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Calamitic Organometallic Liquid Crystals of β -Diketonate Dicarboxylrhodium(I) Complexes

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A series of new rodlike organometallic complexes based on the β -diketone ligands with terminal metal have been synthesized. The mesomorphism of the ligands and complexes has been investigated using DSC and polarizing microscopy. Most of the complexes display nematic mesogenic behavior identically with that exhibited by ligands. The effect of the carbon number of the terminal chain on the mesomorphism is discussed.

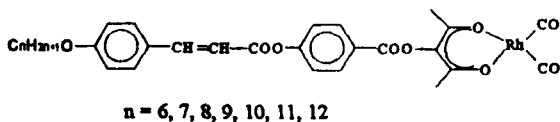
Keywords: Organometallic complex; liquid crystal; β -diketone

Metallomesogens are liquid crystalline materials with potential application in optical or electrooptical devices. Rodlike molecules containing metallic rigid cores in the molecular skeleton have traditionally been regarded as the most suitable geometry to give rise to mesogenic behavior [1, 2]. It is well known that β -diketonate complexes give rise mostly to discotic liquid crystals, which often show centrosymmetric structures [3–5]. We have previously reported the rod-like γ -substituted β -diketonate metallo-mesogenic complexes with terminal metal Rh(I), whose structure is non-centrosymmetric [6].

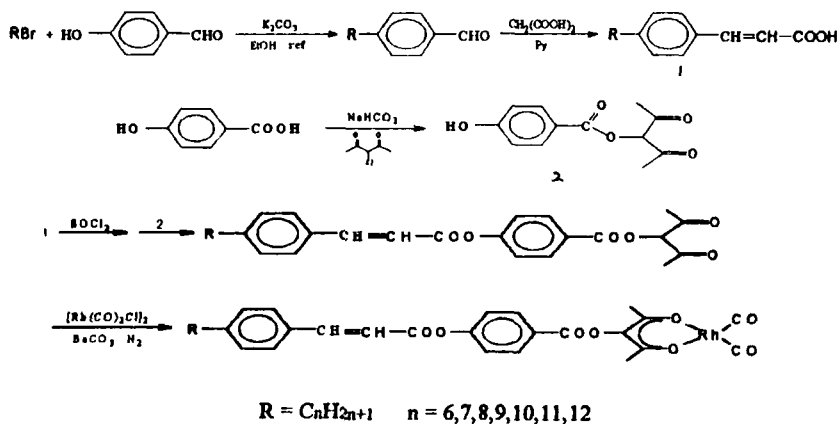
The relationship between molecular structure and mesophase behavior of organic compounds has been extensively studied for many years [7]. The much newer area of mesogenic metal complexes with different molecular

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structure is currently studied. After synthesis and characterization of the β -diketonate complexes with a bridging ester bond, we have now extended these studies and have succeeded in synthesis of another new calamitic family with a bridge bond $\text{CH}=\text{CHCOO}$, which have the terminal metal Rh(I) .



The synthetic procedure leading to the title complexes is outlined in Scheme I.



SCHEME I

RESULTS AND DISCUSSION

Synthesis and Characterization

The ligands were prepared by the reaction of 4-alkoxy cinnamyl chloride with 3-(4'-hydroxybenzoxy)-2,4-pentanedione in dry benzene refluxing for 12 hr. The complexes were obtained by reacting appropriate ligands with μ -dichlorotetracarbonyldirrhodium in dry acetone with an excess of barium carbonate.

The infrared spectra of the ligands have two stretching vibration frequencies at 1730 and 1632 cm^{-1} , which are respectively assigned to the ester group $\nu(\text{COO})$ and the carbon-carbon double bond $\nu(\text{C}=\text{C})$. After

chelation, the stretching vibration frequencies of the ester group and C=C bond shift to 1740 and 1628 cm^{-1} respectively. The stretching vibration frequencies of the carbonyl group in the chelated β -diketonate ring are lowered to 1588 cm^{-1} . It is shown that the carbonyl and C=C bond in the conjugated chelated β -diketonate ring posses double bond and single bond character, accounting for large frequency shifts of the β -diketonate ring absorption after the chelation of the ligand with metal [8]. The infrared spectra of the β -diketonate complexes show absorption around 2098, 2010, 1992 cm^{-1} , which are characteristic of the carbon monoxide stretching region.

