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## Liquid Crystals

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### Mixed-valent diruthenium (II,III) aliphatic carboxylates: columnar mesophases in dodecylsulfate and octylsulfonate derivatives

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# Mixed-valent diruthenium (II,III) aliphatic carboxylates: columnar mesophases in dodecylsulfate and octylsulfonate derivatives

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Two series of polymeric mixed-valent diruthenium (II,III) aliphatic carboxylates of formula  $Ru_2[O_2C(CH_2)_{n-2}CH_3]_4X$  (where  $X$ =dodecylsulfate (DOS) anion and  $n=8, 9, 16$  and  $18$ , or  $X$ =octylsulfonate (OS) anion and  $n=8, 10, 12, 14$  and  $18$ ) were synthesized and characterized. Their liquid crystalline properties and crystalline (Cr) structures were analysed; the Cr phases are lamellar in all cases. For long chain DOS derivatives ( $n=16$  and  $18$ ) hexagonal and rectangular columnar mesophases ( $Col_h$  and  $Col_r$ ) with melting temperatures close to  $140^\circ C$  were observed. For long chain OS derivatives ( $n \geq 10$ ) a  $Col_h$  mesophase was observed, with melting temperatures between  $140$  and  $190^\circ C$ .

## 1. Introduction

Mixed-valent diruthenium tetracarboxylates of formula  $Ru_2(O_2CR)_4X$ , where  $X^-$  is an anion, have been widely studied due to their interesting electronic structure, and spectroscopic, magnetic and mesomorphic properties (see review [1]). In previous studies of their LC properties, we have shown that the melting temperatures, the nature of the mesophases obtained and their corresponding thermal ranges were dependent on the efficiency of the intracolumnar filling of the intermolecular space [2–5]; related results have been obtained by Aquino and co-workers [6]. We succeeded in fulfilling this requirement by different strategies: the use of long chain axial anions, of bulky equatorial carboxylates, or a combination of both [3, 4].

One of the axial ligands used was DOS, see the scheme (a). In a previous study [3] we synthesized and preliminarily characterized two series of carboxylate complexes:  $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4DOS$  (for  $n=8, 9, 16$  and  $18$ ), and  $Ru_2(3,4-B2OCn)_4DOS$  (where 3,4-B2OCn is a 3,4-di( $n$ -alkoxy)benzoate, for  $n=12, 15$  and

16). We showed that these compounds are mesogenic, for those belonging to the first series above *c.*  $140^\circ C$  (for  $n \geq 9$ ) while those belonging to the second family are liquid crystalline even at room temperature.

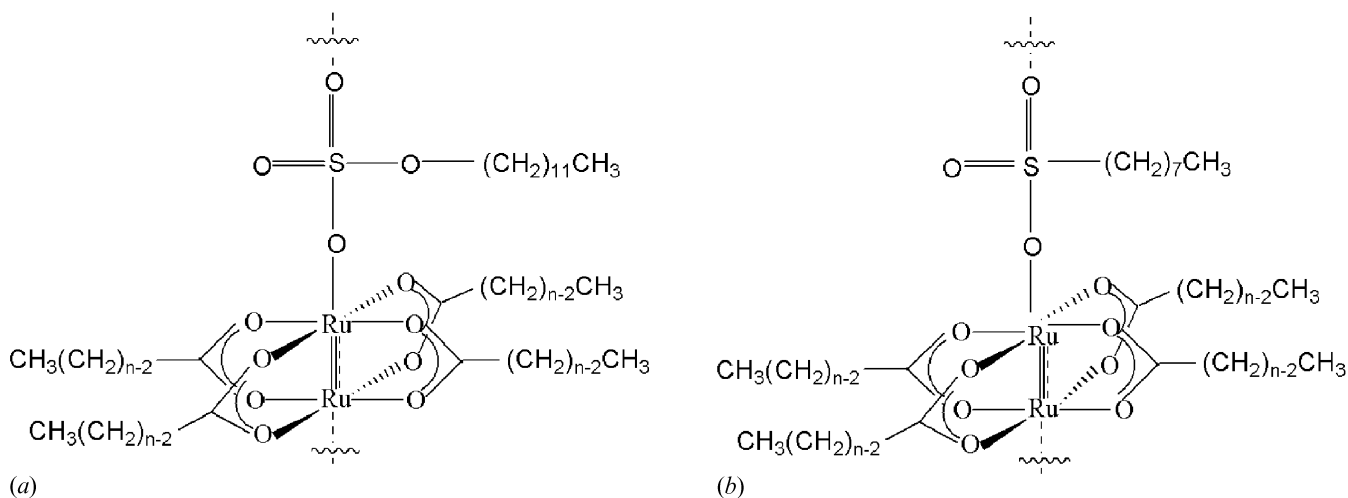
In the present work we have extended this study on the aliphatic series and present here a detailed structural characterization of their crystal (Cr) and liquid crystalline (LC) phases. We have also synthesized and characterized a new series of aliphatic carboxylate complexes:  $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4OS$  (for  $n=8, 10, 12, 14$  and  $18$ ), see the scheme (b). Comparison of the two series gives a better understanding of the role played by the long chain axial anion on the mesomorphic properties and Cr structures of these compounds. The Cr structure of the  $Ru_2(O_2C(CH_2)_8CH_3)_4OS$  derivative has recently been solved [7]; this information is useful for the analysis of both the Cr and LC structures.

