Mixed-Valent Diruthenium (II,III) Long-Chain Carboxylates. 1. Molecular Design of Columnar Liquid-Crystalline Order

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Six series of binuclear mixed-valent diruthenium tetracarboxylates of formula $Ru_2(O_2CR)_4X$, containing different combinations of equatorial carboxylates (RCO_2^-) and anions (X^-) have been synthesized and characterized, and their liquid-crystalline properties have been examined by optical microscopy under polarized light, differential scanning calorimetry, and powder X-ray diffraction studies. Three series derived from linear aliphatic carboxylates, $Ru_2(O_2C-(CH_2)_{n-2}-CH_3)_4X$ with X = Cl ($n = 5-9$, 12, 16), $X = O_2C-R$ ($R = (CH_2)_{n-2}-CH_3$, $n = 6-12$, 14, 15, 16), and X = DOS (DOS = dodecyl sulfate, $n = 6$, 8, 9, 12, 16, 18), were studied. The nature of the counterion X strongly affects the appearance of the liquid-crystalline order: the chloro complexes are not mesomorphic, whereas the complexes with RCO_2 or DOS anions exhibit a columnar hexagonal mesophase above ca. 150 °C. A structural model for the mesophase of the $Ru_2(O_2C-(CH_2)_{n-2}-CH_3)_5$ series is proposed. Three other types of $Ru_2(O_2CR)_4X$ complexes were obtained with a 3,4-dialkoxybenzoate as equatorial ligand ($RCO_2 = 3,4\text{-}(CH_3(CH_2)_{n-1}O)_2PhCO_2$) and with X = Cl ($n = 12$, 15, 16), X = RCO_2 ($n = 12$, 15, 16) and X = DOS ($n = 12$, 15, 16). All complexes of the three latter types are mesogenic, with transition temperatures lower than those found for the aliphatic analogues, and the pentakis(dialkoxybenzoate) derivatives are liquid crystalline at room temperature, indicating that the nature of the equatorial ligands is also a determinant of the mesogenic character. The results are interpreted in terms of the ability of the axial and equatorial ligands to efficiently fill the interdimeric space, thereby creating adequate conditions for columnar order.

Introduction

The challenging possibility of combining the anisotropy and fluidity of liquid-crystalline phases with the properties derived from the presence of d electrons offered by transition-metal complexes is at the origin of the increasing interest and rapid expansion of metallomesogen[1] chemistry in the context of materials chemistry. A large part of the recent research in this field has been directed toward the investigation of mesomorphic properties (particularly the influence of the new molecular geometries arising from coordination chemistry) and, to a less extent, of physical properties.[1] Among the various metallomesogens already explored, the binuclear carboxylates of divalent transition metals, of general formula $M_2(RCO_2)_4$, have been widely studied for M = Cu(II),[2−5] Rh(II),[2,3,6] Ru(II),[2,3,7,8] Mo(II),[8] and Cr(II).[8] It has been shown by several structural techniques[2,4,9] that these derivatives exhibit a columnar hexagonal mesophase above ca. 100 °C, where molecular units are regularly stacked along columns. Interest-

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ingly, the structure of this mesophase is independent of the nature of the metal. All the binuclear carboxylates of this class exhibit the so-called "lantern structure" which is exemplified by the crystal structure of copper acetate.[10] The unsolvated species present the same supramolecular organization, as found for example in the case of copper[11] or rhodium[12] derivatives, where dimeric species are coordinated in axial positions by oxygen atoms of neighboring molecules, thus giving rise to polymeric chains. This polymeric arrangement is retained in the liquid-crystalline phase, in which the peripheral aliphatic chains are melted, resulting in the apparition of a closely packed hexagonal 2D array of columns.[2,3,9]

Among the metals above-mentioned, ruthenium deserves a special interest, as it offers the opportunity of combining the one-dimensional nature of the columnar structure with the peculiar electronic properties of the binuclear cores. As a matter of fact, the diruthenium tetracarboxylates may present two stable oxidation states: the divalent (II,II) state, as already described above, and a mixed-valent (II,III) state, where the complex is cationic and requires a counteranion X^- for electroneutrality, thus giving a general formula $Ru_2(RCO_2)_4X$. Both species exhibit the "lantern structure" and contain a multiple metal−metal bond. The bond order is 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 species and three unpaired electrons in the mixed-valent derivatives.[7,13,14]

In previous papers,[7] we have investigated in detail the Ru(II,II) mesogens, and we turn now to the mixed-valent derivatives. Herein we present an extensive investigation of different types of mixed-valent diruthenium carboxylates, in which we have probed the influence of various elements of the molecular unit (namely, the anion and the equatorial carboxylates) on mesomorphic behavior. Part of these results have been presented in a preliminary communication.[15] In a companion paper[16] we describe the magnetic properties of these species, in relation with the nature of the anion.

The compounds described here are obtained by combination of a counterion chosen among chloride, dodecyl sulfate (DOS), or carboxylate (RCO_2, identical with the equatorial carboxylates) and of equatorial ligands that are either linear chain carboxylates $CH_3(CH_2)_{n-2}CO_2$ or 3,4-dialkoxybenzoates of general formula 3,4-$(C_nH_{2n+1}O)_2$-$PhCO_2$ (Ph = 1,3,4-trisubstituted phenyl ring); the latter will be noted below as B2OC*n*, *n* being the number of carbon atoms in the alkoxy chain. For the sake of clarity, short-chain carboxylates will be noted OAc for acetate, prop for propionate, and but for butyrate.

Experimental Section

Synthesis. $RuCl_3{\cdot}3H_2O$ (Aldrich, Fluka) was used as supplied. Recrystallized aliphatic fatty acids of commercial origin were used; all other chemicals were of analytical grade, including solvents. Manipulations under inert atmosphere (Ar) were carried out in a Jacomex glovebox (40 m^3/h) with an oxygen concentration less than 2 ppm, measured with a Herman-Moritz OA 1440 oxygen sensor; in some cases, the inert atmosphere was warranted simply by gently bubbling Ar or N_2 into the solution before work. $Ru_2(prop)_4Cl$,[17] as well as the three "precursor complexes" involved in our synthetic scheme (see Results and Discussion), namely $Ru_2(OAc)_4Cl$,[17] $[Ru_2(OAc)_4(H_2O)_2]BPh_4$,[18] and $Ru_2(but)_4Cl$,[19] were synthesized following published methods. All the compounds were characterized by IR and UV/vis spectroscopies, as well as by elemental analyses on C, H, and Ru and on S, Cl, or B when appropiate. Elemental analyses and yields of the synthesized compounds are included as Supporting Information in Table S1.

