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On some transition metal complexes having orientational properties

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The orientation properties of some complexes of chromium (III) or cobalt (II) with oxygen-containing ligands are presented. The orientation obtained is mostly homeotropic. The possibility of anchoring by coordination of liquid crystal (LC) molecules to the transition metal ion within the alignment layer is discussed on the basis of spectroscopic arguments.

1. Introduction

Coordination of mesogenic ligands to transition metal ions has been widely used in recent years in order to obtain new mesophases [1–7]. However, there are relatively few examples of metal complexes producing molecular orientation of liquid crystal materials [8].

In this paper we present the orientational properties of some complexes containing chromium (III) or cobalt (II) as the central ion and having acrylic acid (AcA), poly(acrylic acid) (PAcA), polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP) as ligands: when deposited onto the substrate these complexes produce homeotropic orientation.

Alignment of LC molecules on treated surfaces is generally a complex phenomenon and different mechanisms have been discussed in the literature [9–13]. Chemical bonding, even on metal surfaces, has already been considered an important factor in this alignment [14]. The presence of transition metal ions within the alignment layer could raise the question of anchoring by coordination of the LC molecules to these ions. Such an alignment mechanism is proposed here on the basis of spectroscopic arguments.

2. Experimental

The above chromium and cobalt complexes were obtained as aqueous solutions by the reaction between a salt of the corresponding metal and the ligand solution (1·5 wt%), usually at a molar reactant ratio of 1 : 1, as mentioned in the text. At least three preparations were made of each solution. In the case of PAcA, care had to be taken over the M_W distribution, since some precipitation could occur; in the PVP case, the extent of precipitation was much lower. The solutions were used several days after reactant mixing in order to allow the equilibria to be reached.

Chemicals were of p.a. grade. Chromium nitrate and cobalt chloride or acetate were purchased from Merck and UCB, respectively; acrylic acid was obtained from

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Merck, polyvinylpyrrolidone, from Fluka AG ($M_W = 100\,000$), and all of them were used as received. The poly(acrylic acid) (M_W up to $1{\cdot}5 \times 10^6$) was prepared in the laboratory.

The alignment was tested on MBBA as well as on some commercial nematic mixtures having relatively low clearing points and different dielectric anisotropies. Most of the mixture components contain the cyano group as the main function, but some other groups were also present. The characteristics of these LCs are given in table 1.

The alignment layers were deposited by spinning the solution onto glass plates ($25 \times 35\,\mathrm{mm}^2$) of the soda lime type. Several deposited plates were made from every solution of each complex. After deposition, the plates were dried at 120°C for 1 h. In certain cases, the glass plates were previously coated with a PVA layer deposited by spinning (3000 rpm) from an aqueous solution (3 wt%) and then dried at 120°C for 30 min.

At least five experimental cells of 15 μm thickness were manufactured each time for testing the alignment properties of the deposited layers, these layers being obtained from each kind of solution from each preparation. These cells were filled by capillary action using the LC in the isotropic phase. The observations were made after cooling.

The orientational properties of the alignment layers investigated were studied microscopically either between crossed or parallel polarizers or by conoscopy. Cell uniformity was considered as a rough test of the quality of substrate deposition. For each particular LC, we simply judged that the substrate deposition was reproducible if a uniform homeotropic orientation was achieved each time when the layers were obtained under the same conditions (that is, composition and amount of the solution, spinning rate, treatment temperature and duration).

We have sought to establish complex formation between transition metal ions and the above mentioned organics, as well as coordination of the LC molecules to the same ions by using optical absorption spectroscopy. The electronic spectra were recorded for solutions in common solvents having different dielectric constants and donor properties (for example, water, isopropyl alcohol, acetone, chloroform or benzene) using a Specord UV-vis and a Cary 17D spectrometer. The spectra were fitted with Gaussian curves. IR spectra were obtained either from KBr pellets or solutions using a Specord 75 IR spectrometer.

