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My 20 years of research in the chemistry of metal containing liquid crystals

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Contents

Abstract

Twenty years ago, in 1977, I began, with important exterior collaborations, original research on metal containing liquid crystals, also known as metallomesogens. I wished to synthesize in this paper my 20 years of research in this field. These compounds combine the known properties of organic liquid crystals with those introduced by the presence of one or more

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metals (colour, magnetism, polarizability, multiple localized charges) and provide new geometrical shapes including square planar, octahedral, square pyramidal, lantern structures which are unobtainable in purely organic compounds. We have synthesized both rod-like and disc-like metallomesogens, and observed examples of almost all the main mesophase types. If 1977 was the beginning of a systematic research into metallomesogens, the phenomenal growth occurred in early 1980, when many laboratories entered the field.

Keywords: Liquid crystal; Mesomorphic properties; Metallomesogen; Transition-metal complexes

1. Introduction

Twenty years ago, liquid crystals were in great expansion and I was fascinated by these compounds. My laboratory, supervised by A. Rassat, was specialized in the chemistry of paramagnetic molecules and I wished to synthesize paramagnetic liquid crystals. After unsuccessful attempts with liquid crystals labelled by nitroxides, I thought to label them with paramagnetic metals. It was the beginning of my work on metallomesogens.

Even if the first organotransition metallomesogens were reported, by Vorlander [1] in 1923, and Malthête and Billard [2] in 1976, the work developed in our laboratory by U.T. Mueller-Westerhoff and myself on nickel and platinum dithiolenes is widely accepted as being the beginning of systematic research in this field. Since then, many laboratories have entered the field and examples of all the main mesophase types have been observed. Aside from paramagnetism, the presence of one or more metals opens many exciting possibilities: geometries and hence shapes not easily found in organic chemistry can result from coordinating a metal, and many of the d- and f- block transition metal complexes are in an oxidation state which gives coloured compounds.

Profound effects arise from the large and polarizable concentration of electron density that every metal atom possesses, since the molecular polarizability is a key factor in determining whether a molecule will form a liquid crystal. As a result of this, the physical properties of the compound will be enhanced and many interesting possibilities concerning optical [3] (strong birefringence, dichroism, nonlinear optical behaviour), magnetic [4] (paramagnetism, orientation in magnetic field), electrical [5] (one-dimensional conductors), and electro-optical [6] (ferroelectric behaviour) properties, may result. This paper aims to give an overview of the work carried out in our laboratory since 1977 on metallomesogens, with important exterior collaborations. For more details on this field and principally on the basic concepts and facts of the liquid crystal states, the readers are referred to seven recent reviews [7–13].

2. Dithiene complexes of nickel, palladium and platinum

In general, dithiolato complexes are square planar, and one can imagine a planar terphenyl like structure for complexes of that type (Fig. 1). So, first in Grenoble

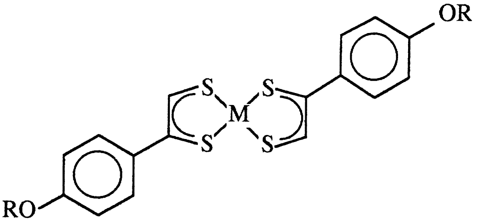

Fig. 1. Four-chain dithiolene complexes.

and mostly in Mueller-Westerhoff's laboratory at IBM in San Jose (California), dithiene complexes of nickel, platinum and palladium were synthesized and their mesomorphic properties investigated [14,15].

Starting materials for the synthesis of the bis-(*p*-alkyl-styryl-1-1,2-dithiolato) nickel, palladium and platinum complexes were benzene derivatives substituted by different alkyl chains. Friedel–Crafts acylation with acetyl chloride and $AlCl_3$ lead to the *p*-alkyl acetophenone, which was brominated by Br_2 in acetic acid to the bromoacetyl derivative. This compound reacts with potassium ethyl xanthate in ethanol and the xanthate obtained is cyclized by HBr in acetic acid to the dithiocarbonate. This dithiocarbonate is cleaved by sodium methoxide to form the styryl dithiolates, which reacted with the respective transition metal halides or tetrahalometallates, to give initially the dianions of the complexes. The neutral compounds were obtained by oxidation by air or iodine [16]. The pure nickel complexes are green in solution and form dark crystals of high reflectivity. The palladium complexes are bronze coloured crystals, which dissolve with wine-red colour, and the platinum analogs are purple in solution as well as in the solid.