Synthesis of Dialkoxybenzoic Acids. *Methyl 3,4-dihydroxybenzoate, 3,4-$(HO)_2C_6H_3COOMe$:* Hydrochloric acid was bubbled for 3 h through a solution of 3,4-dihydroxybenzoic acid (15 g, 97 mmol) in 250 mL of methanol at 0 °C. After evaporation of the methanol the product was purified from a silicagel column, eluted with diethyl ether.

Methyl dialkoxybenzoates, 3,4-$(C_nH_{2n+1}O)_2C_6H_3COOCH_3$: Methyl dihydroxybenzoate (4 g, 24 mmol) was dissolved in 20 mL of cyclohexanone containing 25 g of K_2CO_3; 1-bromododecane (16 g, 65 mmol) or 1-bromohexadecane (20 g, 66 mmol) was then added dropwise, and the solution was refluxed for 3 h. After filtration of potassium carbonate, diethyl ether was added and the solution was cooled to 4 °C. The white

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solid thus obtained was filtered and purified by silicagel column chromatography, using diethyl ether/petroleum ether 1:9. The $n = 15$ derivative was obtained in a similar way, but its purification was carried out by recrystallization from cold acetone.

Dialkoxybenzoic acids, 3,4-$(C_nH_{2n+1}O)_2C_6H_3COOH$: 3 g of the corresponding ester was refluxed for 3 h in 300 mL of methanol and 15 mL of water containing 5 g of NaOH (125 mmol). The sodium dialkoxybenzoate precipitate was filtered at room temperature (the absence of the starting ester was checked by IR) and suspended in an ethanol/water mixture. The solution was acidified with HCl 1 M under stirring for 2 h, and then ethanol was evaporated. Affer extraction with three fractions of diethyl ether, the organic phase was dried over Na_2SO_4 and then evaporated to dryness. The resulting acid was recrystallized from *n*-heptane.

Synthesis of $Ru_2(RCO_2)_4Cl$. *$Ru_2(C_5H_9O_2)_4Cl$:* $Ru_2(OAc)_4Cl$ (520 mg, 1.1 mmol) were refluxed in 30 mL of pentanoic acid for 15 min. The solution was then cooled to room temperature, and the precipitate was filtered, washed with *n*-heptane, then with petroleum ether, and finally dried. The product thus obtained was recrystallized from pentanoic acid, washed as before, and then dried under vacuum.

$Ru_2(C_nH_{2n-1}O_2)_4Cl$ ($n = 6-9$): $Ru_2(but)_4Cl$ (1 g, 1.7 mmol) was mixed with 3 mL (>20 mmol) of the corresponding fatty acid (liquid at room temperature). The mixture was degassed, heated at 120 °C for 20 min, and then cooled to room temperature. The complex was filtered, washed with *n*-heptane and dissolved in ca. 500 mL of ethyl ether; after filtration, 50 mL of *n*-heptane was added, and the solution was allowed to stand to evaporate the ether. The brown-red powder obtained was filtered, recrystallized twice from the corresponding fatty acid, then washed with *n*-heptane, filtered, and dried under vacuum at 40 °C.

$Ru_2(C_nH_{2n-1}O_2)_4Cl$ ($n = 12$ and 16): The butyrato complex and the fatty acid (solid at room temperature) were stirred under Ar at 130 °C for 15 min. After cooling the solution to room temperature, the resulting solid mixture was stirred with *n*-heptane for half an hour, filtered, and washed with *n*-heptane. For the dodecanoate derivative, the red product was dissolved in 400 mL of ethyl ether and filtered. *n*-Heptane (50 mL) was added to the solution; after slow evaporation of ether, the precipitate was filtered, washed with *n*-heptane, and then dried under vacuum. The hexadecanoate derivative being slightly soluble in ether, its purification was carried out by three successive recrystallizations from methanol.

$Ru_2(B2OCn)_4Cl$ ($n = 12, 15, 16$): 3,4-Bis(hexadecyloxy)-benzoic acid (1.2 g, 2.0 mmol) and $Ru_2(but)_4Cl$ (88 mg, 0.15 mmol) were stirred at 140 °C under argon. As the acid melted, a red solution was obtained and a red precipitate appeared after 5 min. The system was cooled to room temperature after 15 min. The solid mixture thus obtained was stirred with methanol and filtered. The precipitate was dissolved in *n*-heptane, filtered off, evaporated to dryness, redissolved in ethyl ether, filtered again, and evaporated to dryness. The red solid product was taken up in methanol, filtered, and dried under vacuum for 24 h, to give a waxy final product. The $Ru_2(B2OC12)_4Cl$ and $Ru_2(B2OC15)_4Cl$ homologues were obtained in a similar way, starting from 75 mg of $Ru_2(but)_4Cl$ (0.13 mmol) and 0.95 g of the B2OC12H acid (1.9 mmol) for the former, and 100 mg $Ru_2(but)_4Cl$ (0.17 mmol) and 1.0 g of the B2OC15H acid (1.9 mmol) for the latter.

Synthesis of $Ru_2(RCO_2)_5$. *Linear aliphatic chain derivatives $Ru_2(C_nH_{2n-1}O_2)_5$:* A single product formation step was used for all the compounds. The next steps—isolation and purification—were adapted to each case.

Product formation: $[Ru_2(OAc)_4(H_2O)_2]BPh_4$ (300 mg, 0.38 mmol) was dissolved in 3 mL of ethanol. An excess of the corresponding fatty acid (4−6 times) was added to this solution: 3−4 mL of the acid when liquid at room temperature ($n = 6-9$), or as an ethanol solution (2−3 g of acid in 20−100 mL) for the solid acids ($n \geq 10$). The solution was stirred in the dark, at room temperature, for 2−3 days.

Isolation and purification of the heaviest homologues ($n \geq 14$): In the case of the complexes with $n = 14$, 15, or 16, a precipitate began to appear after a few hours. After 3 days, the precipitation was complete; the product was filtered and washed with *n*-heptane. The excess of acid was eliminated by two or three recrystallizations in a 1:1 ethanol/*n*-heptane mixture, until complete disappearance of the 1740 cm^{-1} band (free fatty acid) in the IR spectra.

Isolation and purification of the intermediate homologues ($10 \leq n \leq 12$): After stirring for 3 days, the solution was concentrated by evaporation under reduced pressure and then cooled to 4 °C. The precipitate was filtered and washed with acetone and with *n*-heptane. The dodecanoate derivative was recrystallized as the heavier homologues, whereas the decanoate and undecanoate derivatives were recrystallized from a 1:9 ethanol/*n*-heptane mixture. After two or three recrystallizations (absence of free acid checked by IR), the final product was washed with *n*-heptane and then dried under vacuum.

Isolation and purification of the short-chain homologues ($n \leq 9$): After stirring for 3 days, the solution was evaporated under reduced pressure. The nonanoate and octanoate derivatives precipitated at this stage, whereas the precipitation of the heptanoate or hexanoate compounds was obtained by adding a few mL of *n*-heptane, keeping the mixture at 4 °C overnight. The resulting brown powder was stirred in acetone, filtered, recrystallized from the corresponding fatty acid, washed with *n*-heptane, and dried under vacuum.