According to the ^1H -NMR data of the ligands and the complexes, it is found that the proton chemical shift value of complexes is a little lower than those of the free ligands. We think that the results are due to (1) the aid of interaction of metal atom with CO ligand through the $d-\pi$ and $\pi-\pi^*$ action and (2) the effect of the large electronic field with electronic delocalization on the β -diketonate quasi-aromatic ring. These results lead to the shielding effect of the β -diketonate group on the proton of the complexes.

The elemental analysis, IR, and ^1H -NMR of the ligands and the complexes are consistent with their proposed structures.

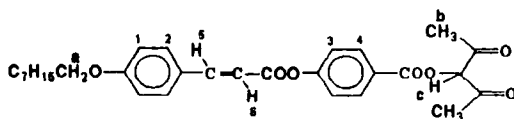
^1H -NMR studies of the ligand and the complex with $n = 8$ are given in Tables I and II, respectively.

The stability of the complexes was studied by thermogravimetric analysis and none of them show weight loss until 210°C.

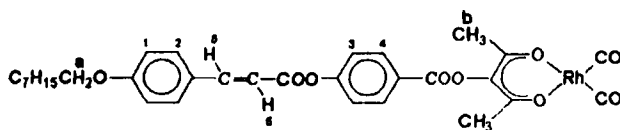
Mesogenic Behavior

All the complexes synthesized, with the exception of the complex $n = 6$, are mesogens. These complexes are stable in air within the temperature range of the measurements. As expected, all of the complexes melted at higher

TABLE I The ^1H -NMR spectra of the ligands in CDCl_3



H_1	H_2	H_3	H_4	δ/ppm H_5	H_6	a	b	c
6.92	8.08	7.40	8.16	6.56	7.47	4.00	2.05–2.38	5.75

TABLE II The ^1H -NMR spectra of complexes in CDCl_3 

H_1	H_2	H_3	H_4	H_5	H_6	a	b
6.50	8.05	7.35	8.29	6.45	7.84	4.00	2.07

temperature than the corresponding ligands. The transition temperature and enthalpies were determined by DSC and the structure of the mesomorphism of the ligands and complexes has been affirmed on the basis of optical textures.

The Ligand

The ligands with $n = 6, 7, 8$ show monotropic mesophases (nematic). When the chain length of the alkoxy group is increased to $n = 9, 10, 11$, they show enantiotropic mesophases, which was identified as a nematic phase. For the higher homologue ($n = 12$), the monotropic phase is again observed as a nematic phase. The transition temperatures of the compounds with the terminal alkoxy group are displayed in Figure 1. As can be seen the clearing temperature decreases with increasing length of the terminal chain up to $n = 12$.

The transition temperatures and enthalpies of the ligands are shown in Table III.

The Complex

It is found that all the complexes show liquid crystalline properties (enantiotropic or monotropic), except for the complex with $n = 6$. The mesophase are identified by their polarizing optical textures as nematic phases. All the complexes show a higher transition temperature than the ligands. On extending the chain length of the terminal chain $n = 7, 8, 9, 10$, an enantiotropic phase was found (nematic (N)). However, the homologues $n = 11, 12$ show a monotropic phase, which is also a nematic mesophase. It

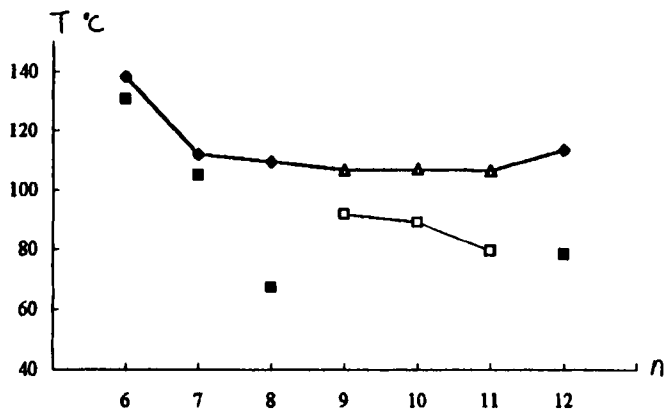


FIGURE 1 Transition temperature as a function of the alkoxy chain length of the ligands.