The mesomorphic properties of the complexes were investigated by the standard methods: hot stage polarized optical microscopy; differential scanning calorimetry and X-ray diffraction. The most general observation is that all the nickel and platinum complexes form well-defined and stable mesophases, while the palladium complexes do not seem to possess any mesomorphic properties. As intermolecular forces play an important role in the mesophase character, we advanced this lack of mesomorphism to the strong Pd–Pd bond. However, Browall [17] found in the solid state of unsubstituted complexes, a Pt–Pt separation of 2.77 Å, shorter than the Pd–Pd distance (2.79 Å). Since information on the M–M distances in the mesogenic phase is missing, it is difficult to assess the potential contribution of any solid state M–M interactions to the mesomorphism or lack of it [9]. For the nickel and platinum series, the complexes with *n*-alkoxy chains ($R = C_nH_{2n+1}$) of six or less carbons atoms are nematic and those with longer chains are smectic. Both the Ni and Pt series show the same break (nematic to smectic) at a $n = 6$ chain length. Transition temperatures of the platinum complexes are higher than those of the nickel complexes by about 30 °C. For both compounds, transition temperatures decrease with increasing of chain length. The nickel complex ($M = Ni$, $n = 6$) shows both mesophase types (smectic 139 °C, nematic 169 °C, isotropic 181 °C).

The X-ray crystal structure [18] of the nickel complex ($n = 8$) showed the expected

M^{II} square planar geometry, with the substituents in a *trans*-conformation. The molecules are arranged zig-zag in layers in the unit cell; this is the arrangement which would be anticipated as the precursor to a smectic phase.

Moreover, the dithiolenes have interesting electron acceptor properties and unusual electronic structures, with strong absorption bands ($\lambda_{max} > 750$ nm, $\epsilon > 25\,000$). So, in order to get charge-transfer complexes between a donor and an acceptor, we synthesized a mesomorphic, strong electron donating substituted tetrathiafulvalene (TTF). We expected that the mixture of the two nematic partners could lead to smectic complexes through enhanced intermolecular interactions. This we have been unable to show, because the charge- transfer interactions appear too weak to lead to stoichiometric complexes [19].

The nematic nickel complex ($n=4$), dissolved in nematic cyanobiphenyl, was shown later to be useful as a near-infrared dichroic dye in active and passive laser devices operating near 800 nm [20,21].

3. *β*-diketonato complexes

At that time, in 1977, a new class of mesogens formed by disc-like molecules was discovered by Chandrasekhar [22].

Some transition metal complexes of *β*-diketones showing a square planar geometry seemed to us good candidates for the search of a discotic shape metallomesogen. Copper complexes of 1,3-(bis(*p*-substituted-phenyl)-*β*-diketones were first investigated.

3.1. Copper and nickel complexes with two or four peripheral chains

The mesogenic 1,3-bis(*p*-substituted-phenyl)-*β*-diketones [23,24] were synthesized by the standard condensation of the *p*-substituted acetophenone with *p*-substituted methyl benzoate in the presence of sodium hydride in anhydrous dimethoxyethane. This method is convenient to prepare symmetric and asymmetric *β*-diketones. The metal complexes were synthesized by addition of a solution of transition metal chloride in ethanol to a solution of the appropriate diketone in the same solvent at pH adjusted with ammonia to 7–8.

The *β*-diketone ligands exhibit a very organized optically biaxial mesophase which is probably a SmE phase.

Then, three copper(II) complexes (Fig. 2) were synthesized, $n=7$, $m=13$; $n=m=10$; $n=m=12$ with $R=Cn$ and $R'=Cm$.