$Ru_2(C_4H_7O_2)_5$. $[Ru_2(OAc)_4(H_2O)_2]BPh_4$ (300 mg, 0.38 mmol) and butyric acid (10 mL) were mixed and degassed. The mixture was refluxed under Ar for 20 min and then kept at 4 °C for a few hours. The precipitate was filtered, washed in *n*-heptane, and dried under vacuum.

Undecylenic acid derivative, $Ru_2(CH_2{=}CH(CH_2)_8CO_2)_5$: $[Ru_2(OAc)_4(H_2O)_2]BPh_4$ (325 mg, 0.4 mmol) and undecylenic acid (4 mL; denoted as $C^{\parallel}_{11}$) were dissolved in 15 mL ethanol. After stirring at room temperature for 3 days, ethanol was eliminated by evaporation at reduced pressure, and the pale-brown precipitate which appeared after an hour at room temperature was filtered, washed with *n*-heptane, and then dried under vacuum.

$Ru_2(B2OC\mathbf{n})_5$. The corresponding 3,4-bis(*n*-alkoxy)benzoic acid (700 mg, 1.16 mmol for $n = 16$, 1.21 mmol for $n = 15$, and 1.42 mmol for $n = 12$) was dissolved in 50 mL of hot ethanol; this solution was deoxygenated and kept to reflux. A degassed solution of 80 mg of $[Ru_2(OAc)_4(H_2O)_2]BPh_4$ (0.1 mmol) in 5 mL of ethanol was added; after 30 min, the brown precipitate formed in the case of $n = 16$ was filtered while hot, washed with hot ethanol, and then dried under vacuum. For $n = 15$ and $n = 12$, the mixture was evaporated to dryness, the solid mixture was stirred in *n*-heptane and filtered off. The clear solution was evaporated to dryness, washed with ethanol, filtered, and dried.

Synthesis of $Ru_2(RCO_2)_4DOS$. *$Ru_2(C_{18}H_{35}O_2)_4DOS$ and $Ru_2(C_{16}H_{31}O_2)_4DOS$:* $Ru_2(C_{18}H_{35}O_2)_4Cl$ (200 mg, 0.14 mmol) or $Ru_2(C_{16}H_{31}O_2)_4Cl$ (400 mg, 0.32 mmol) were dissolved in 10 mL of hot ethanol (solution A). Silver dodecyl sulfate (80 mg, 0.21 mmol, for $n = 18$ or 131 mg, 0.35 mmol, for $n = 16$) was dissolved in 3 mL of ethanol (solution B). B was added dropwise to A, the solution being protected from direct light. After stirring for 4 h, AgCl was filtered off and the solution was concentrated to 2 mL. The pale brown precipitate was filtered and recrystallized in a few milliliters of ethanol.

$Ru_2(C_{12}H_{23}O_2)_4DOS$: $Ru_2(C_{12}H_{23}O_2)_4Cl$ (553 mg, 0.54 mmol) was dissolved in 4 mL of ethanol at room temperature. A solution of 205 mg of AgDOS (0.55 mmol) in 5 mL of ethanol was added dropwise in the dark; after 3 h under stirring, AgCl was filtered off, the solution was concentrated up to ca. 1 mL and then cooled to 4 °C. The resulting precipitate was filtered, washed with very small portions of cold methanol, and then dried.

$Ru_2(C_nH_{2n-1}O_2)_4DOS$ ($n = 9, 8, 6$): The corresponding $Ru_2(C_nH_{2n-1}O_2)_4Cl$ complex (250 mg, 0.29 mmol for $n = 9$, 0.31 mmol for $n = 8$, and 0.36 mmol for $n = 6$) was dissolved in 10 mL of ethanol. AgDOS (150 mg, 0.39 mmol, for $n = 8$ and 9 or 210 mg, 0.56 mmol, for $n = 6$) dissolved in 5 mL of ethanol was added dropwise while protected for direct light. After

