Mesomorphic (η^6-arene)tricarbonylchromium complexes

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The first family of (η^6-arene)tricarbonylchromium complexes containing thermotropic liquid crystals has been prepared and the mesomorphic properties studied. Enantiotropic smectic C and nematic phases were observed. Comparison of their X-ray diffraction characteristics and liquid-crystalline behaviour with those of the metal-free analogues emphasized the influence of the organometallic unit on the mesophase features.

The design of new molecular units, capable of organizing into supramolecular systems exhibiting unique properties, is a current challenge.[1] Such ordered assemblies are expected to provide fundamental information on complex processes occurring at the molecular level, and to stimulate the development of nanoscale technologies.[1]

Among the investigations devoted to organized molecular assemblies (*i.e.* lyotropic and thermotropic liquid crystals, micelles, mono- and multi-layers, membranes),[2] metallomesogens (metal-containing liquid crystals) have recently attracted considerable attention.[3,4] The combination of the properties of metals (polarizability, magnetism, colour, redox activity) with those of liquid crystals (organization) led to most interesting studies, the results of which could have possible future applications, especially in the construction of electrooptical devices. Moreover, careful selection of the metal centre gave novel architectures, as compared to purely organic materials, which allowed further exploration and better understanding of the structure–liquid crystal properties relationship for mesomorphic materials.[3,4]

Our interest in thermotropic organometallic liquid crystals[5] prompted us to consider the (η^6-arene)tricarbonylchromium unit for designing a new class of thermotropic metallomesogens. Its photoreactivity motivated this research; ligand exchange can occur under light irradiation.[6] Ligand substitution may represent an elegant and efficient way for fine tuning the mesomorphic properties.

Little attention has been devoted to chromium-containing metallomesogens. Tricarbonyl(*p*-phenylenediamine)chromium was used to prepare organometallic polyamides which showed lyotropic behaviour.[7] Lyotropic mesomorphism was also reported for an amphiphilic co-ordination-type chromium(III) complex.[8] Thermotropic behaviour has been observed in the case of dichromium tetracarboxylate complexes.[9] To our knowledge, (η^6-arene)tricarbonylchromium complexes containing thermotropic liquid crystals have not previously been reported.

We describe, herein, the synthesis and mesomorphic properties of the first family of thermotropic (η^6-arene)-tricarbonylchromium derivatives, **1** (*n* = 8, 10, 12 or 14), and emphasize the role played by the organometallic framework in the supramolecular organization in the anisotropic state by comparing their liquid-crystal properties with those obtained for their metal-free analogues.[10] A tetracatenar (four chain-containing) ligand was selected with a view to exploring the possibility of designing mesomorphic chromium complexes with columnar liquid-crystalline phases.

Results and Discussion

Syntheses

Targeted organometallic Schiff bases **1** (*n* = 8, 10, 12 or 14) were prepared by condensing $[Cr\{\eta^6\text{-}1,4\text{-}(OCH)_2C_6H_4\}(CO)_3]$ **I** (Scheme 1) with the appropriate aniline derivative[10a] (structure not shown) in toluene, at reflux, and in the presence of a catalytic amount of toluene-*p*-sulfonic acid. Extraction of unreacted starting materials with EtOH gave pure **1** (75–80%), the structure and purity of which were confirmed by ^{1}H NMR spectroscopy and elemental analysis. Dialdehyde **I** was obtained by complexation of $[Cr(CO)_6]$ with 1,4-bis(1,3-dioxolan-2-yl)benzene **III**[11] (prepared from **II**) by adapting the method described for the synthesis of *p*-tolualdehyde diethyl acetal tricarbonylchromium complex[12] (**III** ⟶ **IV**) and subsequent hydrolysis under acidic conditions[13] (**IV** ⟶ **I**). Recently $[Cr\{\eta^6\text{-}1,4\text{-}(OCH)_2C_6H_4\}(CO)_3]$ was efficiently and elegantly prepared in a one-pot, two-step synthesis from $[Cr\{\eta^6\text{-}1,4\text{-}(Bu^n{}_3Sn)_2C_6H_4\}(CO)_3]$.[14]

Mesomorphic properties

The thermal and liquid-crystal behaviour of compounds **1** were investigated by a combination of polarized optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction studies. To avoid sample decomposition, a low light intensity was used during the observations by polarized microscopy and the DSC analyses were recorded for one heating run only.