Both the symmetrically and the unsymmetrically substituted copper complexes present an organized mesophase. We noticed that the unsymmetric compounds have a lower melting point than the symmetric and that the clearing point increases when chain lengths increase. NMR investigations [25] of the spin-lattice relaxation time T, suggested a lamellar mesophase with disc-like molecules organized in columns.

The nickel complexes are not mesomorphic and might possess a pyramidal structure.

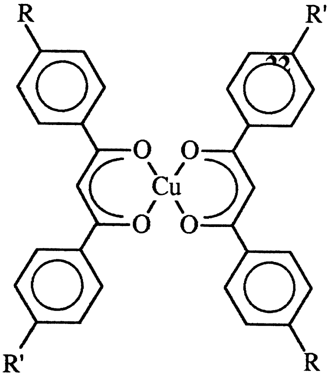

Fig. 2. Four-chain β-diketonate complexes.

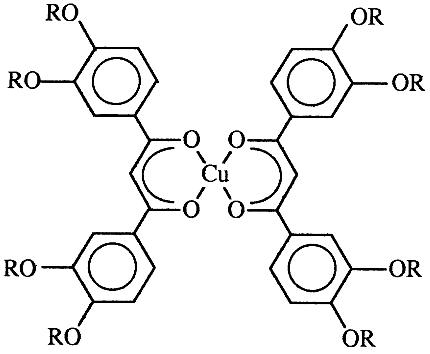

Fig. 3. Eight-chain β-diketonate complexes.

3.2. Copper complexes with eight peripheral chains

A rule-of-thumb prevailed in 1984, that at least six tails were needed on a disc-like core to get a columnar mesophase. Thus, we continued our investigations with copper complexes substituted by eight paraffinic chains.

The complexes [26] shown in Fig. 3 were prepared by similar methods to the complexes with monosubstituted diketones.

When the phenyl substituents of the β-diketonate were each substituted, in 3,4 positions by two alkoxy substituents, giving a total of eight tails, the complexes showed on heating a columnar hexagonal mesophase. This mesophase was miscible with that of the triphenylene hexadecylalkanoate, an organic disc-like molecule of columnar type [27]. A large dissymmetry of the flexible chains results in loss of the mesogenic character, while a slightly dissymmetrical copper complex retains the columnar mesophase. Moreover, changing the alkoxy substituents on the central core from the 3,4 to the 3,5 positions results in the disappearance of the mesomorphic properties. That is probably owing to the steric interactions between chains which

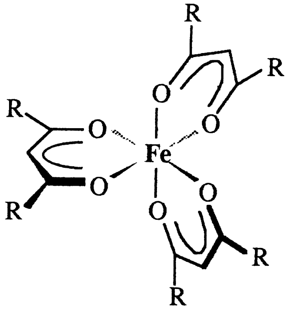

Fig. 4. Iron tris-β-diketonate complexes.

might bend the central core. Substitution of copper by nickel also destroys the liquid crystalline properties.

Small angle X-ray diffraction experiments performed on powdered sample ($M = Cu$, $n = 9$) indicate one intense Bragg reflection indexed 10 in the hexagonal lattice which gives the distance between neighbouring columns $a = 29$ Å. Note that this value is clearly smaller than the molecular diameter obtained from an SASM model with stretched conformations of the aliphatic chains (42 Å).

These binuclear copper(II) carboxylates display a particular tendency to aggregation in apolar solvents, resulting in spectacular gel formation. The structure of the aggregates in the fluid phase and in the gel phase has been investigated by ESR spectroscopy [28]. They are formed with stacked molecules which are linked by axial copper–oxygen coordination bondings.

3.3. Octahedral iron complexes

So far, we had obtained one-dimensional (calamitic) dithiene complexes, two-dimensional (discotic) β-diketonato complexes and we wondered what the properties of a three-dimensional complex with an octahedral geometry would be.

The octahedral iron(III) complex [29] ($R = C_{12}H_{25}C_6H_4$) (Fig. 4) shows two endothermic transitions at -10.5 °C ($\Delta = 13.7$ kJ mol^{-1}) and 37 °C ($\Delta = 40$ kJ mol^{-1}), and a birefringent structure within this range. It was the first octahedral metallomesogen, but unfortunately the nature of the birefringent mesophase has not been identified.

