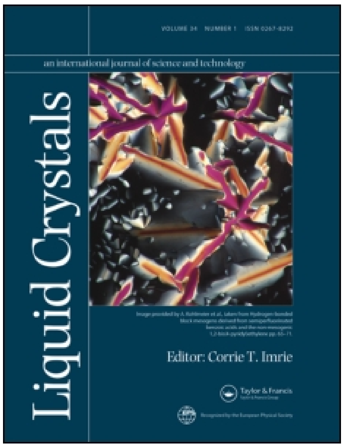

Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Characterization of the first mixed-valent liquid-crystalline materials. Synthesis and structural properties of new binuclear ruthenium carboxylates

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To cite this Article Cukiernik, Fabio D. , Maldivi, Pascale , Giroud-godquin, Anne-Marie , Marchon, Jean-Claude , Ibn-elhaj, Mohammed , Guillon, Daniel and Skoulios, Antoine(1991) 'Characterization of the first mixed-valent liquid-crystalline materials. Synthesis and structural properties of new binuclear ruthenium carboxylates', Liquid Crystals, 9: 6, 903 — 906

To link to this Article: DOI: 10.1080/02678299108055013

URL: http://dx.doi.org/10.1080/02678299108055013

LIQUID CRYSTALS, 1991, VOL. 9, NO. 6, 903–906

PRELIMINARY COMMUNICATIONS

Characterization of the first mixed-valent liquid-crystalline materials

Synthesis and structural properties of new binuclear ruthenium carboxylates

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(*Received 18 January 1991; accepted 25 February 1991*)

The syntheses and structural properties of new binuclear ruthenium (II, III) complexes with long chain carboxylates, of general formula $Ru_2(RCO_2)_4X$ ($R = C_8H_{17}$, $C_{11}H_{23}$ and $X = Cl$, RCOO), are reported. The thermodynamic behaviour of these compounds is strongly influenced by the nature of the counterion X. The chloro complexes ($X = Cl$) are not mesomorphic whereas the carboxylato species ($X = RCOO$) are shown to exhibit a thermotropic columnar mesophase, thus providing the first example of a mixed-valent liquid-crystalline material.

In earlier work from our laboratories, the liquid-crystalline properties of binuclear complexes of fatty acids with transition metals such as Cu(II), Rh(II) and Ru(II) have been fully characterized by optical microscopy, differential scanning calorimetry and X-ray diffraction studies [1–3]. Furthermore, we have taken advantage of the presence of the metal atoms to gain additional information on structural features of the liquid-crystalline phase, by employing copper K edge EXAFS spectroscopy [4], IR and Raman spectroscopies [5] and magnetic susceptibility measurements [3, 6]. Irrespective of the nature of the metal, a discotic hexagonal mesophase was observed, with a characteristic two dimensional hexagonal array of columns, where each column is made up of a rigid backbone of regularly stacked binuclear cores surrounded by melted aliphatic chains. On the other hand, binuclear mixed-valent carboxylates Ru(II)–Ru(III) of general formula $Ru_2(RCO_2)_4X$ ($X = Cl, BF_4, \ldots$) [7–12] exhibit the same classical lantern structure as classical dimetal (II, II) carboxylates. This structural similarity prompted us to undertake a detailed investigation of the mesomorphic properties of Ru(II)–Ru(III) long chain carboxylates, which we assumed to be sensitive

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to the nature of the counterion X. We describe here the synthesis and mesomorphic behaviour of two series of mixed-valent binuclear ruthenium carboxylates: chloro complexes of general formula $Ru_2(RCO_2)_4Cl$ on one hand, and a class of compounds in which the counterion is the same as the four bridging ligands, $[Ru_2(RCO_2)_4(RCO_2)]$, on the other.

Two compounds with different aliphatic chain lengths were prepared in each series: the nonanoate (derived from pelargonic or nonanoic acid) and the dodecanoate (derived from lauric or dodecanoic acid). The chloro derivatives were obtained from the butanoate homologue: $Ru_2(C_3H_7COO)_4Cl$, by a substitution reaction of the four carboxylates ligands with the corresponding fatty acid

$$Ru_2(C_3H_7CO_2)_4Cl \xrightarrow{RCO_2H} Ru_2(RCO_2)_4Cl. \qquad (1)$$

The starting material used in the syntheses of the second series of compounds was a novel tetra-μ-acetato diruthenium (II, III) complex with a weakly coordinating tetraphenylborate (BPh_4^-) counterion. This complex was synthesized according to

$$Ru_2(CH_3COO)_4Cl + NaBPh_4 \xrightarrow{H_2O} [Ru_2(CH_3COO)_4(H_2O)_2](BPh_4) + NaCl. \qquad (2)$$

The second step of the synthesis was the complete substitution of both the counterion and the acetato ligands by the long chain carboxylate anions

$$[Ru_2(CH_3COO)_4(H_2O)_2](BPh_4) \xrightarrow{RCO_2H} Ru_2(RCOO)_5. \qquad (3)$$

$R = C_8H_{17}$ or $C_{11}H_{23}$. All products gave satisfactory elemental analysis (C, H, Ru, B, Cl).

Characterization of the liquid-crystalline properties was achieved by the usual techniques of optical microscopy, differential scanning calorimetry and X-ray scattering. Optical observations were made with an Olympus BH-2 microscope equipped with a Mettler FP 82 hot stage. Differential scanning calorimetry was performed using a Mettler FP 85 calorimeter. Thermograms of samples in sealed aluminium pans were recorded over the temperature range 80–190°C at a scanning rate of 5°C min^{-1}. X-ray diffraction patterns of powder samples of $Ru_2(C_8H_{17}COO)_5$ and $Ru_2(C_{11}H_{23}COO)_5$ in Lindemann capillaries were recorded photographically using a Guinier focusing camera equipped with a bent quartz monochromator (Cu–$K_{\alpha 1}$ radiation from a Philips PW-1009 generator) and an electric oven. We could not detect any mesomorphic behaviour for the chloro complexes: heating these compounds above 230–250°C resulted in decomposition.

