monotropic nematic while the remaining three are monotropic smectic. This smectic phase exhibits a simple fan-shaped texture and is characterised as smectic A phase. The mesophase → isotropic transition temperatures of these as compared to their corresponding copper complexes are about the same except in the case of cyanophenyl derivatives where the difference is about 15°. These palladium complexes decompose at their melting points and hence their enthalpies could not be accurately determined.

CONCLUSION

A number of new metallo organic complexes containing copper (II) and palladium (II) have been synthesised. Most of these exhibit a monotropic nematic phase while the remaining show a monotropic smectic A phase. The β-diketones used to prepare these complexes are also mesomorphic. An enantiotropic nematic phase though over a narrow range was obtained for a binary mixture of two copper complexes.

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