Interestingly, the iron and cobalt complexes, trisubstituted on the phenyl groups of the ligand, synthesized later by T. Swager et al., exhibit a columnar hexagonal disordered mesophase over a wide range of temperatures [30].

4. Dinuclear carboxylate complexes

In 1984, J.C. Marchon suggested that the long-chain homologs of copper acetate might exhibit columnar mesophases owing to the adequate symmetry of their central binuclear cores. Together, we began a systematic study on carboxylate complexes which are known to exist as binuclear molecules with two metal atoms bridged by four bidentate carboxylate groups: CuII, RhII, RuII, etc.

The first description of a thermotropic liquid crystal is documented by Heintz [31] who, as early as 1855, reported the stepwise melting of magnesium myristate.

Thus, in 1910, Vorlander [32] reported the existence of lamellar phases in the anhydrous salts of alkali carboxylates. In 1938, Lawrence [33] noted that copper stearate melted to a plastic fluid before clearing. Later, structural data indicating the existence of columnar and even disc-like mesophases for the anhydrous alkali, alkaline earth, and cadmium salts of long-chain fatty acids were reported by Skoulios et al. [34,35].

The liquid crystalline phase of copper stearate was briefly reinvestigated in 1964 [36], but it was not until 1984 that the mesophase of copper laurate was definitively characterized [37] by a systematic study carried out in Grenoble and in Strasbourg with D. Guillon and A. Skoulios, as columnar by X-ray diffraction [38]. These copper complexes are known to exist in the solid state as dimeric molecules in which two copper atoms are held to each other by four carboxylate groups, leading to a core with a «lantern» structure. Thus, they are the first examples of columnar mesogen bearing only four alkyl chains. This was also the beginning of a comprehensive investigation involving the two laboratories. The inorganic aspects of this research have been briefly reviewed elsewhere [39,40]. The structural aspects are reviewed by A. Skoulios in this volume.

4.1. Copper carboxylates

The general formula $(RCO_2)_4Cu_2$ defines the copper(II) alkanoates studied. In the linear chain compounds C_nCu, R is $CH_3(CH_2)_{n-2}$ with $n = 4$–24. In the branched chain compounds, R is, respectively, $CH_3(CH_2)_3C^*H[CH_2CH_3]$- and $[CH_3(CH_2)_8]_2CHCH_2^-$.

Copper(II) alkanoates were synthesized by reaction of the sodium salt of the corresponding fatty acid with a solution of copper sulphate or acetate in ethanol and ethanol–water respectively, depending on the length of the aliphatic chain. They were obtained as analytically pure samples by recrystallization from heptane.

Optical observations were difficult because of the thermal decomposition of the compounds above 200 °C, at a temperature lower than the clearing point to the isotropic phase.

The transition temperatures between the crystalline phase and the columnar hexagonal mesophase occur between 85 °C and 120 °C [41]. They seem to have only a weak dependence on the length of the aliphatic chain, while it appears that molar enthalpies show a linear dependence on the number, n, of carbon atoms of the chain. The mesophase is stable over a very large temperature range.

The branched chains induce a lower enthalpy and melting point, probably owing to a more efficient filling of the space around the core. Complexes with carbon–carbon double bonds in the alkyl chain of the ligand [42] show similar behaviour.

X-ray diffraction experiments for the linear chain copper alkanoates (C_nCu) with

$n > 5$ indicate a lamellar structure at room temperature. Above the transition temperature the diffraction patterns exhibit in the low region a series of three or four sharp reflections with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, characteristic of a two-dimensional hexagonal lattice. At larger angles, a diffuse band is observed, which corresponds to a Bragg spacing of approximately 4.6 Å attributed to the stacking period h of the dimers within the columns. This value is totally independent of the chain length. We can conclude that the high temperature phase of copper(II) alkanoates is made of columns, all parallels, with a distance of 15–25 Å (depending on the number n of carbons in the chain), in which the polar cores of the complexes are surrounded by disordered aliphatic chains (Fig. 5).