Table 1. Characteristics of the LCs used in this study.

Code	Source	Composition†	Main groups	$\Delta\varepsilon$	T_c/°C
MBBA		Schiff's base	Imine, ether	$-0{\cdot}5$	42
RO-TN570	Roche	Biphenyl mixture	Nitrile	$+13{\cdot}9$	57
RO-TN403	Roche	Biphenyl-pyrimidine mixture	Nitrile, ether	$+19{\cdot}2$	81
RO-TN103	Roche	Ester-pyrimidine mixture	Nitrile, ester	$+25{\cdot}6$	81
ZLI 1565	Merck	PCH mixture	Nitrile	$+11{\cdot}0$	85
ZLI 1285	Merck	PCH/CB/BCH/PCH esters	Nitrile	$+13{\cdot}8$	68
ZLI 1132	Merck	PCH/BCH	Nitrile	$+10{\cdot}3$	70
NP 5	Merck	Azoxy derivative mixture	Azoxy	$-0{\cdot}2$	73

†PCH is phenylcyclohexane, BCH—biphenylcyclohexane, CB—cyanobiphenyl.

Cycles involving heating up to 120°C and cooling down to room temperature were repeated to check the stability of the alignment obtained.

3. Results and discussion

3.1. *Formation of the alignment complexes*

We expected that a coordination complex would be formed between each of the two transition metal ions and the above-mentioned organics, due to the analogy between our systems and many others described in the literature (for example, [4, 6, 8, 15, 16]). Our organic materials could coordinate to the transition ion through their oxygen atoms. This is the case even for PVP, because its nitrogen is sterically hindered.

Since the accurate determination of the structure of the resultant complexes was not the aim of this work, we limited the work to the spectroscopic characterization of the solutions of the complexes as they were obtained some time after mixing of the reactants; thus, several solutions of every complex were studied.

Investigations were carried out in two spectral regions: one relates to the electronic transitions within the transition metal ion and the other involves the ligands. The visible spectra of both transition metal ions in the presence of the different organic materials studied showed the well-known maxima for an environment of the octahedral type, with small variations in the peak positions as a function of the ligand used: therefore, these spectra are not given here. The maxima observed by us were easily ascribed to the corresponding dd spectra according to common ligand field theory [17]. Peak shifts clearly occur as shown by the data of table 2 which gives the peak positions after gaussian fitting of the corresponding spectra. These variations in the position (as well as in the intensity) can be correlated with the influence of the various ligands on the electronic transition energy of the complex ion.

The ligand peaks have also supplied information concerning the complex formation. In figure 1 there are reproduced the spectra of the acrylate complexes in the charge transfer region. When compared with the corresponding spectrum of free AcA, we observe peaks which depend on the transition ion nature, as well as on the counterion, which might enter into the coordination sphere of the transition ion; these peaks can be readily explained if one supposes that the acrylate ions have also been included in the coordination sphere of the chromium or cobalt ions.

To establish the coordination stoichiometry and kinetics further investigations are necessary.

3.2. *The alignment properties of the complexes*

Some of the complex solutions studied, when deposited onto the substrate, give homeotropic alignment properties of LC molecules such as MBBA or those in different commercial mixtures. These results are collected in table 3. The interpretation of these results is difficult due to the fact that mixtures of mesogenic components were mainly used. However, some features should be discussed.

It is interesting to notice that neither the AcA nor the PAcA by themselves gave homeotropic alignment, although such an orientation has already been reported [18] for several carboxylic acids. Similarly, none of the other organic materials had homeotropic orientational properties when they were singly deposited onto the substrate.

Table 2. Position (cm^{-1}) of the main visible absorption bands of the solutions investigated.