## 2. Experimental

### 2.1. Synthesis

The DOS derivatives were synthesized following published procedures [3]. The OS compounds were synthesized by heating under reflux for an hour a

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Scheme. Sketch of the molecular structure of the two series studied: (a)  $\text{Ru}_2(\text{O}_2(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{DOS}$ , (b)  $\text{Ru}_2(\text{O}_2(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{OS}$ .

methanolic solution of the appropriate chloro-complex,  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{Cl}$ , and silver octylsulfonate (10% excess) under  $\text{N}_2$  atmosphere. The  $\text{AgCl}$  precipitate was filtered off and the brown solution evaporated to dryness. The solid thus obtained was dissolved in  $\text{CH}_2\text{Cl}_2$ , the solution filtered again to eliminate excess of  $\text{AgOS}$  and evaporated to dryness. The products were purified by washing several times with water and ethyl ether (for  $n=8-14$ ) or by recrystallization from methanol ( $n=18$ ).

## 2.2. Characterization

The characterization of the synthesized compounds was carried out by elemental analyses for C, H and S at INQUIMAE (Carlo Erba CHNS-O EA1108), see table 1, and by IR spectroscopy as KBr pellets on a Nicolet FTIR 510P spectrometer.

The IR spectra of both series exhibited the following bands in the  $1300-1600\text{ cm}^{-1}$  region:  $1466\text{ cm}^{-1}$  ( $\delta\text{CH}_2$ , asym of  $\text{CH}_2$  and  $\text{CH}_3$ ),  $1376\text{ cm}^{-1}$  ( $\delta\text{CH}_3$ , sym of  $\text{CH}_3$ ),  $1431\text{ cm}^{-1}$  ( $\delta\text{CH}_2$ ,  $\alpha\text{-CO}_2$ ),  $1305\text{ cm}^{-1}$  ( $\gamma\text{CH}_2$ , sym)

and  $c.$   $1500$  and  $1420\text{ cm}^{-1}$  ( $\nu\text{CO}_2$ , asym and  $\nu\text{CO}_2$ , sym). DOS derivatives also exhibited strong bands corresponding to coordinated DOS at  $1305$ ,  $1235-1245$ ,  $1145$  and  $1055\text{ cm}^{-1}$ , and OS derivatives showed the bands corresponding to the coordinated OS at  $1248$  and  $1031\text{ cm}^{-1}$  [8].

## 2.3. Physicochemical measurements

Polarizing optical microscopy (POM) as a function of temperature was carried out between crossed polarizers using a Leitz DMRX microscope equipped with a Leitz 1350 hot-stage. Transition temperatures and enthalpies were obtained by DSC experiments at a heating rate of  $5^\circ\text{C min}^{-1}$ , using a Shimadzu DSC-50. X-ray diffraction (XRD) patterns were obtained with two different experimental set-ups, the powder being filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic  $\text{Cu-K}\alpha_1$  beam ( $\lambda=1.5418\text{ \AA}$ ) was obtained using a Guinier camera (900 W) or a Debye-Scherrer camera, both equipped with a bent quartz monochromator and an electric oven. A first set of diffraction patterns was registered with a gas-curved counter 'Inel CPS 120'; periodicities up to  $60\text{ \AA}$  can be measured, and the sample temperature is controlled within  $\pm 0.05^\circ\text{C}$ . The second set of diffraction patterns was registered on image plates; periodicities up to  $90\text{ \AA}$  can be measured, and the sample temperature is controlled to within  $\pm 0.3^\circ\text{C}$ . Exposure times were varied from 1 to 24 h. The XRD patterns were obtained from room temperature to  $200^\circ\text{C}$ .