EXAFS experiments [43,44], obtained at the copper-K edge, on four copper complexes ($n = 6$, 12, 18, 22) in both their crystalline phase and their columnar hexagonal mesophase, revealed that the copper atoms exhibit intradimer square planar-coordination with four oxygen atoms and an interdimer axial ligation with an oxygen atom of the neighbouring molecule. The binuclear structure and the five-coordination of copper are maintained in the columnar mesophase, and the bond lengths of the dinuclear core remained the same at 20 °C, 70 °C and 120 °C.

Using incoherent quasi elastic neutron scattering [45,46] on selectively deuterated derivatives, M. Bée showed that in the mesophase, the aliphatic chains are completely disordered except for the hydrogen atoms linked to the four carbons closed to the core which undergo very little motion. This might be the reason why a mesophase of rectangular symmetry is found for the butyrate derivative ($n = 3$).

Isotopic labelling has facilitated band assignment in the infra-red spectra [47].

As these compounds are paramagnetic, we performed magnetic susceptibility measurements [48]. A sharp drop of the susceptibility near the solid–mesophase transition temperature was found. This was ascribed to a structural deformation of the dinuclear core. In the light of the EXAFS data, we can conclude that this

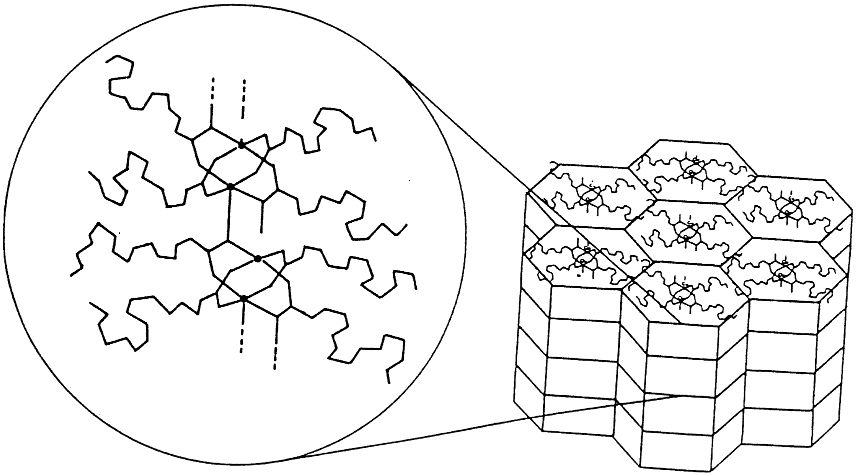

Fig. 5. Structure of copper alkanoates in the columnar hexagonal mesophase.

structural change most likely affects the bond angles rather than the bond distances of the binuclear core.

The copper alkanoates are very inexpensive and their synthesis very simple, so, we thought to prepare highly oriented fibers [49,50] obtained by melt-spinning of its columnar mesophase. Scanning electron microscopy, X-ray diffraction measurements and incoherent neutron scattering indicate that the spun fibers have a high degree of orientation, both in the crystalline and the columnar phase. These fibers can be very long, but unfortunately their mechanical properties are very poor.

4.2. Rhodium carboxylates

The rhodium carboxylates $(RCO_2)_4Rh_2$ with $R=CH_3(CH_2)_{n-2}$ for $n=4$–24 have also a binuclear structure, but possess a metal–metal bond. So, we continued our investigations, and found that they behave very similarly to the copper complexes and form on heating columnar mesophases of the same structures [51].

These compounds were synthesized by heating rhodium acetate $Rh_2(OAc)_4$, $2H_2O$ (1 M) in the corresponding carboxylic acid (4.5 M) at 120 °C for 2 h. Ligand exchange was followed by extraction of unreacted rhodium acetate in water. The green precipitate is recrystallized from the neat fatty acid or from heptane, depending of the length of the aliphatic chain, and give an analytically pure sample in 50–80% yield. A high yield was important because, unlike copper, rhodium acetate is very expensive. The complexes will be noted as C_nRh for the sake of simplicity.