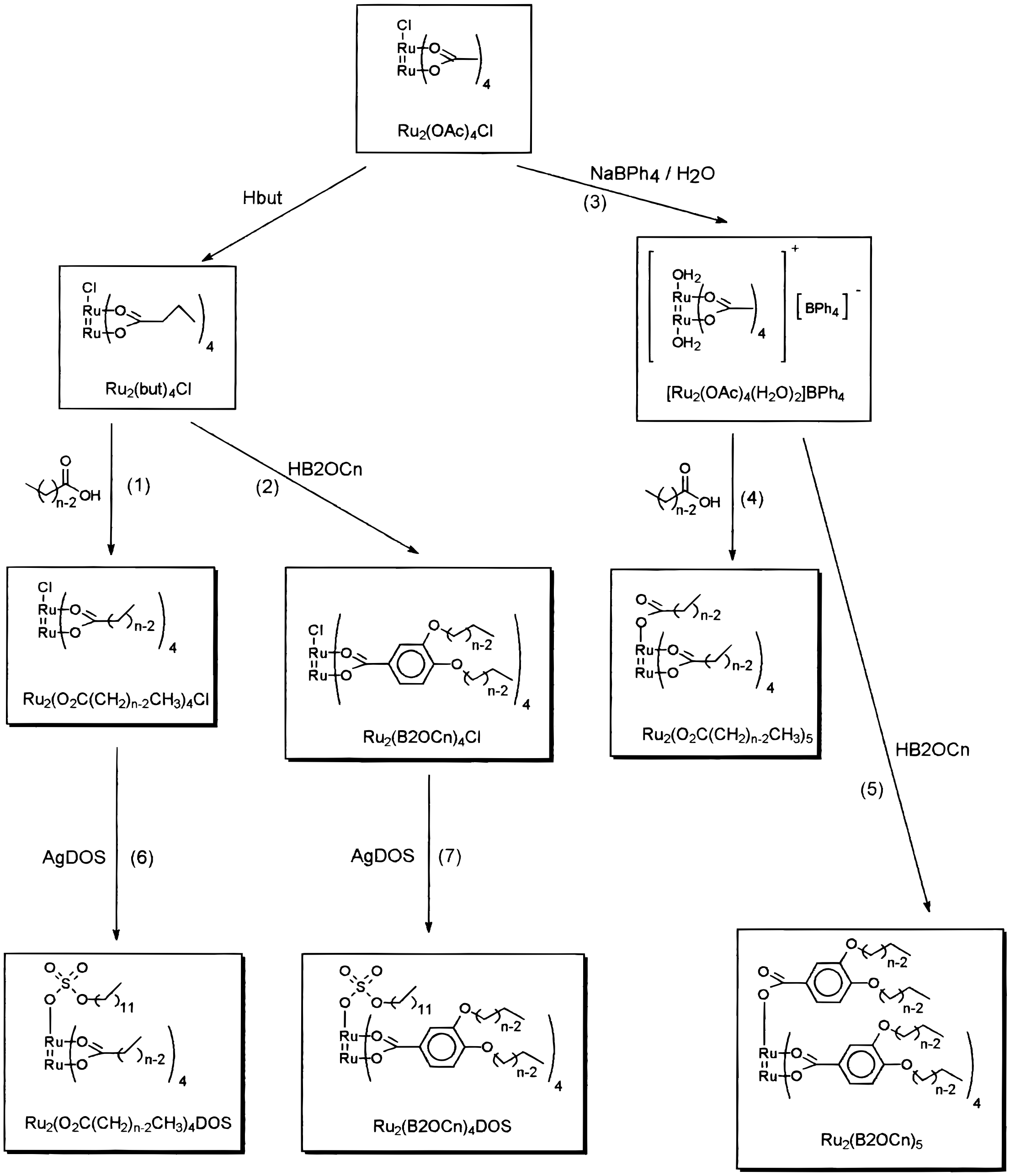

Figure 1. Scheme showing the strategy developed for the synthesis of long-chain mixed-valent binuclear diruthenium tetracarboxylates.

stirring for 2 h, AgCl was filtered off, and the solution evaporated to dryness. The solid was dissolved in a few milliliters of ethyl ether ($n = 9$), dichloromethane ($n = 8$), or acetone ($n = 6$) and the excess AgDOS was removed by filtration. The filtrate was evaporated to dryness; the brown powder was taken up with *n*-heptane, filtered, and dried.

$Ru_2(B2OC12)_4DOS$: $Ru_2(B2OC12)_4Cl$ (200 mg, 0.091 mmol) was dissolved in 10 mL of refluxing ethanol (under N_2). AgDOS (58 mg, 0.155 mmol) dissolved in 10 mL of deoxygenated ethanol was added dropwise while protected from direct light. After refluxing for 3 h, AgCl was removed by hot filtration, and the solution was evaporated to dryness. The solid was dissolved in ethyl ether, filtered, evaporated to dryness and taken up in acetone, filtered, and dried, yielding a pale-brown powder.

$Ru_2(B2OC15)_4DOS$ and $Ru_2(B2OC16)_4DOS$: $Ru_2(B2OC15)_4Cl$ (250 mg, 0.1 mmol) or 160 mg of $Ru_2(B2OC16)_4Cl$ (0.06 mmol) was dissolved in a mixture of 10 mL of *n*-heptane and 10 mL of ethanol. AgDOS (80 mg, 0.214 mmol) for the $Ru_2(B2OC15)_4DOS$ derivative or AgDOS (50 mg, 0.134 mmol) for the $Ru_2(B2OC16)_4DOS$ derivative, dissolved in 10 mL of ethanol + 10 mL of *n*-heptane, was added dropwise while protected from light. After stirring for a few hours, AgCl was filtered off and the solution was evaporated to a few milliliters. The pale-brown precipitate was filtered, washed with ethanol and *n*-heptane, and dried.

Physicochemical Measurements. IR spectra were recorded on Nicolet 150P or Perkin-Elmer 1650 FTIR spectrometers (KBr pellets). An Olympus BH-2 microscope equipped with a Mettler FP82 heating device (driven by a Mettler FP80 system) was used for polarized light optical microscopy (OM/PL) observations. Thermodynamic parameters of the phase transitions were measured by DSC on either a Mettler FP85 or a Shimadzu DSC-50 calorimeter. For X-ray diffraction (XRD) experiments, the powdered samples were contained in Lindemann capillaries; the patterns were recorded with a Guinier focusing camera equipped with a bent quartz monochromator using Cu Kα_1 radiation, either photographically or, in some cases, with a linear position-sensitive INEL detector (see Results and Discussion).

Results and Discussion

Synthesis. Figure 1 summarizes the synthesis of all the mixed-valent diruthenium tetracarboxylates described here, starting from three precursor complexes.

The $Ru_2(RCOO)_4Cl$ series ($R = CH_3(CH_2)_{n-2}$ for n = 5−9, 12, 16, 18) was obtained by a straightforward substitution of the four equatorial carboxylates in the starting butyrato analogue by the corresponding long-chain carboxylate (reaction 1). The dialkoxybenzoates (B2OC*n* with n = 12, 15, 16) were synthesized in a similar way (reaction 2).

For the synthesis of the pentacarboxylates $Ru_2(RCOO)_5$ ($R = CH_3(CH_2)_{n-2}$ with n = 6−12, 14, 15, 16), two steps were necessary, first to substitute the chloride anion of the starting $Ru_2(OAc)_4Cl$ material by the less complexing tetraphenylborate anion (denoted BPh_4, reaction 3) and then to exchange simultaneously this weakly coordinating anion and the four acetato ligands with the corresponding long-chain carboxylate (reaction 4). The B2OC*n* analogues (n = 12, 15, 16) were synthesized by the same procedure (reaction 5).

The DOS containing compounds, $Ru_2(RCOO)_4DOS$ ($R = C_{n-1}H_{2n-1}$; n = 6, 9, 12, 16, 18) or $Ru_2(B2OCn)_4DOS$ (n = 12, 15, 16), were prepared by reaction of the corresponding chloro complex $Ru_2(RCOO)_4Cl$ or $Ru_2(B2OCn)_4Cl$, prepared as shown in reactions 1 and 2, with AgDOS (reactions 6 and 7).

Spectroscopic Characterization. The main spectroscopic characterization was carried out by IR. We describe here only the carbonyl stretching spectral region between 1400 and 1700 cm^{-1}. For the chloro complexes, several strong bands appear between 1400 and 1500 cm^{-1}, but they cannot be completely resolved, even by using a fully deuterated fatty acid. These intense absorption bands contain both symmetrical and asymmetrical carbonyl stretching modes, superimposed with bands due to the bending modes of the CH_2 and CH_3 groups of the peripheral alkyl chains (ca. 1470 cm^{-1}). Nevertheless, both carbonyl stretching vibrations appear between 1400 and 1500 cm^{-1}, and this close proximity points to a symmetrical coordination of the bridging carboxylates within the binuclear core.[20] In the case of the $Ru_2(B2OCn)_4Cl$ derivatives, two additional bands can be seen at 1520 and 1400 cm^{-1} corresponding to vibrational modes of the aromatic ring.

The pentacarboxylate series present very similar IR spectra: the only difference is an additional band at 1520 cm^{-1}, which can be attributed to a carbonyl stretching mode of the axial carboxylate counterion.