Table 1. Elemental analysis and yields of the  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4X$  compounds.

Anion $X^-$	$n$	C/%		H/%		S/%		Yield/%
		exp	(calc)	exp	(calc)	exp	(calc)	
DOS	8	50.38	(50.80)	8.15	(8.24)	3.90	(3.09)	68
	9	52.12	(52.58)	8.49	(8.55)	3.78	(3.92)	73
	16	61.09	(61.30)	10.12	(10.09)	2.22	(2.15)	81
	18	62.90	(63.00)	10.50	(10.39)	2.07	(2.00)	ND
OS	8	49.14	(49.62)	7.80	(8.02)	3.41	(3.31)	91
	10	53.50	(53.36)	8.63	(8.68)	2.26	(2.97)	93
	12	56.90	(56.40)	8.89	(9.21)	2.51	(2.69)	90
	14	58.56	(58.91)	9.91	(9.66)	2.48	(2.46)	93
	18	63.57	(64.78)	10.38	(10.62)	2.11	(1.92)	58

## 3. Results

The phase sequences, transition temperatures, enthalpy changes and structural parameters were examined by POM, DSC and XRD. The results are

Table 2. Phase sequence, structural parameters and transition data of  $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4DOS$  and  $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4OS$  compounds. The phase nature (crystalline Cr, columnar hexagonal mesophase  $Col_h$ , columnar rectangular mesophase  $Col_r$ , lamellar lam, unidentified liquid crystalline phase LC or isotropic I) is followed by its structural parameters at one selected temperature [in °C within square brackets].  $d$  is the interlamellar distance for lamellar phases (in Å);  $D$  is the intercolumnar distance (in Å) for the  $Col_h$  phase;  $a$  and  $b$  are the parameters of the rectangular phase (in Å);  $S$  is the columnar surface (in Å<sup>2</sup>) in both cases. All these parameters are accompanied by their estimated uncertainties (within parenthesis). Transition temperatures (in °C) and enthalpies [in kJ mol<sup>-1</sup>] are included between the corresponding phases. Also abbreviated: decomposition (dec), not determined (ND).

$n$	Phase sequence, structural parameters and transition data
<i>Ru<sub>2</sub>(O<sub>2</sub>C(CH<sub>2</sub>)<sub>n-2</sub>CH<sub>3</sub>)<sub>4</sub>DOS compounds</i>	
8	Cr <sub>1</sub> lam, $d=25.3$ (2) [20] • 121 [36] • Cr <sub>2</sub> lam, $d=21.1$ (2) [130] • 194 [18] • I+dec
9	Cr <sub>1</sub> lam, $d=27.6$ (2) [30] • 116 [34] • Cr <sub>2</sub> lam, $d=22.8$ (2) [130] • 156 [19] • LC <sup>a</sup> +dec
16	Cr <sub>1</sub> lam, $d=40.8$ (2) [25] • 57 [ND] • Cr <sub>2</sub> lam, $d=40.8$ (2) [90] • 142 [65] • Col <sub>h</sub> , $D=29.8$ (2); $S=770(10)$ [150] • 163 [ND] • I+dec
18	Cr <sub>1</sub> lam, $d=45.2$ (2) [25] • 36 [24] • Cr <sub>2</sub> lam, $d=45.2$ (2) [90] • 143 [118] • Col <sub>r</sub> , $a=61.3$ (2); $b=30.6$ (2); $S=937$ (12) [150] • 162 [8] • Col <sub>h</sub> , $D=27.7$ (2); $S=665$ (10) [160] • 202 [14] • I+dec
<i>Ru<sub>2</sub>(O<sub>2</sub>C(CH<sub>2</sub>)<sub>n-2</sub>CH<sub>3</sub>)<sub>4</sub>OS compounds</i>	
8	Cr <sub>1</sub> lam, $d=22.8$ (2) [50] • 161 [30] • Cr <sub>2</sub> lam, $d=23.0$ (5) [180] • 218 [24] • I+dec
10	Cr <sub>1</sub> lam, $d=26.8$ (2) [50] • 169 [46] • Cr <sub>2</sub> lam, $d=27.2$ (5) [180] • 186 [4] • Col <sub>h</sub> , $D=19.5$ (2); $S=329$ (7) [200] • 208 [10] • I+dec
12	Cr <sub>1</sub> lam, $d=30.8$ (2) [50] • 157 [58] • Cr <sub>2</sub> lam, $d=31.5$ (7) [160] • 174 [6] • Col <sub>h</sub> , $D=22.9$ (2); $S=454$ (8) [190] • 211 [12] • I+dec
14	Cr <sub>1</sub> lam, $d=34.3$ (2) [50] • 150 [64] • Cr <sub>2</sub> lam, $d=35.0$ (8) [160] • 166 [6] • Col <sub>h</sub> , $D=24.0$ (2); $S=499$ (8) [180] • 192 [6] • I+dec
18	Cr <sub>1</sub> lam, $d=44.1$ (2) [50] • 98 [23] • Cr <sub>2</sub> lam, $d=44.1$ (8) [130] • 140 [47] • Col <sub>h</sub> , $D=27.0$ (2); $S=625$ (9) [180] • 196 [6] • I+dec