Solution composition†	I band	II band
$[Cr(H_2O)_6]^{3+}$	17084	23946
Cr:AcA (1:1)	17132	24212
Cr:PAcA (1:1)	17300	24450
Cr:PVA (1:1)	17032	23992
Cr:PVP (1:1)	17225	24150
$[CoCl_x(H_2O)_y]^{2-x}$	19051	21265
$[Co(CH_3COO^-)_x(H_2O)_y]^{2-x}$	18856	20727
Co:AcA (1:1)	18829	20831
Co:AcA (1:2)	19084	21196
Co:PAcA (1:1)	19006	21065
Co:PVA (1:1)	18918	21033
Co:PVP (1:1)	19200	21300

†The molar ratio in the case of polymer ligands refers to the monomer units. In the formulae of the octahedral complex ions x varies between 0 and 4, while y is related to x by the equation $x+y=6$.

Cobalt(II) acetate or chromium(III) nitrate (by deposition from aqueous solution) induces homeotropic orientation which is maintained only for a few days at room temperature.

We have found that the orientational properties of the layers deposited using complexes containing PAcA do not seem to depend on the polymer chain length over the range studied.

The stability of the observed homeotropic alignment differs as a function of the complex and nature of the LC: thus, the orientation obtained using the solution containing the complexes of PVA with cobalt or chromium is unstable. On the other hand, the complexes of the other ligands studied lead to an orientation which is stable for at least 6 months at room temperature. In some few cases, the stability is preserved even after several heating cycles over the clearing point and cooling cycles down to room temperature. In the case of the Cr:PAcA alignment layer the MBBA molecules underwent chemical degradation during the several months of storage; the optical anisotropy of the LC was therefore destroyed.

The conclusions from our experiments are therefore that the most stable homeotropic alignment is obtained with Cr:PVP (1:1) and Cr:PAcA (1:1) solutions: the alignment was preserved after heating the corresponding cells at 120°C for more than 1000 h.

Up to now, we have failed to correlate the stability of the homeotropic alignment obtained with any structural factors.

3.3. *Coordination of LC molecules to the transition metal ions from the alignment layer*

Since the coordination properties of the nitrogen atom of Schiff's bases or nitriles are already known, and since MBBA possesses in addition an oxygen donor atom, we supposed that the LC molecules themselves might coordinate to the transition ions of the aligning layer. Such behaviour was not checked in the cell, but in solution.

The spectra in figure 2 show that the UV absorption peaks of MBBA are shifted and greatly enhanced in intensity in the presence of transition metal ions, especially chromium. It is noted that all spectra were recorded after the same lapse of time, obviously rather short, after mixing the LC with the solution of transition metal salt, since it is known that MBBA is chemically very sensitive. However, we did not observe any modification of the electronic spectrum of MBBA in the same solvent, even after two days. The IR spectrum of MBBA in the presence of transition metal ions indicates no chemical alteration of the LC molecule. Consequently, the spectral modifications observed in figure 2 have been assigned to the interactions of the lone pair of electrons of the LC molecule with the transition metal ion, so forming a coordination complex.

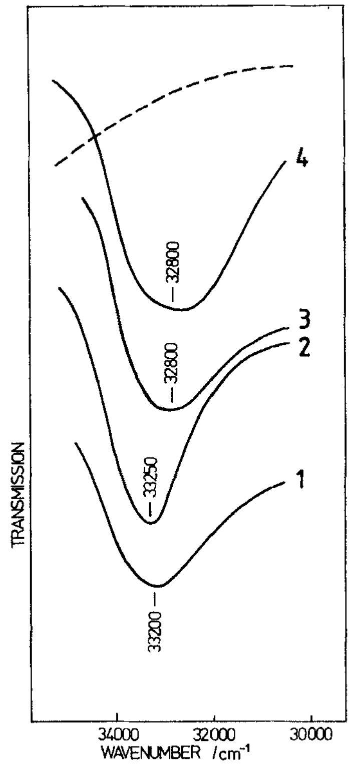


Figure 1. Difference spectra in the charge transfer region between each of the complexes formed from the following reactant mixtures (1) Co acetate: AcA (2 : 1); (2) Cr acetate: AcA (1 : 1); (3) Co chloride: AcA (1 : 1); (4) Cr: AcA (1 : 1)—and free AcA (aqueous solutions). The dashed curve represents the spectrum of free AcA.