The IR spectra of the $Ru_2(RCOO)_4DOS$ complexes present the same trends as those of the chloro complexes. Three additional intense bands are seen at 1060, 1145, and 1295 cm^{-1}, associated with the sulfate group.[21]

A more thorough vibrational study of these complexes by IR and Raman spectroscopies is in progress, more particularly in the low-energy region, to examine the metal−metal bond and the metal−oxygen interaction.[22]

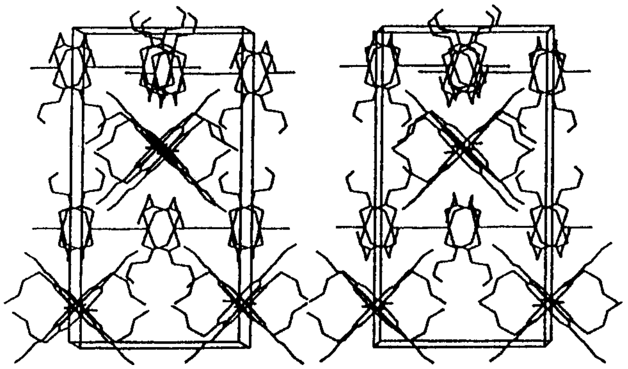

Figure 2. Stereoscopic view of the supramolecular structure of the crystalline phase of $Ru_2(O_2C_5H_9)_4Cl$, as determined by X-ray diffraction, showing the presence of perpendicular polymeric chains.

Liquid-Crystalline Properties. The mesomorphic properties were investigated by polarized optical microscopy (OM/PL) and differential scanning calorimetry (DSC). Most of the compounds exhibiting mesomorphic properties were then studied by powder X-ray diffraction (XRD).

The linear chain carboxylates with a chloride anion do not present any mesophase prior to their clearing point at 260 °C, which is accompanied by decomposition. To understand this absence of mesomorphic properties, we have turned our attention to the crystal structures of the shorter chain homologues $Ru_2(OAc)_4Cl$,[23] $Ru_2(prop)_4Cl$,[24] and $Ru_2(but)_4Cl$.[14e,25] In all cases, the crystalline structure is made up either of zigzag or of linear chains, with alternating cationic ruthenium carboxylate and chloride anion:

$$\text{---}\ Cl\ \text{---}\ Ru_2(RCOO)_4\ \text{---}\ Cl\ \text{---}\ Ru_2(RCOO)_4\ \text{---}$$

For the acetato and propionato complexes, all the chains are parallel in the lattice, whereas for the butyrato compound, there are two perpendicular sets of chains.

The crystal structure of the valerato complex $Ru_2(C_4H_9COO)_4Cl$ has been recently reported in the context of magnetostructural correlations in ruthenium mixed-valent carboxylates.[16] Of particular importance for the present work is the presence of two sets of perpendicular cation−anion chains (Figure 2). This result supports the assumption that higher homologues in this series present the same kind of criss-crossed crystal lattice, which is not suitable for the formation of a columnar phase.

The basic reason these chains are criss-crossed is related to the compacity of such structures. The packing of chloride anions and bulky cationic $Ru_2(RCOO)_4^+$ moieties create void spaces between the dimers. An efficient way to fill that space and to warrant an optimum compacity within the three-dimensional array is therefore to organize the cation−anion chains perpendicular to each other. With that arrangement, the

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Table 1. Temperature (°C) and Enthalpy (kJ mol^{-1}) of the Crystal-to-Mesophase Transition for the $Ru_2(O_2C-(CH_2)_{n-2}-CH_3)_5$ Series and Structural Parameters Determined by XRD Studies (Interlamellar Spacing *d* in Å of the Lamellar Phase and Intercolumnar Distance *D* in Å in the $D_{h.o}$ Mesophase)

n	temp	enthalpy	*d*	*D*
6	167	21	15.8	*a*
7	155	26	18.0	*a*
8	156	33	22.5	*a*
9	150	45	22.6	*a*
10	148	*a*	27.3	30.1
11	152	60	30.0	31.8
12	150	69	32.4	33.9
14	143	84	37.3	36.0
15	136	98	37.7	36.7
16	142	107	42.2	38.7
$11^{\|\|}$	119	*b*	*a*	*a*

[a] Not measured. [b] Decomposition occurs at 125 °C.

space around a chlorine atom may be efficiently filled with the aliphatic peripheral chains of neighboring compounds, belonging to adjacent perpendicular cation−anion chains.

Adequate filling of this interdimer space is probably a key factor favoring the appearance of columnar mesophases. We can propose three possible strategies to achieve this, using (1) a bulky anion, with long aliphatic chains, (2) a bulky equatorial carboxylate ligand, and (3) a combination of both large anions and carboxylate equatorial ligands. We have therefore developed several series of compounds as representative of these three strategies.

First, we have chosen to replace the small chloride anion by two types of bulky anions: a long-chain carboxylate (the same as the equatorial carboxylates of the dimer) and the dodecyl sulfate anion (noted below as DOS). The general formula of the compounds derived from the former is $Ru_2(RCOO)_5$ with $R = CH_3(CH_2)_{n-2}$, and the series derived from the latter will be denoted $Ru_2(RCOO)_4DOS$.

The second strategy was to keep the chloride anion, but to choose bulky equatorial carboxylates: 3,4-dialkoxybenzoato ligands of general formula 3,4-$(C_nH_{2n+1}O)_2$-PhCOO.

Finally, combinations of bulky equatorial carboxylates and counterion were obtained in two series: the pentakis(dialkoxybenzoate) complexes, of general formula $Ru_2(B2OCn)_5$, and dialkoxybenzoates with a DOS anion, of formula $Ru_2(B2OCn)_4DOS$.

First Case: Aliphatic Chain Carboxylates with Bulky Anions. *$Ru_2(RCOO)_5$.* All the aliphatic chain pentacarboxylates described above were found to exhibit a transition from the crystalline phase to a viscous birefringent phase. The transition temperatures and enthalpies are reported in Table 1. These temperatures are higher than those determined for the divalent analogues[7] $Ru_2(RCOO)_4$, which were close to 100 °C, and as a general trend, they decrease as the chain length increases. It is interesting to note that the inclusion of a terminal unsaturation in the fatty acid ($C^{\|\|}_{11}$, undecylenic acid) lowers the crystal to liquid-crystal transition temperature by approximately 30 °C, compared to the saturated undecanoate homologue. This result is in agreement with trends already found for side-chain unsaturated alkanoyloxybenzenes,[26] substituted cyclohexanes,[26] and divalent copper and ruthenium carboxylates.[5c]

The transition enthalpies are of the same order, for a given chain length, in the pentacarboxylates and in the divalent tetracarboxylates, despite the presence of a fifth alkyl chain in the former. Their evolution with the chain length is linear and we can therefore calculate the fusion enthalpy per methylene group ΔH_{CH_2}. The equation of this curve may be written as

$$\Delta H(n) = \Delta H_0 + 5n\Delta H_{CH_2}$$

By a linear regression, the slope of that curve was found to be 8.7 ± 0.2 kJ mol^{-1}, which gives a value of 1.7 kJ mol^{-1} for ΔH_{CH_2}. This value is lower than that obtained for divalent tetracarboxylate species (2.5 kJ mol^{-1} for copper analogues).[4] This discrepancy may be due to differences in the structure of the mesophase, leading to different intermolecular interactions, as we will see below.