<sup>a</sup>Decomposition in the LC phase precluded XRD structural characterization. Microscopic observations suggest a columnar mesophase.

summarized in table 2, and analysed here for each series of compounds.

### 3.1. $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4DOS$ series

The structural characterization of the phases of all the derivatives studied was performed by XRD, as the high viscosity and uncharacteristic textures of the mesophases prevented their identification by POM. A limited thermal stability at temperatures above the clearing point precluded measurements on cooling. At temperatures below the melting point all the compounds showed one or more Cr lamellar phases (characterized by a series of peaks with distances in the reciprocal spacing ratio 1:2:3:4...). They also showed broad signals at 7.9, 4.5 and 3.9 Å. The interlamellar distance is nearly independent of temperature, but grows linearly with the number of carbon atoms in the carboxylic chains, figure 1(a).

The compounds with  $n=16$  and 18 are mesogenic. The compound with  $n=16$  exhibits a  $Col_h$  ( $p6mm$ ) mesophase characterized in XRD by a series of sharp peaks with distances in the reciprocal spacing ratio  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}\dots$  and two additional broad signals, one at 7.0(1) Å probably due to the intracolumnar periodicity and a second broader one at 4.5 Å typical of alkyl chains in a liquid-like order. The compound with  $n=18$  shows both a  $Col_r$  ( $c2mm$ ) (peaks that could be indexed as 20 (s), 11 (vs), 31 (vw), 40 (m), 02 (m), 22 (w) and 13 (vw) and additional signals at 7.1 and 4.5 Å) and a  $Col_h$  ( $p6mm$ ) mesophase [4, 5] above 150°C, with only one additional signal at 4.5 Å. In the latter case, the absence of a signal close to 7 Å together with the short intercolumnar distance suggests that an increment in the intracolumnar period might be operative.

### 3.2. $Ru_2(O_2C(CH_2)_{n-2}CH_3)_4OS$ series

For the compound with  $n=18$ , POM observations showed a room temperature Cr phase that became darker at 100°C, and then more fluid and birefringent near 140°C; at  $c.$  195°C the clearing point was reached. For the shorter chain length homologues  $10 \leq n \leq 14$  similar behaviour was found, but a second transition between the two Cr phases was also seen. For the compound with  $n=8$ , no fluid anisotropic phase was observed. The Cr phases of all the compounds were identified as lamellar by XRD. As in the previous case, the interlamellar distance grows linearly with the chain length, figure 1(b).

The mesophase of all the mesogenic compounds was identified as a  $Col_h$  ( $p6mm$ ); the structural determination was difficult due to their thermal instability and poorly developed XRD patterns. In all cases, the signal corresponding to the molten aliphatic chains at 4.5 Å

