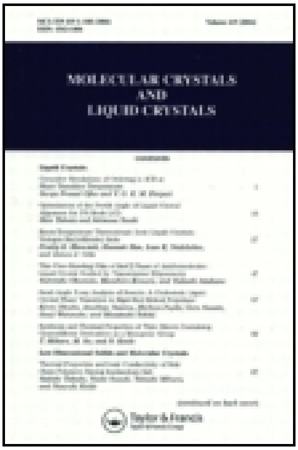

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Metal-tricarbonyl Group Incorporated Mesogens Synthesis and Liquid Crystal Properties of π-Tricarbonylchromium Cholesteryl p-Alkoxybenzoate

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Metal-tricarbonyl Group Incorporated Mesogens Synthesis and Liquid Crystal Properties of π-Tricarbonylchromium Cholesteryl *p*-Alkoxybenzoate

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A series of title complexes have been synthesized and characterized. The complexes of cholesteric mesophase exhibit lower temperature ranges than that of the corresponding ligands, some of which possess smectic phase. The clearing points of the complexes and ligands obey the even – odd effect.

Keywords: Organometallic complexes, liquid crystal, tricarbonylchromium derivative, cholesteric phase.

There are two possible consequences of incorporating metals into liquid crystal molecules. In many cases metals bring together free ligands to form symmetrical calamitic or discotic mesogens, in which metals usually are located at the center of molecular rigid cores. The metallomesogens with these characters usually exhibit significantly higher transition temperatures over those of free ligands[1], an undesirable consequence for potential applications. On the other hand, unsymmetrical complexes with metal-small ligand gropus coordinated with calamitic mesogens possess lower transition temperatures than that of corresponding organic mesogens[2]. Chromium-tricarbonyl moiety can easity be incorporated to form the unsymmetric metallomesogens by complexation with benzene ring existing in many organic mesogens. In this paper, we present a series of cholesteric metallomesogens containing chromium-tricarbonyl moieties. The results show that this series of complexes have lower mesophase temperature ranges than that of the free ligands.

RESULTS AND DISCUSSION

The complexes were synthesized by routine methods (Fig. 1).

They are all stable yellow solids but decompose gradually in solution. Table 1 collects the elemental analysis data of the complexes and ligands. The DSC and polarized microscopic data are listed in Table 2, as Figures 2 and 3 shown.

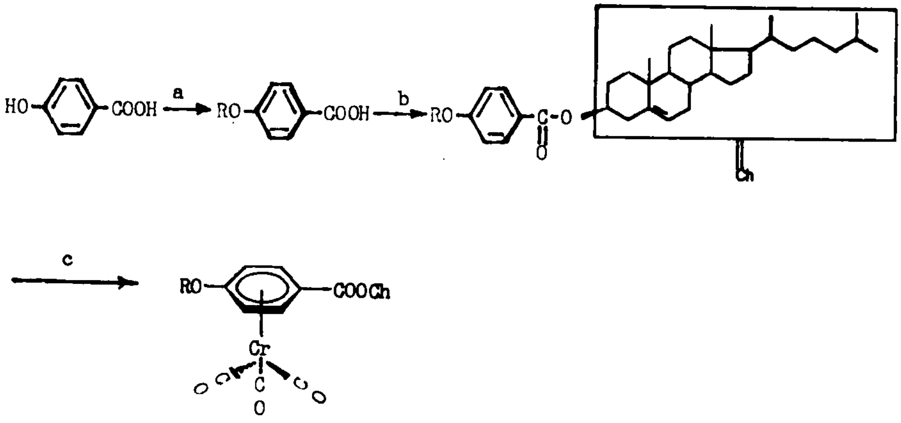

FIGURE 1 Synthesis route of the complexes. (a) R-Br/K_2CO_3/Ethanol, R = C_nH_{2n+1}; (b) $SOCl_2$; Cholesterol/pyridine/benzene; (c) $Cr(CO)_6$/THF : dibytyl ether = 1 : 10.

