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Cholesteric Metallomesogens Containing Optically Active Metal-Tricarbony Moieties

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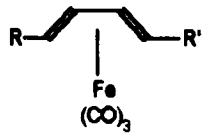
Diastereoisomers, iron tricarbonyl, cholesteryl sorbate 4, (+)-isomer and 5, (−)-isomer, have been synthesized and resolved by fractional crystallization. The stereostructures of the complexes were proposed by chemical method and CD spectra. DSC and polarized microscope revealed that 5 shows enantiotropic cholesteric phase. The two isomers possess same mesophase behaviors on cooling. Thermal racemization of 5 has been observed, but it is inhibited in some extent by the cholesteryl group. Chromium tricarbonyl cholesteryl (p-methyl) benzoate 8 shows similar phase transition with 4.

Keywords: Metallomesogens, DSC, stereochemistry, cholesteric phase.

Metal-containing liquid crystals (metallomesogens) receive increasing attention owing to their combined properties of organometallic complexes and mesogens.[1] One subject of this area is chiral metallomesogens with ferroelectric or paramagnetic chiral smectic C phase.[2,3] More recently, the metallomesogens with cholesteric mesophase have been reported.[4] Traditionally, asymmetric center, the essential part of chiral liquid crystal, is derived from optically active chiral carbon. However, different kinds of chiral reagents are usually expensive and not readily available, thus it restricts the sysnthesis and applications of chiral mesogens. On the other, some chiral metallic complexes of non-chiral carbon can be easily prepared by resolving the racemic mixtures. If this kind of asymmetric factor can be incorporated into chiral liquid crystal, new properties and possibilities are expected. For example, asymmetric butadiene iron-tricarbonyl complexes are easily accessible and stable molecules combining chiral centers, lateral dipole moments $\pi \rightarrow Fe(CO)_3$ and rigid cores together. Thus they are expected to be excellent precursors for building up ferroelectric liquid crystal materials.[5] The first mesogens containing iron-tricarbonyl moiety **1** was synthesized by Timinski and Malthete.[6] Enantiomers **1a** showed nematic phase, while **1b** showed S_A as well as nematic phases at very significantly lower temperatures.

In this paper, we present cholesteric metallomesogens with $M(CO)_3$(M = Fe, Cr) moieties, optically active butadiene iron-tricarbonyl moiety is successfully incorporated into cholesteric mesogens.



1

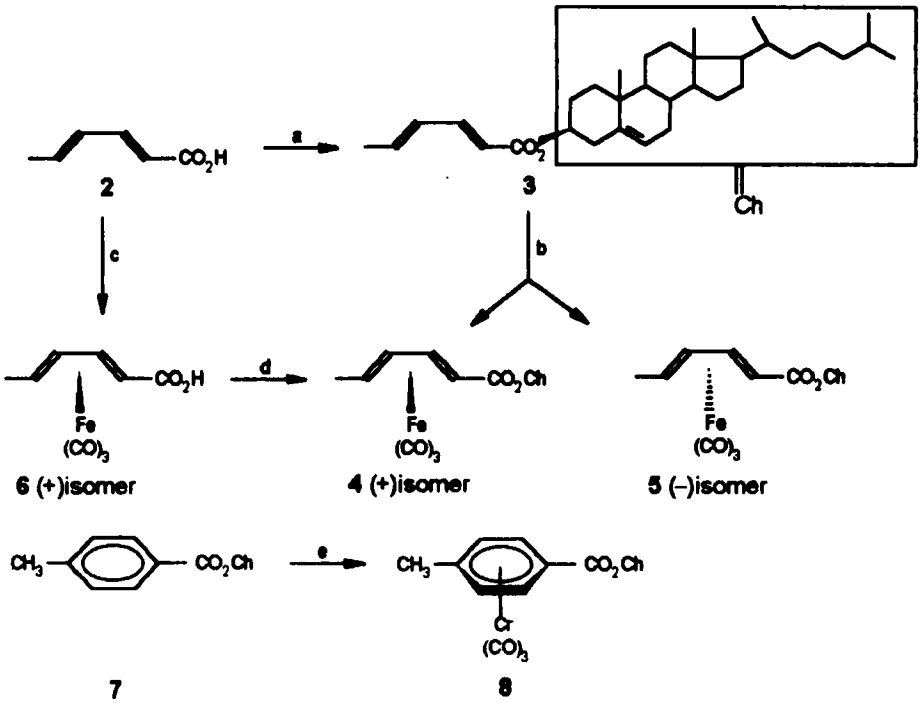
1a: R=Me, R'=$CO_2C_6H_4CH{=}NC_6H_4C_8H_{17}$

1b: R=$C_nH_{2n+1}OC_6H_4N{=}CH$

R'=$C_nH_{2n+1}OC_6H_4O_2C$

RESULTS AND DISCUSSIONS

By common methods, complexes **4**, **5**, and **8** have been synthesized.