All of the complexes exhibited mesomorphism (Table 1). The derivatives **1** (*n* = 8 or 10) showed enantiotropic smectic C and nematic phases, whereas **1** (*n* = 12 or 14) presented enantiotropic smectic C phases. The mesophases were identified from their optical textures. Both liquid-crystalline phases gave typical schlieren textures. The transition between the smectic C and nematic phases was clearly detected owing to the formation of transition bars (illustrative examples of phases and phase transitions can be found in ref. 15). Crystal-to-crystal and crystal-to-liquid crystal transitions overlapped. Therefore, broad melting transitions were obtained. Compounds **1** showed good thermal stability within the mesomorphic state but decomposed in the isotropic fluid.

X-Ray diffraction studies confirmed the nature of the mesophases. Decomposition occurred upon long exposure to irradiation as previously observed for related molecular complexes in solution.[6]

Nematic phase. The compounds oriented easily in a magnetic

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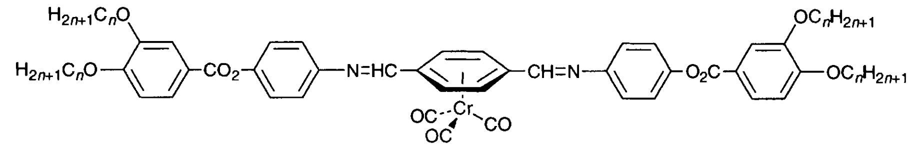
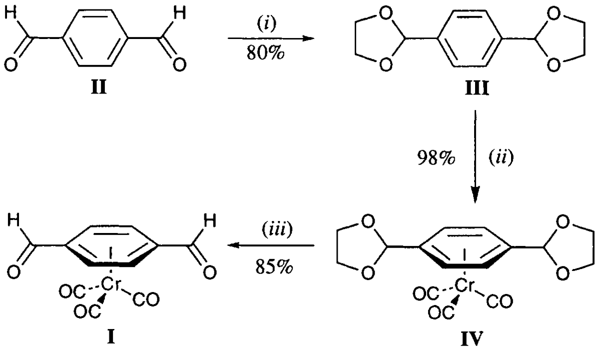


1 (n = 8, 10, 12 or 14)



Scheme 1 (*i*) Ethylene glycol, traces of HCl; (*ii*) $[Cr(CO)_6]$, di-*n*-butyl ether–heptane, reflux; (*iii*) tetrahydrofuran (thf), concentrated HCl

Table 1 Phase-transition temperatures[a] for complexes **1** and for the corresponding metal-free compounds[b]

	Complexes **1**		Metal-free compounds	
n	Transition[c]	T/°C	Transition	T/°C
8	$C \longrightarrow S_C$	95	$C \longrightarrow S_C$	137
	$S_C \longrightarrow N$	102[d]	$S_C \longrightarrow N$	198.5
	$N \longrightarrow I$	140[d]	$N \longrightarrow I$	206.5
10	$C \longrightarrow S_C$	94	$C \longrightarrow S_C$	125
	$S_C \longrightarrow N$	110	$S_C \longrightarrow I$	185
	$N \longrightarrow I$	131		
12	$C \longrightarrow S_C$	92	$C \longrightarrow S_C$	127.5
	$S_C \longrightarrow I$	118	$S_C \longrightarrow \varphi_{ob}$	128.5
			$\varphi_{ob} \longrightarrow \varphi_h$	161
			$\varphi_h \longrightarrow I$	186
14	$C \longrightarrow S_C$	95[d]	$C \longrightarrow \varphi_h$	123
	$S_C \longrightarrow I$	99	$\varphi_h \longrightarrow I$	176

[a] C = Crystal state, S_C = smectic C phase, N = nematic phase, φ_{ob} = oblique lamello-columnar phase, φ_h = hexagonal columnar phase, I = isotropic liquid. [b] From ref. 10. [c] First heating run. [d] Determined by polarized optical microscopy.