TABLE 1

The Elemental Analysis of Ligands and Complexes

	Ligands			Complexes		
n	C	H	Yield (%)	C	H	Yield (%)
1	80.62(80.72)	10.12(10.06)	78	69.60(69.49)	8.03(7.97)	24
2	80.48(80.85)	10.32(10.08)	73	70.01(69.85)	8.36(8.06)	19
3	80.59(80.97)	10.89(10.28)	81	70.34(70.18)	8.48(8.49)	35
4	80.01(80.19)	10.58(10.38)	80	70.31(70.46)	8.47(8.36)	30
5	79.76(81.20)	10.46(10.48)	67	70.32(70.56)	8.08(8.46)	25
6	81.06(81.31)	10.46(10.57)	80	71.31(71.04)	8.65(8.60)	47
7	81.17(81.40)	10.77(10.66)	84	71.52(71.35)	8.39(8.65)	50
8	81.38(81.50)	10.84(10.74)	85	71.77(71.62)	8.93(8.75)	43
9	81.85(81.59)	10.82(10.83)	76	71.95(71.84)	8.90(8.91)	20
10	81.70(81.68)	10.69(10.90)	85	72.11(72.12)	8.76(8.95)	55
11	81.86(81.76)	10.96(10.97)	89	72.51(72.34)	8.94(9.05)	52
12	81.89(82.09)	10.92(11.08)	87	72.52(72.59)	9.11(9.14)	46

At first sight on the Figure 2, the ligands exhibit wide ranges of mesophases, the phase transitions obey even–odd rule from terminal carbon number 2 to 11. Smectic phases exist when $n > 6$, and the longer the terminal carbon chain is the wider the smectic phase range. The corresponding organometallic complexes have much lower melting and clearing points and narrower mesophase ranges. Moreover, no smectic phases were observed in comparision with free ligands, although in some extent, even–odd rule was observed. The chromium tricarbonyl groupds in the organometallic complexes are coordinated perpendicularly through π-electron of benzene ring to the long axes of the ligands, thus are unfavorable to formation of smectic phases and lower clearing points. It is reported that the chromium tricarbonyl moiety coordinated

TABLE 2

DSC and Optical Microscopic Results of Ligands and Complexes

	Ligands		Complexes	
n	Transition	T, °C, (H, kJ·mol^{-1})	Transition	T, °C, (H, kJ·mol^{-1})
1	C—Ch			
	Ch—I			
2	C—Ch	134(24.87)	C—Ch	110(11.90)
	Ch—I	230	Ch—I	153
3	C—Ch	134.9(18.22)	C—Ch	105(21.00)
	Ch—I	223.5(0.34)	Ch—I	178
4	C—Ch	129(21.91)	C—Ch	108(5.66)
	C—Ch	226	Ch—I	194
5	C—Ch	132(10.74)	C—Ch	110(6.47)
	Ch—I	217	Ch—I	186
6	C—Ch	121.6(18.50)	C—Ch	117(28.29)
	Ch—I	222	Ch—I	210.9(0.99)
7	C—S	129(25.00)	C—Ch	111(36.79)
	S—Ch	138(1.18)	Ch—I	197(0.89)
	Ch—I	210		
8	C—S	132(38.00)	C—Ch	112(32.56)
	S—Ch	156(0.97)	Ch—I	205(0.98)
	Ch—I	215		
9	C—S	139(32.77)	C—Ch	115(10.89)
	S—Ch	166(0.57)	Ch—I	182(0.50)
	Ch—I	194(0.75)		
10	C—S	112(33.45)	C—Ch	96(28.83)
	S—Ch	175.4(0.63)	Ch—I	189(0.87)
	Ch—I	206(1.10)		
11	C—S	114(23.80)	C—Ch	98(24.2)
	S—Ch	177(0.68)	Ch—I	181(0.90)
	Ch—I	202(0.99)		
12	C—S	128(34.43)	C—Ch	105(35.68)
	S—Ch	176(0.46)	Ch—I	176(0.82)
	Ch—I	196(0.62)		

laterally to polymer main chain improved the solubility[3]. It is also true that the complexes show better solubility to many solvents.