SCHEME I Synthetic routes of complexes. (a) $SOCl_2$; cholesterol/C_6H_6/Py. (b) $Fe(CO)_5$/*n*-dibutyl ether; fractional crystallization. (c) $Fe(CO)_5$/n-dubutylether; α-(–)- pheny ethyl amine. (d) $SOCl_2$/Py; cholesterol/C_6H_6/Py (e) $Cr(CO)_6$/n-dibutyl ether: THF = 10:1.

Two diastereoisomers, **4** and **5** are separated by recrystallization from acetone and column chromatograph. CD and UV spectra of them are depicted in Figure 1.

The CD curves of **4** and **5** have the same patern but opposite in sign. Moreover, CD patern of 4 is similar to that of (+)–trans, trans, 2,4-hexadienic acid iron-tricarbonyl **6**,[7] it indicates that stereostructure of butadiene iron-tricarbonyl moiety in 4 has the same absolute configuration as that of **6**. This was further approved by the fact that esterification of **6** with cholesterol afforded **4** instead of **5**.

It is reported that butadiene iron-tricarbonyl complexes undergo thermal racemization.[8] This is also observed, when **5** was heated and left at 130°C (mesophase) under, N_2, the specific rotation reduced from $-82°$ to $-68°$ after 4 hours and to $-41°$ after 24 hours and longer. But specific rotation is $+16°$ for the 1:1 mixture of 4 and 5. The optically active cholesteryl may inhibit the racemization of **5**. The fact that the yield of **5** was higher than that of **4** in the reaction of **3** with $Fe(CO)_5$ supports this argument.

Phase transition and DSC results are collected in Table 1. Figure 2 shows DSC curves of **4**, **5**, and their mixture.

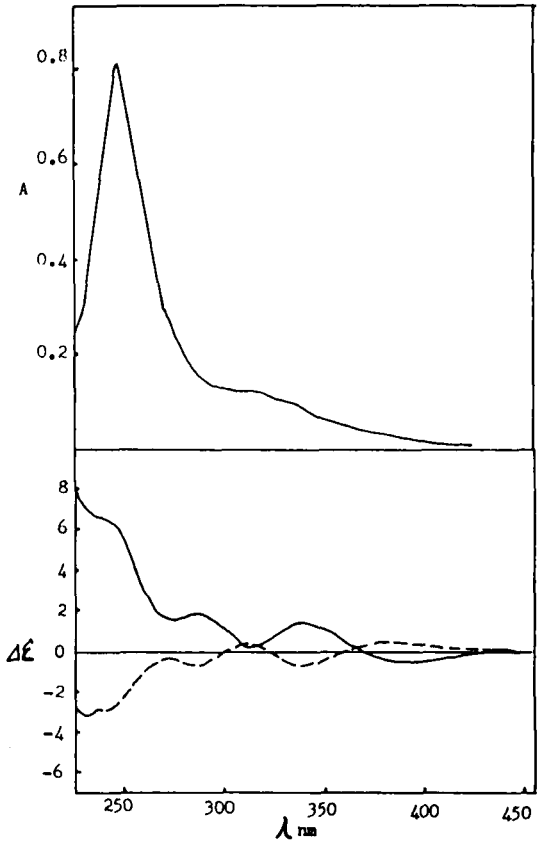


FIGURE 1 UV and CD spectra of diastereoisomers 4 and 5. 4, ——, 5, - - -; solvent, $CHCl_3$; 20°C.