field. The diffracted intensity is distributed between four spots at low angles and two diffuse arcs at wide angles (Fig. 1, right). The wide-angle arcs are the section of a torus. The maximum intensity corresponds to a scattering vector modulus of *ca.* $(2\pi/4.5)$ Å^{-1} and characterizes the distribution of the molecules in a plane perpendicular to the director (n). The plane of the torus, the equatorial plane, is perpendicular to the director which itself is also, in this case, parallel to the magnetic field. The four spots at small angles are symmetrically located around the incident X-ray beam. They are sections of two tori with the meridian as common revolution axis. The scattering vector of each of these small-angle spots makes an angle of 49° with the meridian and its length is $(2\pi/33.4)$ Å^{-1}. These diffuse spots are characteristic of a periodic lamellar structure with a period of 33.4 Å. The normal to the layer (c) is tilted at 49 ± 1.5° with respect to the director. The spots are aligned in pairs on layer lines perpendicular to the meridian. The periodicity of these layers along the meridian corresponds to a mean distance between molecules along the director which is of the order of the length of the ligand (52 Å). The width of the diffuse spots is governed by the extension of the lamellar structure. Therefore, in the nematic phase the existence of four diffuse spots characterizes a local smectic C lamellar ordering (smectic C fluctuations, *i.e.* the so-called cybotactic groups). Similar results were obtained from **1** (n = 10). In this case an additional, non-oriented, mesophase was also detected which could be due to the presence of the metal-free organic compound[10] because of metal loss.

Fig. 1 Schematic representation of the diffraction pattern of a single domain of the nematic phase; the pattern is symmetrical about the director (n). Left, usual nematic diffraction pattern; right, nematic with local smetic C ordering as shown by the four spots at small angles (see text)

Smectic C phase. As one approaches the smectic C phase (on cooling the sample) the small-angle diffuse spots sharpen, which means that the correlation length of the smectic C fluctuations is increased. A modification of the texture occurs when the true smectic C phase appears: the smectic layers orient parallel to the sample tube walls; the layer periodicity is the same as in the nematic phase.

The variation of the d-layer spacing as a function of the alkyl chain length for compounds **1** (n = 8, 10, 12 or 14) as well as for the metal-free analogues[10] is presented in Fig. 2. A difference of 2 Å was systematically observed between both systems. This difference could result from a different tilt angle (*ca.* +4° in the case of metal-free species) as a consequence of different quadrupoles between the free and complexed organic compounds. Indeed, according to Barbero and Durand,[16] the tilt angle is increased as the quadrupolar modulation through the layer is increased (an optimum value of 55° was predicted). Another possibility would be that the global conformation of the organic ligand is more extended when complexed to a bulky group which increases the steric hindrance in the aromatic sub-layers. In the free organic compound the discrepancy between the molecular area at the aromatic and paraffinic chain level favours a zigzag conformation of the molecule where the long axes of the chains make an angle with the core long axis. The smectic layer could thus contain a mixture of molecules with extended and zigzag conformations, so that the apparent length of the molecule is shorter than in an assembly of molecules all in extended conformation (note that the difference between the two conformations is not due to the paraffinic chains themselves, but to the relative orientation of the different components of the compound). Besides, molecules in zigzag conformation can form clusters, evidence of which can be seen in the X-ray diffraction pattern of the metal-free mesophases: defective columns of molecules parallel to the director and with a shorter repeat distance than the apparent molecular length L $[= d/\cos \alpha$ (d = layer spacing, α = tilt angle)] are inserted in the smectic layers. Obviously, the defective columns release the packing constraint resulting from the difference between the chain and core areas. The diffraction patterns of the mesophase of the complexes do not show any feature which could be the signature of defective columns.