TABLE III Optical, thermal and thermodynamic data for the ligands

<i>n</i>	transition ^a	temp ^b , °C	ΔH^b (kJ/mol)
6	C-I	138.3	20.34
	I-N ^c	130.5	
7	C-I	111.9	28.33
	I-N ^c	105.0	
8	C-I	109.2	23.49
	I-N	67.3	0.44
9	C-N	91.9	18.07
	N-I	106.5	3.52
10	C-N	89.2	21.03
	N-I	106.9	4.39
11	C-N	79.6	14.48
	N-I	106.4	8.80
12	C-I	113.2	28.46
	I-N	78.6	2.48

^a C, crystal; N, nematic; I, isotropic liquid; ^b DSC data from first scan; ^c not detected by DSC.

is found that the clearing point temperatures of the complexes become lower with the increase of the terminal carbon number. Also, the transition temperature ranges of the complexes become narrower with the increase of the terminal carbon number.

The transition temperatures and enthalpies of the complexes determined by DSC are summarized in Table IV and Figure 2.

One of the textures observed with a polarizing optical microscope is shown in Figure 3.

TABLE IV Optical, thermal and thermodynamic data for the complexes

<i>n</i>	transition ^a	temp ^b , °C	ΔH^b (kJ/mol)
6	C-I	185.8	38.71
7	C-N	115.5	25.57
	N-I	167.3	1.24
8	C-N	84.2	27.69
	N-I	132.5	2.51
9	C-N	103.4	21.56
	N-I	144.6	4.31
10	C-N	101.5	27.40
	N-I	142.4	2.17
11	C-I ^c	139.6	31.91
	I-N ^c	102	
12	C-I	138.2	44.36
	I-N	102.1	1.58

^a C, crystal; N, nematic; I, isotropic liquid; ^b DSC data from first scan; ^c not detected by DSC.

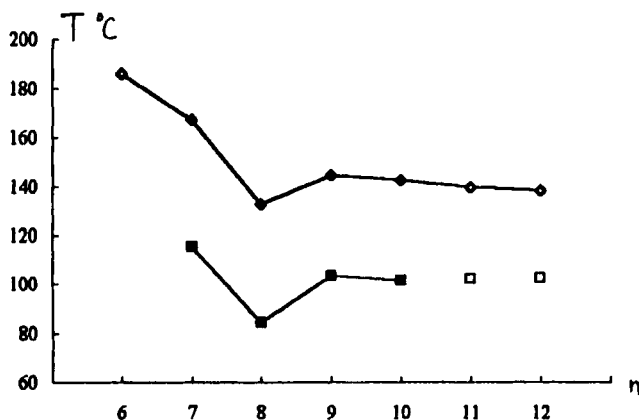


FIGURE 2 Transition temperature as a function of the alkoxy chain length of the complexes.

EXPERIMENTAL SECTION

Techniques

The ^1H -NMR spectra were recorded on a Varian FT-80A spectrometer, using CDCl_3 as solvent and TMS as an internal standard. The IR spectra (Nujol) were performed on a NICOLET FT-MX-IE spectrometer. Elemental analyses were obtained with a CARLO ERBA-1106 micro-analyzer. The thermotropic behaviors were determined by DSC using Perkin-Elmer 7 series analysis system operated at a scanning rate of $10^\circ\text{C}/\text{min}$. The textures of mesophase were observed under ORTHLUX-II