An unexpected difficulty appeared during our initial studies of the mesomorphic properties: an intramolecular redox reaction takes place above the transition temperature, to give the divalent species $Ru_2(RCOO)_4$ as the main product. The elucidation of this reaction was achieved by the combination of several techniques. First by DSC, two endothermic peaks were observed during the first heating: one at ca. 150 °C, attributed to a crystal to mesophase transition, and a second peak that occurred around 175 °C. In the following heating cycles, only one reproducible peak could be observed, around 100 °C. To characterize the product formed after heating above 175 °C, the sample was recrystallized under an inert atmosphere from hot heptane. Its IR spectrum, the magnetic susceptibility data between 6 and 300 K as well as the elemental analysis were consistent with a divalent species $Ru_2(RCOO)_4$. This intramolecular redox reaction has been observed for several chain lengths.

This problem also affected our first X-ray diffraction results, which have been published in a preliminary communication for the $n = 9$ and $n = 12$ pentacarboxylates.[15] Our classical technique was then to record X-ray diffraction patterns during 24 h, at temperatures above the transition temperature. The resulting pattern was in fact that of the divalent species, thus corresponding to a hexagonal columnar structure. The intercolumnar distances were higher than those obtained for the $Ru_2(RCOO)_4$ species, and we attribute this to the presence of decomposition products included within the columnar structure. This kind of swollen mesomorphic structure has already been described for $Cu_2(RCOO)_4$ and $Rh_2(RCOO)_4$ species.[27] Further structural studies of $Ru_2(RCOO)_4$ compounds swollen by paraffins, as well as a detailed study of the thermal decomposition, are currently underway. Precise structural characterization was therefore performed later with a linear localization detector, which allows us to record diffraction patterns much faster (in about 15 min each), at various temperatures. This recording time is

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much smaller than the decomposition time at any given temperature, as it was determined by magnetic susceptibility measurements versus time of measurement, at different temperatures.

For the whole series, the crystalline structure at room temperature was found to be lamellar, and the measured interlamellar spacings *d* are similar to those found for the $Ru_2(RCOO)_4$ species (see Table 1). This result indicates that the presence of a fifth aliphatic chain does not perturb the lateral packing.

The crystallographic structure of the propionato analogue $Ru_2(prop)_5$ has been published recently in the literature.[28] The dimeric units are bridged through the axial carboxylate counterion, to give alternating cation–anion chains in a way similar to the $Ru_2(RCOO)_4Cl$ series:

$$\cdots RCOO{-}Ru_2(RCOO)_4{-}RCOO{-}Ru_2(RCOO)_4\cdots$$

A second interesting feature is that these chains are parallel one to each other. The crystal structure of the benzoato analogue ($R = C_6H_5$) has also been published[29] and shows the same features. By analogy with these crystalline structures, we can thus propose that in the long-chain $Ru_2(O_2C{-}(CH_2)_{n-2}{-}CH_3)_5$ complexes, the carboxylate anion axially bridges the dimers,[30] and the metallic cores and COO groups are located in polar sheets separated by two layers of aliphatic chains. This model is in good agreement with the lamellar spacing reported above.

The high-temperature diffraction patterns are characteristic of an ordered hexagonal columnar mesophase. The packing distance is 4.3 Å and the measured intercolumnar distances *D* are reported in Table 1. From these values, the columnar surface can be calculated, and it was found that this area is approximately 3 times larger than that calculated for the $Ru_2(RCOO)_4$ analogue corresponding to the same chain length, as shown in Figure 3.

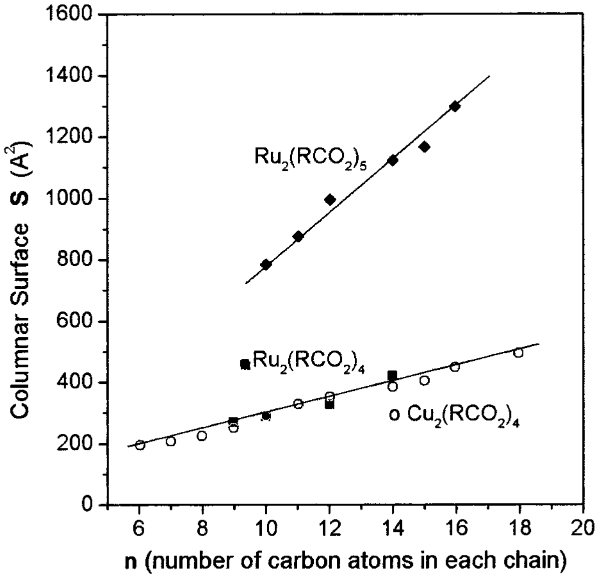

Figure 3. Dependence of the surface area of each column on the total number of carbon atoms in the aliphatic chains for divalent diruthenium tetracarboxylates and mixed-valent diruthenium pentacarboxylates.

To understand the molecular arrangement in the mesophase, it is useful to examine the crystalline structure of the $Ru_2(prop)_5$ analogue (Figure 4a). It is reasonable to assume that the polymeric chains are retained in the mesophase of the higher homologues. This hypothesis finds support in the examination of their magnetic behavior in both the crystalline and liquid-crystalline phases, as published elsewhere.[16] Vibrational IR and resonance Raman studies also show[22] that the binuclear structure and the polar cores arrangement are essentially retained in the mesophase (even if a small bending of the interdimeric carboxylate cannot be excluded). The repeating distance *l* (see Figure 4a) within these chains is 8.8 Å, which cannot explain the value of 4.3 Å found experimentally and which corresponds approximately to half of this distance *l*. Now let us consider two adjacent polymeric chains, axially shifted by half a dimer, and with interdigited peripheral chains (see Figure 4b): the repeating distance is *l*/2, which is close to the value of 4.3 Å. It is now possible to calculate how many such coupled chains are present in one column of the mesomorphic structure.