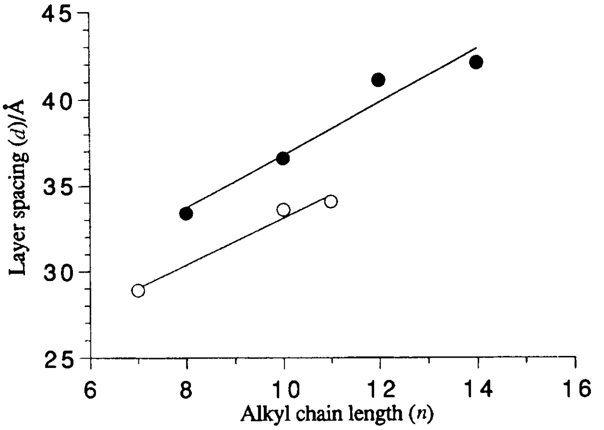


Fig. 2 Variation of the layer spacing (*d*) as a function of the alkyl chain length (*n*) in the smectic C phase for compounds **1** (●) and for their metal-free analogues (○); for **1** (n = 8), the period was measured in the nematic phase from the cybotactic groups

Finally, comparison of the thermal data for complexes **I** with those of the metal-free compounds (Table 1) revealed that introduction of the chromium tricarbonyl core into the organic segment lowered both the melting and clearing transitions. This behaviour is most likely due to the bulky organometallic subunit which acts as a spacer between the mesogenic molecules, decreasing the intermolecular interactions. This tendency is further confirmed by the fact that complexes **1** exhibited nematic and/or smectic phases whereas for their organic counterparts columnar phases were also observed: despite the presence of a tetracatenar ligand, the chromium tricarbonyl system prevented columnar-like stacking.

Conclusion

We have reported the first family of tricarbonylchromium (η^6-1,4-disubstituted benzene) complexes containing thermotropic liquid crystals. They gave enantiotropic nematic and/or smectic C phases. The role played by the metal centre was explained by comparing the X-ray diffraction data and mesomorphic behaviour of the organometallic derivatives with those of the corresponding metal-free analogues. Owing to the photoreactivity of the basic (η^6-arene)tricarbonylchromium system, light-induced ligand-exchange reactions could be used for mesophase engineering.

Experimental

Materials

Aniline derivatives[10a] and 1,4-bis(1,3-dioxolan-2-yl)benzene[11] were prepared following literature procedures. The solvents were dried according to standard methods prior to use.

Instrumentation

Transition temperatures and enthalpies were determined with a differential scanning calorimeter (Mettler DSC 30) connected to a Mettler-TA 4000 processor, rate 10 °C min^{-1}, under N_2; treatment of the data used the Mettler TA72.2/.5 graphware. Optical studies were made using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2. A point-focused monochromatic X-ray beam [λ(Cu-Kα) = 1.541 Å] was obtained[10a] by the reflection on a doubly bent graphite monochromator. The sample was held in a Lindemann glass capillary tube (diameter 1.0 mm) inserted for alignment in the gap of a permanent magnet (0.3 T) and maintained at a constant temperature within ±0.5 K. The diffracted X-rays were collected on flat rectangular photographic film. The sample, its environment and the film were in a closed evacuated camera in order to suppress the background due to air scattering. The NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer with $SiMe_4$ as internal reference, IR spectra on a Perkin-Elmer 1720 FTIR spectrometer and UV/VIS spectra on a Perkin-Elmer Lambda 5 spectrophotometer. Elemental analyses were performed by Mikroelementaranalytisches Laboratorium, ETH-Zurich and the Service de Microanalyse de l'Université Louis Pasteur de Strasbourg.

Syntheses

Complex IV. A solution of 1,4-bis(1,3-dioxolan-2-yl)benzene **III** (12.0 g, 0.054 mol) and $[Cr(CO)_6]$ (12.0 g, 0.054 mol) in di-*n*-butyl ether (432 cm^3)–heptane (192 cm^3) was heated at reflux in a Strohmeir apparatus for 2 d under argon and in the absence of light. The solution was cooled to *ca.* 90 °C and filtered over hot Celite. The filtrate was cooled to room temperature which led to the formation of bright yellow crystals. The solid was filtered off (the following day to allow for completion of crystallization) and dried under high vacuum to give analytically pure complex **IV** (19.0 g, 98%) (Found: C, 50.15; H, 3.85. Calc. for $C_{15}H_{14}CrO_7$: C, 50.30; H, 3.95%). IR (MeCN): $\tilde{\nu}$/cm^{-1} 2965 (CH_2), 1968 (CO) and 1905 (CO). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_2Cl_2): 317 (12 000) and 229 (19 000). NMR ($CDCl_3$): ^{1}H, δ 4.06 (d, 8 H, J = 8.6, CH_2), 5.51 (s, 4 H, complexed aromatic) and 5.54 (d, 2 H, J = 8.66 Hz, CH); ^{13}C-{^{1}H}, δ 65.75 (CH), 101.29 (CH, complexed aromatic), 107.68 (CC, complexed aromatic) and 231.82 (CO).