A high temperature liquid-crystalline phase was observed, however, for both pentacarboxylato species: a transition from the crystal to a new birefringent phase was detected at 149°C by careful observation of the dodecanoate under the microscope, and this phase transition was studied by DSC for the nonanoate and dodecanoate compounds. The corresponding values of temperature and enthalpy are listed in table 1, together with the data obtained earlier [3] for the Ru(II, II) analogues, also reported for comparison. The clearing point could not be observed for these products as decomposition occurred near 170°C. Thus, the thermal stability range of this phase is very narrow, compared to the mesophase of the Ru(II)–Ru(II) analogues, for which neither clearing nor decomposition could be detected by heating up to 250°C.

X-ray diffraction studies were carried out on powdered samples of pentakis-nonanoate and pentakis-dodecanoate diruthenium (II, III) in the crystalline phase,

Table 1. Temperatures and enthalpies of the transition crystal–mesophase for mixed-valent derivatives $Ru_2(RCOO)_5$ and Ru(II, II) analogues $Ru_2(RCOO)_4$.

	$Ru_2(RCOO)_5$		$Ru_2(RCOO)_4$†	
R	$T/^\circ C$	$\Delta H/kJ\,mol^{-1}$	$T/^\circ C$	$\Delta H/kJ\,mol^{-1}$
C_8H_{17}	149	15	96	40
$C_{11}H_{23}$	149	66	90	41

† Data from [3].

Table 2. Interlamellar distances in the crystalline phase for mixed-valent derivatives $Ru_2(RCOO)_5$ and Ru(II, II) analogues $Ru_2(RCOO)_4$.

	$d/Å$	
R	$Ru_2(RCOO)_5$	$Ru_2(RCOO)_4$†
C_8H_{17}	22·5	24·5
$C_{11}H_{23}$	32·3	31·7

† Data from [3].

Table 3. Intercolumnar distances in the mesophase for mixed-valent derivatives $Ru_2(RCOO)_5$ and Ru(II, II) analogues $Ru_2(RCOO)_4$.

	$d/Å$	
R	$Ru_2(RCOO)_5$	$Ru_2(RCOO)_4$†
C_8H_{17}	18·2 18·6	17·6
$C_{11}H_{23}$	21·2	19·4

† Data from [3].

from room temperature to 130°C. The diffraction pattern is characteristic of a lamellar structure, and no change in the features of this structure could be detected over the entire temperature range of the phase. The interlamellar distances measured for both compounds are reported in table 2 and compared to the interlamellar distances of the Ru(II)–Ru(II) analogues. It turns out that the spacings of the Ru(II)–Ru(III) derivatives are close to those of the Ru(II)–Ru(II) derivatives, in spite of the presence of a fifth alkyl chain in the former.

The X-ray diffraction patterns of the mesophase exhibit in the small angle region a series of sharp reflections related to a two dimensional packing of columns. For the dodecanoate derivative, the lateral packing is hexagonal, as usual, with a cell parameter of 21·2 Å, whereas for the pelargonate derivative it is slightly distorted into a centred rectangular lattice with cell parameters $a = 31{\cdot}7$ Å and $b = 18{\cdot}8$ Å, with an interdiagonal angle of 61·4°. Thus the intercolumnar distances are found to be equal to 18·6 Å and 18·2 Å (see table 3). Though slightly larger, these distances are comparable to those found with the Ru(II)–Ru(II) analogues. This suggests that the fifth alkyl chain should be located inside the column, thus leading to an increase of the intracolumnar stacking period of the binuclear complexes, and presumably to a different type of order along the cores of the columns. However, no supporting evidence of stacking order along the columns could be found by examination of the X-ray patterns in the mesophase.

The absence of mesomorphic properties for the $Ru_2(RCO_2)_4Cl$ complexes can be related to their crystalline structure, which we assume to be analogous to that found for the chloro tetra-μ-butanoato diruthenium (II, III) [9]. In the latter, the Ru_2^{5+} bimetallic cores are linked to one another across the axially bridging chloride anion providing an array of perpendicular infinite linear chains in the crystal. This structural arrangement cannot be a good precursor for a columnar mesophase, where the column axes are all parallel.

The structural similarities in both crystalline and mesomorphic phases between the mixed-valence ruthenium pentacarboxylates, $Ru_2(RCO_2)_5$, and the Cu(II, II) [1], Rh(II, II) [2], Ru(II, II) [3] or Mo(II, II) [13] tetracarboxylates are striking, despite their obviously different metal:carboxylate stoichiometry which should lead to differences in their supramolecular organization. So far, we have not been able to obtain suitable single crystals of any pentacarboxylate species for a structure determination which could precisely indicate the location of the additional carboxylate group and its coordination mode. The crystallographic structure of a mixed-valent benzoato derivative $Ru_2(C_6H_5COO)_5$, C_6H_5COOH [12] clearly shows that the carboxylate counterions bridge dimeric units, to give linear chains of molecules parallel to each other, and we assume a similar organization for the aliphatic pentacarboxylato analogues.

Insight into the internal structure of the columnar cores will hopefully be gained through further experiments on a more extended homologous series of compounds, by EXAFS spectroscopy and wide angle X-ray diffraction studies.

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