The volume *V* of the section of one column, centered on one node of the hexagonal array, with transversal section area *S* and height *h*, can be expressed as

$$V = Sh = pV_0 \qquad (1)$$

where V_0 is the volume of one dimer and *p* the number of dimers within that columnar section. With the hypothesis of additivity of molar volumes, the volume V_0 can be given by

$$V_0 = V_{pc} + 5V_{CH_3} + 5(n-2)V_{CH_2} \qquad (2)$$

where *n* is the number of carbon atoms in one aliphatic chain, V_{pc} is the volume of the polar core, V_{CH_2} and V_{CH_3} being the molar volumes respectively of the methylene and methyl groups. By replacing V_0 in eq 1 by the expression of eq 2, we obtain therefore the cross-section area of a column:

$$S = p(V_{pc} + 5V_{CH_3})/h + (5p/h)V_{CH_2}(n-2) \qquad (3)$$

The first term is fixed, whereas the second one increases linearly with *n*; this is what was experimentally observed by plotting the cross section $S = 3^{1/2}D^2/2$ as a function of *n*. The slope of this curve, calculated by a linear regression, is 72 ± 4 Å.² If we assume that the aliphatic chains are disordered in the mesophase, we can thus use for V_{CH_2} a value of 29 Å³ which corresponds to the volume of a methylene group in a disordered aliphatic chain.[31] With $h = 4.3$ Å experimentally determined, we can deduce $p = 2.1 \pm 0.2$.

The only way to incorporate two dimers in a columnar section height of 4.3 Å is to put four cation–anion chains in one column. We propose therefore the following

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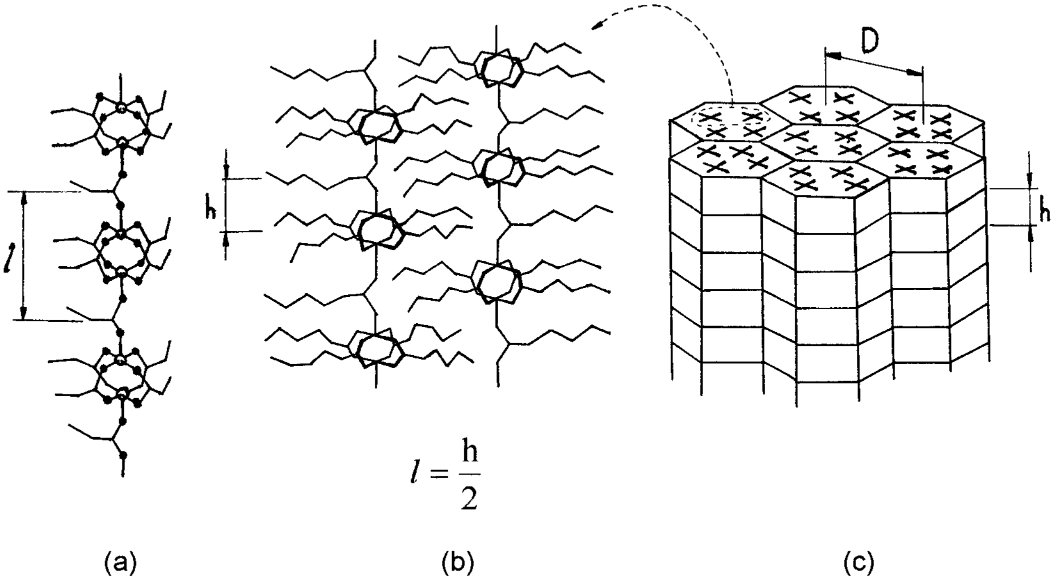

Figure 4. Schematic representation of the structural model proposed for the thermotropic mesophase of mixed-valent diruthenium pentacarboxylates. (a) Polymeric dimer-anion chain found in the crystalline structure of $Ru_2(prop)_5$ (adapted from ref 28): (○) Ru; (●) O. (b) Two polymeric chains shifted by half a dimer, as supposed to be present in the mesophase of the long-chain mixed-valent diruthenium pentacarboxylates. (c) Columnar hexagonal mesophase of these compounds: each column is built up by four polymeric chains (see text).

Table 2. Temperature (°C) and Enthalpy (kJ mol^{-1}) of the Crystal-to-Mesophase Transition for the $Ru_2(O_2C{-}(CH_2)_{n-2}{-}CH_3)_4DOS$ Series

n	temp	enthalpy
6	145	7
8	121	37
9	153	36
12	152	63
16	140	65
18	143	118

model to describe the molecular arrangement in the mesophase: the alternating chains of ···dimer–carboxylate···, present in the crystalline phase, are retained in the mesophase. Each column of the hexagonal array is made up of four molecular chains entangled and axially shifted by half a dimer, as schematically represented in Figure 4c.

$Ru_2(RCOO)_4DOS$. Six compounds have been studied in that family: $Ru_2(CH_3(CH_2)_{n-2}COO)_4DOS$ with n = 6, 8, 9, 12, 16, and 18. They all exhibit a transition to a birefringent viscous phase at ca. 140 °C. The transition temperatures and enthalpies, obtained by DSC, are reported in Table 2. The temperatures are similar to those found in the related series of pentacarboxylates.

In the $n = 16$ compound, a small endothermic peak at 45 °C appears in the thermogram during the first heating; then during the subsequent heatings of the same sample, an exothermic peak appears at 50 °C. This may be related to a crystal–crystal transition, an interpretation that finds a support by examination of the powder diffraction patterns of the crystalline phase at different temperatures (see below). Even if this peculiar behavior was found only in the hexadecanoate derivative (and, to lesser extent, in the octadecanoate analogue), all the members of this series exhibited a first endothermic transition at temperatures below 120 °C, which is presumably due to a crystal-to-crystal phase transition (seen by OM/PL and XRD) and then the crystal-to-liquid crystal phase transition at higher temperatures. The clearing point is detected at ca. 200 °C for all the compounds of this series, and it is accompanied by decomposition.

The XRD patterns of the crystalline phase of the n = 16 compound have been recorded at three different temperatures: 30, 70, and 110 °C. The small-angle region is the same for the three temperatures: it shows a series of sharp reflections in the reciprocal spacings 1:2:3:4, which is characteristic of a lamellar structure. From these, we have calculated an interlamellar spacing of 39.8 Å, which is similar to the value found for the pentakis(hexadecanoate) (42 Å). The wide-angle region obtained at 30 °C is different from that recorded at 70 and 110 °C, and it indicates slight differences in the crystalline structure between 30 and 70 °C.

The diffraction patterns obtained in the mesophase cannot be interpreted in a straightforward fashion, but they suggest that the mesophase is of the hexagonal columnar type. A detailed structural study of this mesophase is now underway.

Second Case: Bulky Carboxylates with Small Anion: Chloride. Three dialkoxybenzoate compounds of general formula $Ru_2(B2OC\mathit{n})_4Cl$ have been studied: n = 12, 15, and 16. For the n = 16 compound, an endothermic peak (ΔH = 95 kJ/mol) is observed at 27 °C. All the compounds exhibit a very slow transition, beginning at ca. 50 °C, to a phase that was shown, by X-ray diffraction, to be of a lamellar type. However, the XRD signals in the small-angle region were rather diffuse and indicative of a lamellar structure that was developed on a small scale only. The XRD pattern of the same lamellar structure exhibited a broad reflection at 4.7 Å in the wide-angle region.