TABLE 1

DSC results of ligands and complexes

Compound	Phase Transition	T, °C	ΔH, kj·mol^{-1}
3	K → Ch	147	109.4
	Ch → I	200*	
4	K → I	193	99.3
	I → Ch	131	− 1.4
	Ch → S	93	− 1.3
	S → K	80	− 27.5
5	K → Ch	117	34.8
	Ch → I	133	1.5
	I → Ch	132	− 1.6
	Ch → S	99	− 1.8
	S → K	86	− 27.8
7	K → Ch	162*	
	Ch → I	236*	
8	K → I	169.	61.9
	I → Ch	162	− 0.6
	Ch → S	134	− 2.7
	S → K	106	− 48.8

* Microscope data.

All the three complexes have similar phase trasitions on cooling run. **5** exhibits an enantiotropic mesophase on heating, while two mesophases were recorded on cooling. **4** and **8** show two monotropic mesophases, reflecting that the mesogen properties of this kind of molecules are dominated mainly by the overall molecular shapes. The mesogenic properties of 1:1 mixture of **4** and **5** are of interest. DSC curves of the mixture exhibit three endothermal peaks representing the phase transition of **4** (**116**, **131**) and **5** (**175**) respectively. Three exothermal peaks on cooling reflect the same mesophase behaviors of **4** and **5**. Mesophase textures of the mixture are showed on figure **3**. Cooling from isotropic liquid phase, the mixture changes to typical cholestric phase at 132°C (plate a) and to smectic phase at 100°C. On reheating, crystal separates out and grows up along with the raise of temperature (b). At 132°C liquid crystal phase diminishes. The crystal remains until 175°C (c).

In comparison with the free ligands, the corresponding organometallic complexes have lower transition temperatures, but narrower or even no enantiotropic mesophases. The coordinated metal-tricarbonyl moieties are perpendicular to the long axes of calamitic molecules and therefore, unfavor to the formation of mesophases.

EXPERIMENTAL SECTION

Instruments: NMR, Varian FT-80A; IR, Nicolet MX-1E infrared spectrometer; Microanalysis, Carlo Erba 1106 microanalyzer; DSC, Prekin-Elmer 7 Series thermal-analysis system with a heating or cooling rate of 10 K/min under N_2; texture, Leitz POK II polarizing microscope with hot stage; specific rotation, Perkin-Elmer 241 Polarimeter; CD, Jasco J-500C Dichrograph.

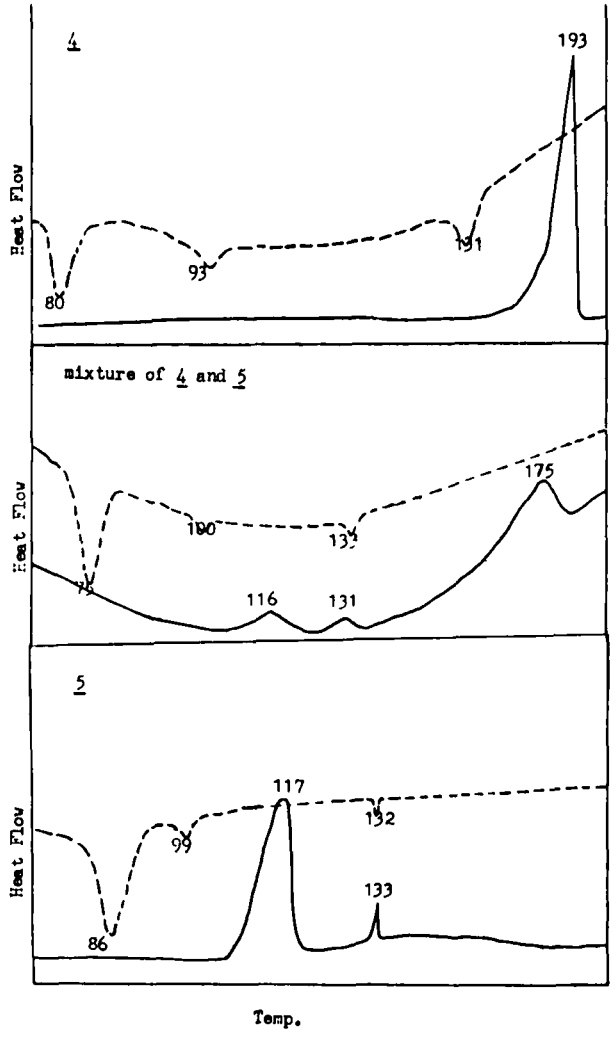


FIGURE 2 DSC curves, - - - -: cooling run, ——: heating, 10K· min^{-1} under N_2.