We have observed a phase transition for all the linear and branched chain species. The observations of the texture is difficult using an optical polarizing microscope, owing to the high clearing point of the compounds. Nevertheless, we have been able to observe textures with developable units, indicating a columnar structure.

The thermograms have been reported for the entire series of rhodium(II) alkanoates. All show a transition between 65 °C and 155 °C. This peak corresponds to a transition from the crystalline to a mesomorphic state. The reverse transition (mesophase to crystal) occurs at a somewhat lower temperature, because of slow nucleation and crystal growth kinetics. The values of the transition temperatures are similar to those of copper carboxylates and close to 100 °C. As for copper, it appears a minimum for a chain length of eight carbons. The branched chain compound has a lower melting point and a lower enthalpy. The values of the enthalpies are lower than for copper compounds. This result shows that the energetic contribution of the bimetallic core is significant. Further, the mesophases were stable in a large temperature range, and they started to decompose only above 220 °C.

For the linear chain rhodium alkanoates with $n>5$, the X-ray patterns at room temperature indicate a lamellar structure independent of temperature, but which increases linearly with the chain length. At higher temperature the X-ray patterns are consistent both with the disordered of the aliphatic chains and with the ordering of the polar cores in the columns.

If the core is substituted by *p*-alkyl phenyl groups instead of linear chains, the complexes $Rh_2[(O_2CC_6H_4\text{-}4OC_nH_{2n+1})_4]$ for $n=8$–14, display a columnar mesophase of rectangular symmetry [52]. One such complex with eight chains shows two columnar phases, one rectangular at room temperature and a hexagonal one above 138 °C.

As for copper complexes, Rh K-edge EXAFS measurements [53] showed no change in the coordination of rhodium on passing from the solid state to the mesophase, even if Raman experiments showed a clear change in the Rh–Rh stretching vibration throughout the phase transition [54].

To study the dynamic behaviour about the M–M bond, ^{13}C high-resolution solid-state NMR spectroscopy measurements [55] have been reported in both the crystalline and liquid crystalline states of the Rh soaps. This investigation provides the first evidence that the dimetallic cores undergo a fast axial bond exchange in this type of liquid crystalline material.

As mesogens can also be organized by the influence of solvent to generate micelles and then lyotropic liquid crystal phases, D. Guillon and A. Skoulios tried mixtures of rhodium eicosanoate or copper dodecanoate with solvents such as toluene, decahydronaphtalene, and (+) camphene [56]. The mesophase found at high temperature changes from columnar to nematic when the weight fraction of the solvent is increased beyond a value of about 50%. This study is a way to bridge the gap between thermotropic and lyotropic systems.

4.3. Ruthenium carboxylates

The work on copper and rhodium tetraalkanoates was extended to ruthenium complexes because the diruthenium tetracarboxylates are known to present two stable oxidation states: the divalent (II,II) state, and a mixed-valent state (II,III), where the complex is cationic and requires a counter-anion X^- for electroneutrality, giving a general formula $Ru_2(RCOO_2)_4X$. Both contain a multiple metal–metal bond of order 2 in the case of the divalent state, and 2.5 in the case of the mixed-valent state. Moreover, these carboxylates are paramagnetic with two unpaired electrons in divalent compounds and three in the mixed-valent species. In view of the interest of these compounds, two theses have been prepared on this topic by P. Maldivi [57] and F. Cukiernik [58].

4.3.1. Diruthenium (II,II) carboxylates

A wide series of diruthenium (II,II) tetracarboxylates of general formula $Ru_2(RCOO)_4$ was prepared [59]. The carboxylate substituents include linear alkyl chains which will be noted C*n*Ru ($n=4$ to 19), two unsaturated chains ($R=CH_2=CH(CH_2)_8$ and $R=(CH_3)_2C=CHCH_2CH_2CH(CH_3)CH_2^-$), as well as fluorinated chains $R=C_7F_{15}^-$. A pyrazine adduct was also obtained with the dodecanoate analogue.