Another transition from this lamellar phase was observed, at higher temperature, to a columnar hexagonal mesophase, as characterized by X-ray diffraction. The X-ray pattern shows, in the small-angle region, three sharp reflections positioned in the ratio $1:3^{1/2}:4^{1/2}$, and a broad reflection in the wide-angle region. The

Table 3. Temperature (°C) and Enthalpy (kJ mol^{-1}) of the Lamellar-to-Columnar Mesophase Transition of the $\mathrm{Ru_2(B2OC}n\mathrm{)_4Cl}$ Compounds and Structural Parameters Determined by X-ray Diffraction Studies (Interlamellar Spacing d in Å of the Lamellar Phase and Intercolumnar Distance D in Å)

n	temp	enthalpy	d	D
12	157	2.2	29.6	27.5
15	150	2.8	32.6	30
16	157	4	31.3	30.9

thermodynamic data of this transition, obtained by DSC, are reported in Table 3, as well as the structural parameters, given by X-ray diffraction, of the lamellar mesophase (interlamellar distance) and of the columnar mesophase (intercolumnar distance).

This intercolumnar distance, of about 30 Å, is short compared to the diameter of one molecule with fully extended aliphatic peripheral chains, which was for example evaluated to 50 Å in the case of the $n = 15$ derivative. This could be related to the fusion of the chains and to the possible interdigitations between adjacent columns, as already observed in the columnar mesophase of divalent $\mathrm{M_2(RCOO)_4}$ complexes.[2-4,6,7,9]

Third Case: Bulky Equatorial Carboxylate with Bulky Counterion. Two series belonging to this category were studied: $\mathrm{Ru_2(B2OC}n\mathrm{)_4DOS}$, with a linear chain anion, and $\mathrm{Ru_2(B2OC}n\mathrm{)_5}$, with a bulky anion.

Three homologues of the series $\mathrm{Ru_2(B2OC}n\mathrm{)_5}$ ($n = 12$, 15, and 16) have been characterized by optical microscopy and DSC. They all show a transition between two birefringent and very viscous phases, at ca. 30 °C for the $n = 12$ compound, at 42 °C ($\Delta H = 130 \pm 5$ kJ mol^{-1}) for the $n = 15$ and at 48 °C ($\Delta H = 130 \pm 5$ kJ mol^{-1}) for the $n = 16$ complex. The clearing point appeared at ca. 210 °C, with decomposition of the sample.

An X-ray diffraction study has been carried out for the $n = 15$ homologue. At room temperature, an ordered columnar hexagonal mesophase was observed with, in the low-angle region of the XRD pattern, three reflections in the ratio $1:3^{1/2}:4^{1/2}$ and in the wide-angle region, a sharp reflection at 4.3 Å, superposed with a broad band. The intercolumnar distance was found at $D = 32.5$ Å. Above 50 °C, the pattern exhibited in the low-angle region an additional reflection at $7^{1/2}$, and at wide angles, the sharp reflection disappeared, while a broad one at 4.3 Å was present, showing that the order along the columnar axis became liquidlike, probably due to the melting of the peripheral alkoxy chains. The intercolumnar distance measured from this X-ray pattern was $D = 35.2$ Å, indicating that the dimensions of the hexagonal array increased with temperature, which may be related to an increase of the dynamical disorder of the peripheral chains.

Similar results were found for the $\mathrm{Ru_2(B2OC}n\mathrm{)_4DOS}$ series ($n = 12$, 15, and 16): they also exhibit a liquid-crystalline phase at room temperature, as shown by XRD. DSC experiments on the $n = 16$ derivative showed a first very intense endothermic peak at 41 °C ($\Delta H = 220$ kJ/mol) and a second, much smaller endothermic peak at ca. 160 °C ($\Delta H = 2.5$ kJ/mol). The kinetics of recrystallization from the intermediate to the room-temperature phase is very slow, taking several days. A detailed characterization of the structure of these phases is now under way.

Conclusions

We have shown in this work that a strong correlation exists between the molecular structure of the mixed-valent diruthenium carboxylates and their mesomorphic properties. For the aliphatic derivatives the mesogenic character depends, first of all, on the nature of the anion: complexes containing chloride as counterion, $\mathrm{Ru_2(C}_n\mathrm{H}_{2n-1}\mathrm{O_2)_4Cl}$, do not show any thermotropic mesophase whereas complexes with a long-chain carboxylate as the anion, i.e., $\mathrm{Ru_2(C}_n\mathrm{H}_{2n-1}\mathrm{O_2)_5}$ or dodecyl sulfate $\mathrm{Ru_2(C}_n\mathrm{H}_{2n-1}\mathrm{O_2)_4DOS}$, exhibit thermotropic hexagonal columnar mesophases. Moreover, the macroscopic structural informations obtained by powder XRD, combined with the use of “local probes of the polar cores” allowed us to propose a model for the mesophase of the pentacarboxylate derivatives.

Bulky carboxylates, possessing several aliphatic chains (namely, the 3,4-dialkoxybenzoates) were shown to enhance the formation of mesophases in these systems. Thus, it was possible to induce mesomorphism in the chloride series, obtaining mesogenic chlorocarboxylates $\mathrm{Ru_2(B2OC}n\mathrm{)_4Cl}$, in contrast to the nonmesogenic character of the linear aliphatic analogues $\mathrm{Ru_2(C}_n\mathrm{H}_{2n-1}\mathrm{O_2)_4Cl}$. Furthermore, the transition temperature from the crystalline to the liquid-crystalline phase of the pentacarboxylates was considerably lowered by using this type of carboxylates; indeed, room-temperature liquid crystals were obtained, even if the nature of their mesophases is not yet completely established.

These results can be understood in terms of a general principle: the key parameter that can be tuned in order to enhance the mesomorphic behavior of these compounds is an efficient filling of the space around a rigid “skeleton” of stacked polar cores within a columnar structure. The problem of the void space between dimers created by an axial ligand—in the present case, by the chloride anion- was also pointed out in the case of divalent copper[5a] or ruthenium[7b] carboxylates containing axially coordinated pyrazine. We have shown in this work that an adequate combination of axial ligands/anions and equatorial carboxylates may lead to an efficient intracolumnar filling of the interdimeric space.

The present strategy may be used further in order to decrease the transition temperatures (by using, for example, trialkoxybenzoates as equatorial ligands, and/or alkyl-containing anions) and also to confer mesogenic character to compounds containing small axial ligands such as pyrazine. We are presently carrying out such studies.

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Supporting Information Available: Elemental analysis and yields of ligands and complexes (2 pages). Ordering information is given on any current masthead page.

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