In zero order approximation, free ligands are equivalent to a simple calamite, there are not difference between molecule and it's image. However, owing to molecular chirality, the alkane group is not in the plane with the steroid group, then the whole molecule is twisted. In forming the liquid crystal phase, the orientational order of molecular unarrangement increased with increasing alkyl chain length. When $n > 6$ a smectic phase will appear. On the other hand, when the tricarbonylchromium moiety was coordinated by π-electron of benzene ring to the free ligand to form the organometallic complexes, the whose molecule becomes very twisted. The orientational order of molecular arrangement decreases in the process of forming mesogen, the smectic phase also disappears. Cholesteric phase can be considered as twisted nematic phase, the director of molecular orientation in space changes periodically according to a helical way. For this reason there are not nematic phases. It was seen that the twist degree of the calamite increased with the incorporation of tricarbonylchromium

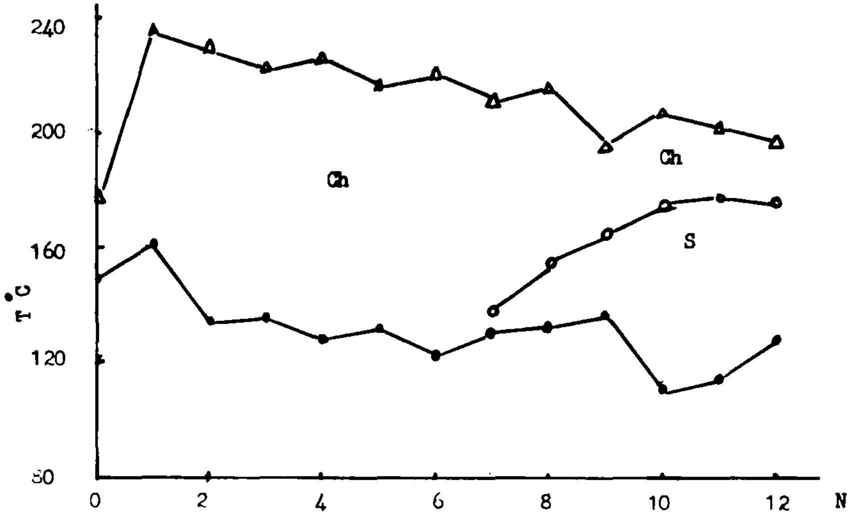

FIGURE 2 Effects of terminal carbon atom number (N) on the mesomorphism of free ligands.

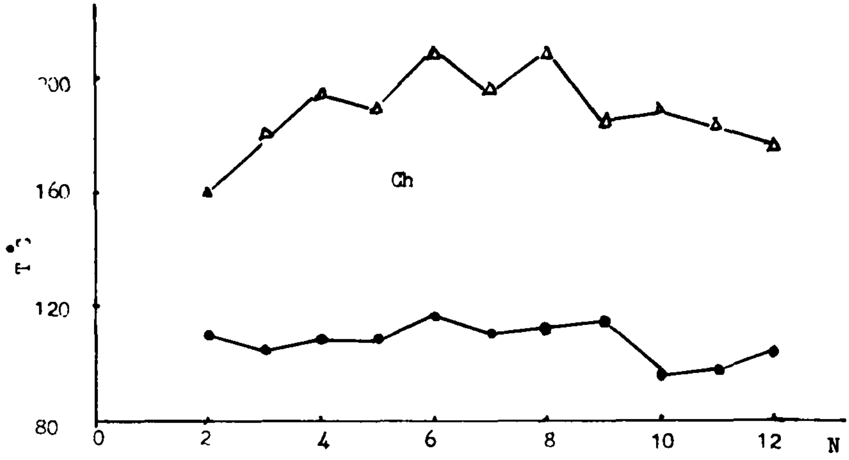

FIGURE 3 Effects of terminal carbon atom number (N) on the mesomorphism of organometallic complexes.

moiety to free ligand, the dipole–dipole interaction between molecules becomes weaker, therefore the melting and clearing points are lowered.

The typical cholesteric phase textures are depicted on Figure 4.