Most of the complexes of linear fatty acids and of perfluorooctanoic acid were prepared under argon, starting with ruthenium(II,II) butyrate, by substitution of the four carboxylate ligands by the corresponding fatty acid. Ruthenium butyrate is readily obtained by chromium(II) reduction of chlorodiruthenium(II,III) tetrabutyrate in a water–methanol solution.

The unsaturated compounds were obtained by a similar procedure, but starting with ruthenium(III) acetate. The light-brown, air-sensitive complexes were usually recrystallized from heptane and correct elemental analysis (Ru, C, H) were obtained for all compounds. In addition, they all exhibit carbonyl absorptions around 1550 and 1420 cm^{-1} in the infra-red, in good agreement with those published for shorter analogues.

The pyrazine complex was prepared by adding a stoichiometric amount of pyrazine to an ethanol solution of dodecanoate complex. With a branched chain complex the adduct exhibit a mesophase whose structure could not be elucidated at room temperature [60]. The liquid crystal behaviour is lost with straight chains [61].

As the ruthenium (II,II) tetracarboxylates are thermally unstable under oxygen, making difficult their observation with a hot-stage polarizing optical microscope, the detection of their mesophases was carried out by differential scanning calorimetry.

A thermotropic phase transition between 95 °C and 150 °C was observed for all complexes except the perfluoro compounds. Unsaturation in the peripheral chains depresses transition near room temperature. The dependence of the transition temperature with the chain length is the same as that already observed for copper and rhodium complexes.

X-ray diffraction measurements have been performed on four powdered samples at room temperature for the crystalline phase and at 120 °C for the mesophase. The X-ray patterns at room temperature are similar to those of copper and rhodium carboxylates, indicating a lamellar structure. The interlamellar spacing increases with n, number of carbon atoms. At high temperature, at the low-angle region several reflections are indicative of a columnar hexagonal mesophase. The X-ray pattern shows also the presence of a packing order within the columns, with a repeating distance of 4.6 Å.

The measurements of the magnetic susceptibility [62] as a function of temperature, between 6 and 400 K, show a sharp change in the magnetic moment at the solid–mesophase transition ascribed to a core distortion rather than an ordering effect, as we have suggested earlier for the copper soaps.

4.3.2. *Mixed-valent diruthenium (II,III) carboxylates*

The general formula of mixed-valent ruthenium carboxylates is $Ru_2(RCOO)_4X^{\ominus}$ with X = anion. The anion has a strong influence on the mesomorphic behaviour. Three series derived from linear aliphatic carboxylates were studied [63]. The chloro complexes ($X=Cl^{\ominus}$) (n = 5–9, 12, 16) are not mesomorphic, whereas the complexes with a carboxylate ($X=RCOO^{\ominus}$) (n = 6 to 12, 14, 15, 16) or an alkylsulphate ($X=C_{12}H_{25}OSO_3^{\ominus}$) as the anion, exhibit a columnar mesophase on heating. Three other types of complexes were also studied with the same anions, but with 3,4-dialkoxybenzoate as ligand ($R=3,4\text{-}(CH_3(CH_2)_{n-1}O)_2Ph$) noted B2OC*n*.

The $RU_2(RCOO)_4Cl$ series, ($R=CH_3(CH_2)_{n-2}$) for n = 5–9, 12, 16, 18), was obtained by the substitution of the four equatorial carboxylates in the starting butyrato analogue by refluxing during 15 min in the corresponding fatty acid. The brown–red powder was recrystallized from the appropriate acid or from heptane. The dialkoxybenzoates B2OC*n* with $n=12$, 15, 16 were synthesized in a similar way.

For the synthesis of the pentacarboxylates $RU_2(RCOO)_5$ $R=CH_3(CH_2)_{n-2}$ for ($n=5$–9, 12, 16, 18), two steps are necessary. First, we substitute the chloride anion of the starting material $Ru_2(RCOO)_4Cl$ by the less complexing tetraphenylborate anion (BPh_4) and then we exchange simultaneously the four acetato ligands and the weakly coordinated anion by the corresponding fatty acid, in the pure liquid for $n=6$–9 or in ethanol solution for $n\geq 10$. The solution was stirred in the dark for 2 or 3 days at room temperature.