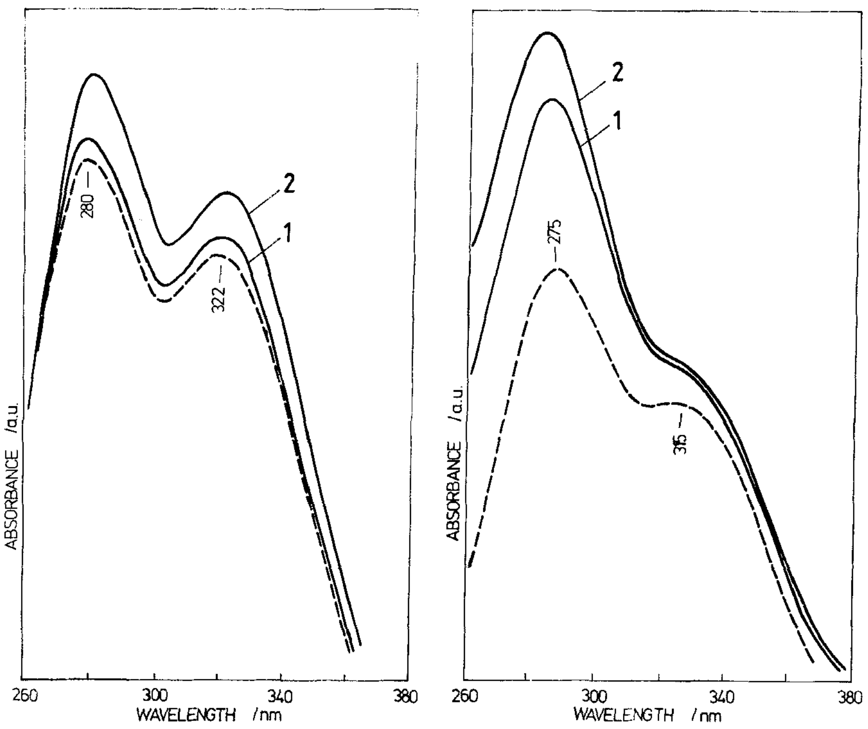
Table 3. Orientational properties of the complexes studied.

Glass pretreatment	Alignment layer	Liquid crystal	Alignment†	Orientation stability
PVA	Chromium nitrate	MBBA	⊥	Unstable
PVA	Cobalt acetate	MBBA	⊥	Unstable
PVA	AcA	MBBA	∥ ×	
		RO-TN 570	∥ ×	
PVA	PAcA	MBBA	∥ ×	
	PVP	MBBA	∥ ×	
		ZLI 1565	∥ ×	
PVA	Co : PAcA (1 : 1)	MBBA	⊥	‡
		ZLI 1285	⊥	‡
		NP 5	⊥	Unstable
PVA	Co : AcA (2 : 1)	MBBA	⊥	‡
		ZLI 1285	⊥	‡
		ZLI 1565	⊥	‡
		RO-TN 570	⊥	‡
		RO-TN 403	⊥	‡
		ZLI 1132	⊥	‡
	Co : PVA (1 : 1)	MBBA	⊥	Unstable
		ZLI 1132	∥ ×	
	Co : PVP (1 : 1)	MBBA	⊥	Unstable
		RO-TN 570	⊥	Nonuniform, unstable
PVA	Cr : PAcA (1 : 1)	MBBA	⊥	MBBA degradation
		ZLI 1132	⊥	‡
		RO-TN 570	⊥	‡§
PVA	Cr : AcA (1 : 1)	MBBA	⊥	
		RO-TN 103	⊥	‡
		ZLI 1565	⊥	‡
		ZLI 1132	⊥	
		ZLI 1285	⊥	‡
	Cr : PVA (1 : 1)	MBBA	⊥	Unstable
		ZLI 1285	⊥	
		ZLI 1132	∥ ×	
		NP 5	∥ ×	
	Cr : PVP (1 : 1)	MBBA	⊥	
		RO-TN 570	⊥	‡§

† ⊥, Homeotropic; ∥ ×, parallel nonuniform.