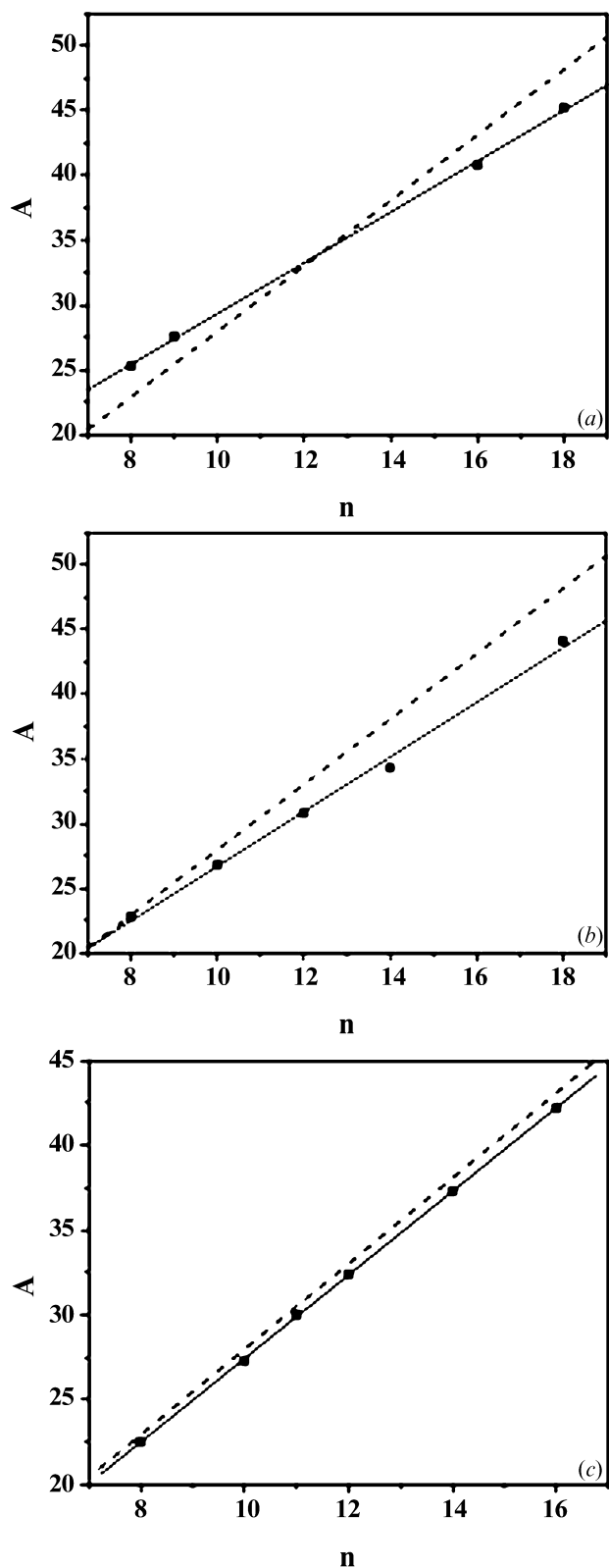


Figure 1. Interlamellar distance of the crystalline phase as a function of the number of carbon atoms ( $n$ ) in the carboxylic chains: (a) DOS derivatives ( $\text{Cr}_1$  phase), (b) OS derivatives, (c) pentacarboxylate derivatives.

was seen. Only for the  $\text{CoI}_h$  mesophase of the  $n=18$  derivative was another peak at *c.* 7.3 Å, corresponding to the intracolumnar periodicity, observed.

## 4. Discussion

### 4.1. Crystalline phase

Both series show a lamellar Cr structure at room temperature, the interlamellar distance increasing linearly with  $n$ , as shown in figure 1. Both observations agree with the results already found for the pentacarboxylate analogues [3], a series of compounds with a closely related structure: the axial linear carboxylate is replaced here by either DOS or OS anions. In the pentacarboxylate series, the comparison of the experimental interlamellar spacing with the molecular length calculated (as  $5.27 \text{ \AA} + 1.26 \times 2(n-1) \text{ \AA}$  where  $5.27 \text{ \AA}$  is twice the distance between the centre of the dimer to the carboxylic C and  $1.26 \text{ \AA}$  is the typical  $\text{CH}_2\text{-CH}_2$  distance in an aliphatic chain) for the compounds with the aliphatic chains in an extended conformation, figure 1(a), leads to the conclusion that the aliphatic chains are tilted at *c.*  $17^\circ$  from the normal to the polymeric axis [3].