The B2OC*n* analogues ($n=12$, 15, 16) were synthesized by the same procedure. The DOS containing compounds, $Ru_2(RCOO)_4DOS$ ($R=CH_3(CH_2)_{n-2}$ with $n=$ 6–12, 14, 15, 16) were prepared by reaction of the corresponding chloro complex $Ru_2(RCOO)_4Cl$ or $RU_2(B2OCn)_4Cl$, prepared previously, with silver dodecylsulphate in ethanol by stirring the solution for 4 h. The pale-brown precipitate was recrystallized in ethanol.

The mesogenic properties have been studied in the same way than for the analogues of copper and rhodium. The linear chain carboxylates with a chloride anion do not present any mesophase prior to their clearing point near 260 °C. In order to understand this absence of mesomorphic properties, we have turn our attention on the packing of the molecules. After a study of the crystal structure of $RU_2(C_4H_7COO)_4Cl$ it appears that this packing between chlorine anions and carboxylate cations create empty spaces between the dimers. Therefore, three possible ways were studied to fill this interdimer space, which seems the key factor to get a mesophase: a bulky anion with a long aliphatic chain, a bulky equatorial carboxylate ligand or a combination of both [64].

4.3.2.1. *Bulky anions.*

Two families have been studied: a long-chain carboxylate anion and a dodecyl sulphate anion. The general formula of the former compounds is $Ru_2(RCOO)_5$ and the series derived from the latter will be $Ru_2(RCOO)_5DOS$.

All the aliphatic chain pentacarboxylates $Ru_2(RCOO)_5$ were found to exhibit a transition from the crystalline phase to a viscous birefringent phase. The transition temperatures are higher than those determined for the divalent compounds $Ru_2(COO)_4$ whether the transition enthalpies are of the same order. For the other family $Ru_2(COO)_4DOS$, six compounds have been studied with $n=6$, 8, 12, 16, and 18. They present phase transition at a temperature equivalent to those of pentacarboxylates.

4.3.2.2. *Bulky carboxylates with small anion.*

Three dialkoxybenzoate compounds with the chloride as the anion noted $Ru_2(B2OCn)_4Cl$ have been studied $n=12$, 15, 16. All exhibit a lamellar phase at low temperature. At higher temperature, a columnar hexagonal mesophase was characterized by X-ray diffraction.

4.3.2.3. *Bulky equatorial carboxylates with bulky anion.*

Two series were studied: $Ru_2(B2OCn)5$ ($n=12$, 15, 16) and $Ru_2(B2OCn)_4DOS$ ($n=12$, 15, 16). X-ray diffraction carried out at low temperature on the pentacarboxylate series showed an ordered columnar hexagonal mesophase. Decomposition occurs around 210 °C.

Similar results were found with $Ru_2(B2OCn)_4DOS$ series ($n=12$, 15, 16). They all exhibit a liquid crystalline phase at room temperature, not yet completely established. From this study on mixed-valent diruthenium carboxylates, we can conclude that a strong correlation exists between the molecular shape and the mesomorphic properties. Particularly, the filling of the interdimer space is a key factor for appearance of columnar mesophase which can occur at room temperature.

5. Conclusion

It is well understood, that, in the preceeding pages, it was not intended to give a review of the whole area of metallomesogens. For that, the reader is referred to the reviews cited in the introduction to the *Handbook of Liquid Crystals* [65] and to the book Metallomesogens [66]. We have presented, essentially, the work carried out in our laboratory over the last 20 years. As synthetic chemists, our goal was to explore a large variety of new ligands in order to design new metal complexes with low melting points, which might lead to new applications. Although the research into metal-containing liquid crystals is still in its infancy, considerable advances in the understanding of their physical properties have been made. A substantial number of metals have already been incorporated, and still many remain to be explored. A challenge is opened in this interdisciplinary field.

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After such global assistance there appears to be little left to which the author can attach his name, except to the apologies for the errors that may remain.

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