Reagents: All solvents were dried and distilled under N_2 prior to use; THF and n-dibutyl ether from $LiALH_4$, benzene from sodium, pyridine from CaH_2,$Fe(CO)_5$, purchased from factory 857, General Corporation of Chinese Nuclear Industry, and $Cr(CO)_6$(99)%, from Aldrich Chemical Company Inc. were used without further purification.

Cholesteryl sorbate **3** and cholesteryl (p-methyl) benzoate **7** were prepared according to known procedures.[9]

Iron tricabonyl, cholestryl sorbate **4** and **5**: 1.5 g (3.1 mmol) **3**,**4** ml (large excess) $Fe(CO)_5$, 20 ml *n*-dibutyl ether and several drops of $BF_3.OEt_2$ were mixed and refluxed for 4 hrs. until TLC detection showed no ligand **3**, the solvent and unreacted $Fe(CO)_5$

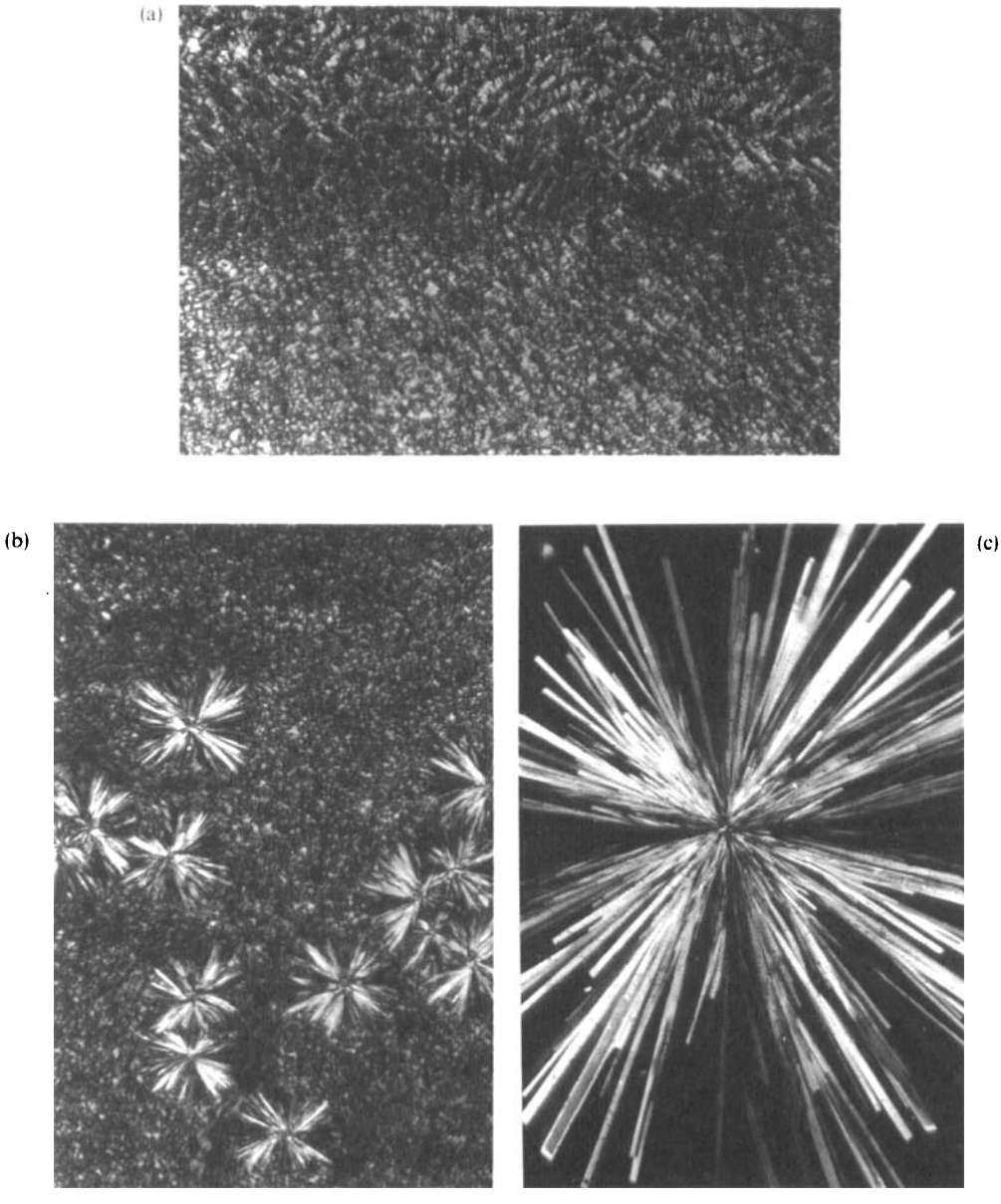


FIGURE 3 Typical textures of the 1:1 mixture of 4 and 5. Observed under Leitz POK II microscope with hot stage. 200_x. (a) 120 °C, cooling run. (b) 120 °C. heating. (c) 170 °C, heating. See color plate II.

were distilled at reduced pressure. The residue was recrystallized twice from acetone to afford 0.55 g (28%) 4. The mother liquid was evaporated to dryness.The crude product of 5 thus obtained were purified by column chnromatograph (silica gel 100–200 mesh, eluent: petroleum ehter: acetone = 30:1) and recrystalized from ethanol to afford 1.0

g (52%) **5**. Total yield: 80%. Structural data; **4**, Anal. Calcd. For $C_{36}H_{55}O_5Fe$: C, 69.66, H, 8.45, Found, C, 69.59, H, 8.46. UV ($CHCl_3$) 300, 243.2 nm. IR (KBr) 2040, 1990, 1960 (C ≡ O), 1700 (C = O)cm^{-1}, ^{13}C-NMR ($CHCl_3$), 217, 215, 210 (C ≡ O), 172 (C = O), 140, 123, (C = C), 88, 83, 58, snf 46.6 (C = C–C = C), 74 (C–O). $[\alpha]_D^{20} = +106$ ($CHCl_3$) **5:** found: C, 69.52, H, 8.62. ^{13}C-NMR, 217, 215, 210 (C ≡ O), 171.8 (C = O), 140, 122.6 (C = C), 88, 83, 58.3, 46.2 (C = C–C = C), 74 (C–O), ppm. IR: 2040, 1980, 1960 (C ≡ O), 1695 (C=O), cm^{-1}. $[\alpha]_D^{20} = -82$($CHCl_3$).