In the case of the DOS series, calculated values for the length of the extended molecules are 22.9, 25.4, 43.1 and 48.1 Å for the compounds with  $n=8, 9, 16$  and 18, respectively. At first sight, these values are quite similar to the obtained interlamellar distances, suggesting that each lamella contains just one polymeric strand. However, a more careful comparison, figure 1(a), shows that the experimental values are larger than those calculated for  $n=8$  and 9 (carboxylic chain length shorter than DOS) but shorter for  $n=14$  and 18 (carboxylic chain length larger than DOS). A possible explanation can be given to account for this discrepancy, based on an efficient way to fill the void space created by the chain length difference. The void space at the end of the shorter chain (carboxylic or DOS) is filled by the terminal  $\text{CH}_2$  and  $\text{CH}_3$  belonging to the longer chain (DOS or carboxylic) of an adjacent polymer (figure 2). This effect is superimposed on a tilt of the aliphatic moieties with respect to the perpendicular to the lamellae, which reduces the interlamellar distance as in the pentacarboxylate series. The XRD peak at 7.9 Å can be ascribed to an intracolumnar repeat distance, while the peak at 3.9 Å is approximately half that one, supporting the proposed model in which two adjacent chains are shifted by half of the intracolumnar stacking in order to allow interdigitation.

The Cr structure of one compound of the OS series,  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}$ , has been solved already (figure 3) [7]. The dimers are arranged in a plane almost normal to the lamellae (tilted by about  $20^\circ$ ). The

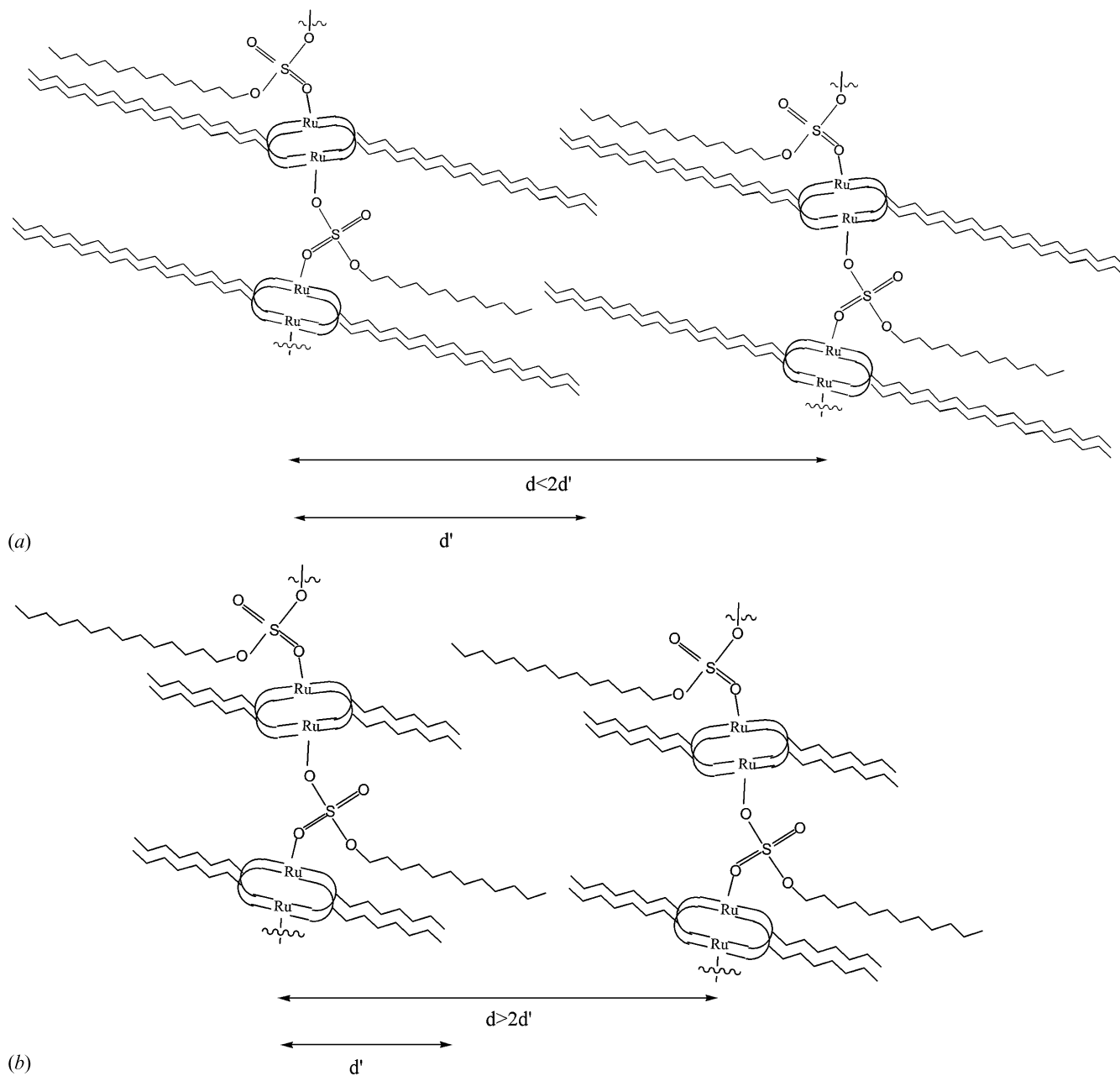


Figure 2. Proposed models for the supramolecular arrangement of the lamellar crystalline phases (illustrated for the DOS series): (a) interdigitation for compounds with equatorial alkyl chains longer than the axial one; (b) interdigitation when equatorial chains are shorter than the axial one.