‡ Stable orientation at room temperature, at least 6 months.

§ Stable orientation after heating at 120°C more than 1000 h.



(*a*) (*b*)

Figure 2. UV absorption spectra of MBBA in the presence of transition ions: (1) cobalt ions; (2) chromium ones. (*a*) in solution in chloroform; (*b*) in solution in isopropyl alcohol. The dashed curves represent the spectra of free MBBA in the corresponding solvents.

On the other hand, the involvement of the cyano group in a similar coordination interaction should alter the CN bond and, therefore, its stretching vibration has to be shifted when compared with that of the uncoordinated cyano group. This behaviour has been observed not only for solutions, but also for the complexes deposited by evaporation of water onto IR transparent plates; the most illustrative spectra are given in figure 3. The spectral region where the CN stretching mode appears is generally well separated from other IR absorptions, but we verified that this range was clear for each component of our systems. Therefore, the additional peaks seen in figure 3 were assigned to the stretching vibration of the LC cyano group coordinated under different environments in agreement with the literature [19].

The components of ZLI 1565 and 1132 have terminal cyano groups as single functions in the molecules, like the components of RO-TN 570: therefore, a similar spectroscopic behaviour is to be expected and has been found for the former two LC mixtures and for the latter mixture. Other commercial mixtures noted in table 1 contain additional oxygen functions or pyrimidine rings which might also be involved in coordination to the transition metal ions. At this stage of the investigations, we have no experimental evidence for such an involvement. The behaviour of the cells filled with the corresponding LC mixtures seems to depend on the nature of

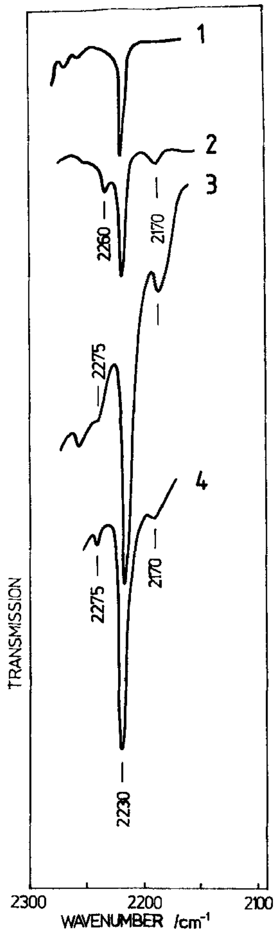


Figure 3. IR spectra of RO-TN 570 in the C ≡ N range: (1) free, in chloroform solution; (2) interacting with Cr : AcA complex in chloroform solution; (3) interacting with Cr : AcA complex deposited onto a KRS5 plate; (4) interacting with Cr : PAcA complex deposited onto a KRS5 plate.

the function(s) in the molecule, although this function is not the only determining factor.

We have concluded that the LCs studied can coordinate to the alignment layer containing transition metal ions. This bonding is always normal to the surface which contains the transition metal ion, and this might explain the homeotropic orientation of the LC molecules. At this stage of the investigations, we can only speculate on the complex lying on the substrate. If four of the carboxy (oxy) groups in the alignment complex are situated in one plane, they reproduce a well-known structure [15]. The axial positions of the octahedron around the central ion might be occupied, one of them by a bond to the substrate surface and the other, by a bond to the LC molecule. The model becomes much more complicated if the complexes are dimeric or polymeric. However, it is difficult at this time to say what particular properties are conferred on these cells through such a strong bonding as coordination.

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