(+) Iron tricarbonyl, sorbic acid 6 was prepared and resolved by fractional crystallization based on known method.[7,10] $[\alpha]_{578} = +209$(lit. +213).

4: To 0.25 g (1.0 mmol) **6** suspended in 10 ml anhydrous benzene was added 0.85 ml PCl_3 and 2 drops of pyridine. The mixture was refluxed for 1 h under N_2. After removal of solvent in reduced pressure, the residue was extracted with 10 ml benzene. To the solution, 0.5 g (1.3 mmol) cholesterol and two drops of pyridine in 10 ml benzene was added. The mixture was refluxed for 3 hrs. and filtered. The filtrate was evaporated and the residue was treated by column chromatograph. Yellow band was collected and evaporated. The solid was recrystallized from mixture of cyclohexane and petroleum ether to afford 0.12 g (19%) 4. M.p. 188–190°C. Elemental analysis, found C, 69.45, H 8.05. $[\alpha]_D = +104°$.

Chromium tricarbonyl, cholesteryl (*p*-methyl) benzoate 8: Mixture of 0.5 g (1 mmol) **6** and 0.20 g (0.9 mmol). $Cr(CO)_6$ in 11 ml solvent (n-dibutyl ether: THF = 10:1) was refluxed for 20 hrs. The product was purified by column chromatograph (silica gel 200–300 mesh. eluent:cyclohexane:ehtyl acetate = 2:1) to get 0.1 g (17%) 7. M.p. 168°C. Anal Cacd. for $C_{38}H_{52}O_5Cr$,C,71.22, H, 8.18. Found: C, 71.19 H 8.48 IR, 1960 and 1899 (C ≡ O), 1720(C = O) cm^{-1}. ^{1}H-NMR, 6.1, 6.0, 5.05, 4.95(C_6H_4), 2.15(CH_3) ppm.

Acknowledgments

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