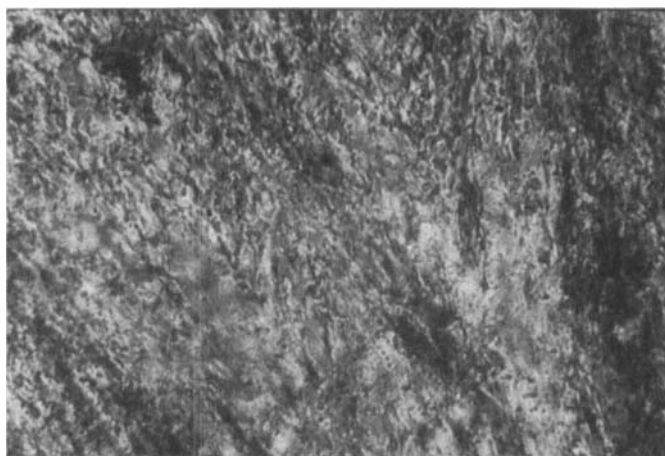


FIGURE 3 Texture of the complex ($n = 8$) under cross polarizers 110°C , on cooling run $\times 220$. (See Color Plate III).

POLBK polarizing optical microscope with a hot stage (self made) and TDA temperature controller.

Synthesis

3-(4-hydroxybenzoxy)-acetylacetone

A mixture of 1mmol potassium *p*-hydroxybenzoate with 1mmol 3-chloro-2,4-pentanedione in 50 ml dry benzene [9] at room temperature was stirred overnight to give a red solution [10]. About 500ml water was added to the reaction mixture and the mixture was extracted several times with chloroform. The combined extracts were dried with sodium sulfate and distilled. The residue was recrystallized from benzene, yield 78.4%. m.p. 109.5°C . $\text{C}_{12}\text{H}_{12}\text{O}_5$ Found C, 60.95; H, 5.11; calcd. C, 61.02; H, 5.08%; IR ν_{max} 3500–3100 (s, OH), 1724 (s, $\text{ArC}=\text{O}$), 1613, 1593, 1571 (s, Ar), 1254, 1169 (s, $\text{Ar}-\text{O}-\text{C}$) cm^{-1} δH : 2.16, 1.97 (6H, d, $2 \times \text{CH}_3$), 6.93–7.98 (4H, m, $1 \times \text{C}_6\text{H}_4$), 13.90 (1H, s, hydrogen of enol form).

The Ligands

The ligands were prepared by reaction of 1mmol 4-alkoxy cinnamyl chloride with 1mmol 3'-(4-hydroxybenzoxy)-acetylacetone in 50ml dry benzene by refluxing for 12 hr. After the solution evaporated, the products were obtained by recrystallization from ethanol, yields about 65 ~ 70%.

TABLE V The elemental analysis (percent) of the ligands and the complexes (calculated values in parantheses)

	<i>n</i>	<i>C</i>	<i>H</i>
Ligands	6	69.74 (69.52)	6.84 (6.44)
	7	70.14 (70.00)	6.52 (6.67)
	8	70.81 (70.44)	7.10 (6.88)
	9	70.51 (70.86)	6.91 (7.09)
	10	71.46 (71.26)	7.17 (7.28)
	11	71.55 (71.64)	7.35 (7.42)
	12	71.93 (72.00)	7.60 (7.64)
Complexes	6	55.49 (55.78)	4.55 (4.65)
	7	56.73 (56.42)	4.90 (4.86)
	8	56.81 (57.06)	5.40 (5.06)
	9	57.84 (57.66)	5.60 (5.26)
	10	58.02 (58.24)	5.28 (5.44)
	11	58.68 (58.79)	5.95 (5.62)
	12	59.42 (59.15)	5.80 (5.78)

The Complexes

A mixtures of dry acetone solutions of ligands (1 mmol) and μ -dichlorotetracarbonyldirrhodium $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [11] (0.5 mmol) with excess of solid barium carbonate were stirred under N_2 at room temperature for 30 min [12]. After filtering and distilling, the remaining mixture was chromatographed on silica gel using chloroform as an eluent. The products were purified by crystallization from ethanol, yields about 80%.

The elemental analysis of the ligands and complexes are collected in Table V.

All the compounds were characterized by IR and ^1H -NMR techniques without significant differences within the same series.

Acknowledgement

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