interlamellar distance ( $c$ -axis of the unit cell) is 26.7 Å, in agreement with the value found on powdered samples (table 2). No appreciable interdigitation between adjacent lamellae was seen in this case. Considering the whole series, the interlamellar distance grows linearly with  $n$ , figure 1(c). This distance can be compared with the length of the totally extended molecule estimated, as previously, as 22.9, 28.0, 33.0, 38.1 and 48.1 Å for the compounds with  $n=8, 10, 12,$

14 and 18, respectively. These values are in all cases, except for the  $n=8$  homologue (when the equatorial and axial chain lengths are equal), a little larger than those measured. The same reasons as in the previous case can be given to explain these differences. Provided that the fifth aliphatic chain corresponding to the OS ligand, being shorter than the carboxylic chains, leaves empty space that might be filled by interpenetration of the aliphatic chains of the adjacent dimer, the

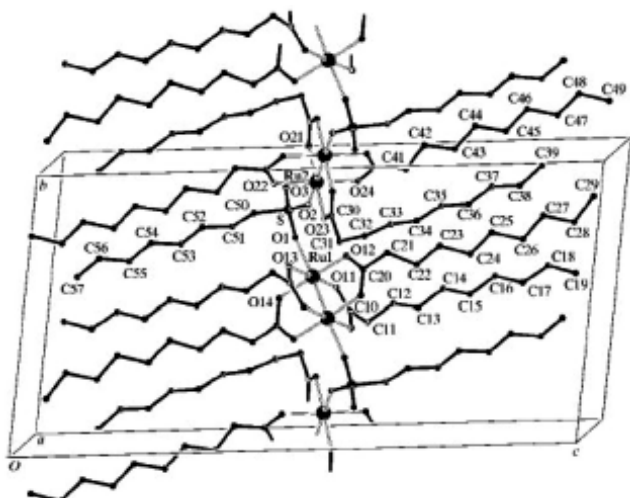


Figure 3. Unit cell present in the crystalline structure of the  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}$  compound (reproduced with permission from reference [7]), showing both the molecular structure, the supramolecular lamellar architecture, and the tilted  $\cdots\text{Ru}_2\cdots\text{OSO}\cdots\text{Ru}_2\cdots$  arrangements.

interlamellar distance decreases with respect to the calculated one, as seen in the Cr structure of the decanoate derivative and presumably also in the DOS and pentacarboxylate series. Additionally, partial disorder (e.g. *gauche* conformations) of the aliphatic moieties may account for this decrease.

#### 4.2. Liquid crystalline phase

The presence of a  $\text{Col}_h$  mesophase for both the  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{DOS}$  and  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{OS}$  series at high temperature is in agreement with the results already found for the  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_5$  analogues. However, some differences arise from the comparison of both series when considering the number of cation–anion chains inside each hexagonal cell. The  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{DOS}$  series will be considered first.

It is possible to estimate the molecular volume of one dimer by addition of the different molecular parts (even if the hypothesis of additive molar volumes should be used with some care in compounds where the rigidity of the central part renders difficult the filling of this space by mobile fluid parts of the molecules), as:

$$V_{\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{DOS}} = V_{\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}} + 4(n-10+1) \times V_{\text{CH}_2}$$

The value used for  $V_{\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}}$  (*c.*  $1600(50) \text{ \AA}^3$ ) is the one obtained from its Cr structure ( $1356.5(1) \text{ \AA}^3$  [7]), but corrected for the difference in temperature between  $-153^\circ\text{C}$  and  $150^\circ\text{C}$ ;  $V_{\text{CH}_2}$  was

estimated as the volume corresponding to totally disordered aliphatic chains in paraffinic compounds at the corresponding temperature ( $29.036 \text{ \AA}^3$  at  $150^\circ\text{C}$ ) [9]; and the difference between the volumes of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  groups was assumed to be negligible. The estimated volume for  $n=16$  is  $2420(100) \text{ \AA}^3$ . Considering the calculated surface per column (table 2) and assuming that the peak at  $7.1(2) \text{ \AA}$  corresponds to the intracolumnar periodicity (for the  $n=16$  analogue), the volume of the section of hexagonal cell is  $5460(250) \text{ \AA}^3$ . This means that each section of column contains 2.25 anion–cation units; in fact, considering that the compound probably has void space close to the rigid cores, the numbers of polymeric strands per column is *c.* 2.