EXPERIMENTAL SECTION

Instruments: NMR: Varian FT-80A; IR : NICOLET FT-MX-1E; Microanalysis; Carlo Erba 1106; DSC; Perkin-Elmer 7 series thermal analysis system with a heating or

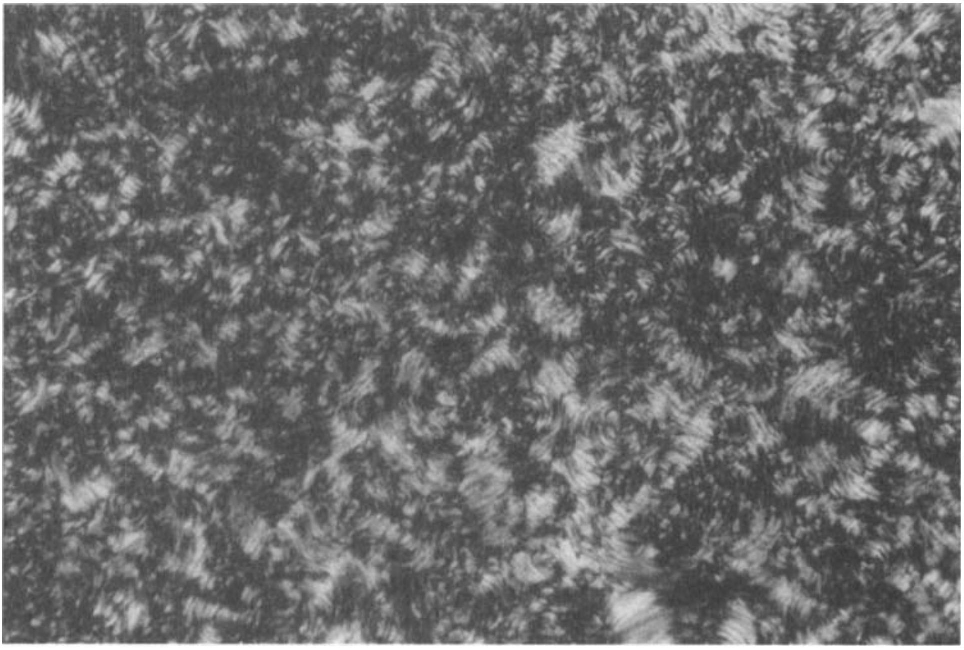

FIGURE 4 The typical texture of the complexes (R = 10), 320X, cooling run, 130°C. See Color Plate III.

cooling rate of 10 K/min under N_2; textures; Leitz POK II polarized microscope with hot stage. THF and *n*-butyl ether are dried over $LiAlH_4$ and distilled under N_2 prior to use, pyridine from CaH_2. $Cr(CO)_6$ are used directly as received from Aldrich Chemical Company Inc. General procedure: *p*-alkoxy benzoic acids are prepared through common methods, by the reaction of alkyl bromide with either *p*-hydroxyl benzoic acid or with *p*-hydroxy methyl benzoate followed by hydrolysis.

Cholesteryl (*p*-alkoxy)benzoate: 1.5 g *p*-alkoxyl benzoic acid was reacted with excess amount of $SOCl_2$ for about 5 hs. then remove the extra $SOCl_2$ by evaporation under reduced pressure. The residue was dissolved by 15 ml benzene, then this solution was added dropwise into the cholesterol (1 : 1 molar ratio to acids) in 20 ml benzene and several drops of pyridine at room temperature. The mixture was refluxed for 3 hs. followed by routine purification treatment to afford products. The yields and elemental analysis data are collected on Table 1.

Chromium tricarbonyl, cholesteryl (*p*-alkoxy)benzoate: mixture of 0.5 g ligand and 0.20 g $Cr(CO)_6$ in 11 ml solvent (*n*-bytyl ether : THF = 10 : 1) was refluxed for 20 hrs. The product was purified by column chromatograph (silica gel 200–300 mesh, eluent: cyclohexane : ethyl acetate = 2 : 1). The yields and microanalysis results are showed on Table 2. IR ($n = 6$, for instance): 1960 and 1896 (C=O), 1720 (C=O) cm^{-1}, ^1H-NMR, 6.1, 6.0, 5.05, 4.95, (C_6H_4) 2.15 (CH_2) ppm.

Acknowledgments

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