Complex I. A mixture of complex **IV** (4.6 g, 13 mmol) and concentrated HCl (12 mol dm^{-3}, 50 cm^3) in thf (100 cm^3) was stirred at room temperature for 30 min. The solution was made alkaline with a saturated Na_2CO_3 aqueous solution (100 cm^3) and extracted with diethyl ether (3 × 100 cm^3). The deep red organic phase was dried over $MgSO_4$. Removal of the solvent under vacuum gave a solid residue. Crystallization of the latter from diethyl ether–pentane yielded pure complex **I** (2.95 g, 85%) (Found: C, 48.65; H, 2.20. Calc. for $C_{11}H_6CrO_5$: C, 48.90; H, 2.25%). IR (MeCN): $\tilde{\nu}$/cm^{-1} 1992 (CO), 1930 (CO) and 1700 (CHO). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_2Cl_2): 443 (3100), 322 (12 000) and 229 (22 000). NMR [$(CD_3)_2CO$]: ^{1}H, δ 6.32 (s, 4 H, complexed aromatic) and 9.72 (s, 2 H, CHO); ^{13}C-{^{1}H}, δ 93.89 (CH, complexed aromatic), 99.44 (CC, complexed aromatic), 190.72 (CHO) and 230.73 (CO).

Compound 1 (n = 8). A solution of complex **I** (100 mg, 0.37 mmol), the appropriate aniline derivative (n = 8, 320 mg, 0.74 mmol), a catalytic amount of toluene-*p*-sulfonic acid and toluene (25 cm^3) were heated under reflux in the dark. Water was removed by means of a Dean–Stark trap. The reaction mixture was allowed to cool to room temperature and the solvent removed under vacuum. The solid residue was suspended in EtOH (25 cm^3) and treated in an ultrasonic bath for 15 min. The mixture was then heated at reflux for 30 min. The solid was filtered off and dissolved in CH_2Cl_2. Evaporation of the solvent under reduced pressure gave the desired compound in 75% yield, as a red solid. IR (KBr): $\tilde{\nu}$/cm^{-1} 2955, 2924, 2854, 1986 (CO), 1909 (CO), 1728 (CO_2), 1625 (C=N) and 1598. ^{1}H NMR (CD_2Cl_2): δ 0.85–0.90 (m, 4 CH_3), 1.2–1.6 (m, 20 CH_2), 1.75–1.95 (m, 4 CH_2), 4.05–4.10 (m, 4 CH_2O), 6.16 (s, 4 H, complexed aromatic), 6.97 (d, J = 8.5, 2 H of benzoyl), 7.27 and 7.28 (overlapped dd, 8 H of aniline), 7.67 (d, J = 1.8, 2 H of benzoyl); 7.81 (dd, J = 8.5 and 1.8 Hz, 2 H of benzoyl) and 8.16 (s, 2 CHN).

Complexes **1** (n = 10, 12 or 14) were prepared similarly; their ^{1}H NMR and IR spectra were similar to those of **1** (n = 8). The elemental analyses are reported in Table 2.

Table 2 Elemental analytical data for complexes **1** (calculated values in parentheses)

		Analysis (%)		
n	Formula (M_r)	C	H	N
8	$C_{69}H_{88}CrN_2O_{11}$ (1173.46)	70.90	7.50	2.40
		(70.65)	(7.55)	(2.40)
10	$C_{77}H_{104}CrN_2O_{11}$ (1285.68)	71.95	8.20	2.20
		(71.95)	(8.15)	(2.20)
12	$C_{85}H_{120}CrN_2O_{11}$ (1397.88)	73.05	8.80	2.00
		(73.05)	(8.65)	(2.00)
14	$C_{93}H_{136}CrN_2O_{11}$ (1510.11)	73.55	8.65	1.85
		(73.95)	(9.10)	(1.85)

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