The assignment of the XRD signal at  $7.1(2) \text{ \AA}$  as the interdimeric distance is consistent with a model in which the equatorial plane of the dimers is tilted, as observed for the Cr structure of  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}$  [7] and discussed already; in this case a distance of  $6.75(1) \text{ \AA}$  between neighbouring dimers was observed. A longer distance for the DOS derivatives suggests a larger  $\text{Ru}_{\text{dimer } 1}\text{–S–Ru}_{\text{dimer } 2}$  angle.

A new feature for these compounds is the presence of a  $\text{Col}_r$  phase for the  $n=18$  derivative below the hexagonal phase, stable from  $143$  to  $162^\circ\text{C}$ . Minor rearrangements in the mesophase are required for the transition between these phases and this agrees with the low associated enthalpy change ( $8 \text{ kJ mol}^{-1}$ , see table 2). The  $\text{Col}_r$  mesophase is probably a consequence of a slight tilt of the whole molecules with respect to the columnar axis or a different arrangement of the four aliphatic chains, e.g. arranged in pairs on opposite sides of the core.

For the  $\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{OS}$  series, no mesomorphic behaviour was seen for the  $n=8$  derivative, while for the long chain length derivatives ( $n=10, 12, 14$  and  $18$ ) a  $\text{Col}_h$  mesophase was observed. A similar analysis to that of the DOS derivatives can be made for this series to calculate the number of cation–anion units inside each cell. The molecular volume was estimated as:

$$V_{\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{OS}} = V_{\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_4\text{OS}} + 4(n-10) \times V_{\text{CH}_2}$$

The estimated volumes for  $n=12, 14$  and  $18$  are  $1800(100)$ ,  $2000(100)$  and  $2500(100) \text{ \AA}^3$ , respectively. Considering the calculated surface per column and assuming that the peak at  $7.3(2) \text{ \AA}$  corresponds to the intracolumnar periodicity, the volumes of the section of hexagonal cell are  $3310(140)$ ,  $3640(150)$ ,  $4560(200) \text{ \AA}^3$ , respectively. The value for the surface of the hexagonal cell of the  $n=10$  derivative is smaller than that expected compared to the other members of the series, and this

may be due to an increase in the intracolumnar stacking, but its corresponding volume was excluded in this comparison. This means that each column probably contains *c.* 2 cation–anion chains (the ratios between both values are 1.85, 1.82, 1.82).

The number of cation–anion chains inside each hexagonal cell for the pentacarboxylates was estimated as four [3]. The difference is probably related to the intracolumnar stacking mode of these three series: while the intracolumnar stacking in the latter series (4.3 or 8.8 Å) corresponds to linear ...Ru<sub>2</sub>...OCO...Ru<sub>2</sub>... chains parallel to the columnar axis, in the former series (OS or DOS) it corresponds to tilted ...Ru<sub>2</sub>...OSO...Ru<sub>2</sub>... arrangements.

### 5. Conclusions

As in a related series studied previously, both the DOS and OS long chain derivatives exhibited a Col<sub>h</sub> mesophase and, for the longest chain DOS derivative, an additional Col<sub>r</sub> phase. This appears to be a consequence of a delicate balance between the disorder provided by the ‘melted’ aliphatic chains and the order derived from the polymeric nature of these compounds. Even if this 1D arrangement of bimetallic centres of interesting electronic structure is promising, their limited thermal stability precludes any practical application.

Subtle differences in the supramolecular architecture of these compounds compared with the related Ru<sub>2</sub>(O<sub>2</sub>C(CH<sub>2</sub>)<sub>n-2</sub>CH<sub>3</sub>)<sub>5</sub> series, gave minor structural differences such as the intracolumnar stacking distance and the number of coordination polymeric strands contained in each column. An efficient filling of the

intermolecular space plays a key role in both the LC and Cr phases.

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