metal-organic compounds

A liquid crystal derived from ruthenium(II,III) and a long-chain carboxylate

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The title compound, *catena*-poly[[tetrakis(μ-decanoato-$\kappa^2 O$:O')-diruthenium(II,III)($Ru-Ru$)]-μ-octanesulfonato-$\kappa^2 O$:O'], [$Ru_2(C_{10}H_{19}O_2)_4(C_8H_{17}O_3S)$], is an octanesulfonate derivative of the mixed-valence complex diruthenium tetradecanoate. The equatorial carboxylate ligands are bidentate, bridging two Ru atoms to form a dinuclear structure. Each of the two independent dinuclear metal complexes in the asymmetric unit is located at an inversion centre. The octanesulfonate anion bridges the two dinuclear units through axial coordination. The alkyl chains of the carboxylate and sulfonate ligands are arranged in a parallel manner. The global structure can be seen as infinite chains of polar moieties separated by a double layer of non-polar alkyl groups, without interdigitation of the alkyl chains.

Comment

Mixed-valence diruthenium(II,III) tetracarboxylates, [Ru_2-(O_2CR)$_4X$] (X^- is an anion), have been extensively studied in recent years because they exhibit interesting electronic structures, spectroscopic features, magnetic behaviour and liquid crystalline (LC) properties (Aquino, 1998). In particular, LC phases (mesophases) have been obtained with long-chain carboxylates, provided that an appropriate combination of the equatorial carboxylate (RCO_2^-) and axial anion (X^-) is used (Cukiernik, Ibn-Elhaj *et al.*, 1998; Chaia *et al.*, 1999; Caplan *et al.*, 1999). For example, aliphatic equatorial carboxylates combined with long-chain axial anions, such as dodecylsulfate or an aliphatic carboxylate, induce mesomorphic behaviour (Cukiernik, Ibn-Elhaj *et al.*, 1998). In some of these cases, a model describing the structural changes taking place through the phase transition has been proposed.

As is usual in LC work, these models were based on the structural parameters of the LC phase (obtained from powder X-ray diffraction experiments), on information provided by local spectroscopic probes and on the crystalline structure of short-chain (non-mesogenic) analogues.

Of the more than 30 structures of mixed-valence diruthenium carboxylates that are known, the great majority deal with short-chain analogues (Bennett *et al.*, 1969; Bino *et al.*, 1979; Togano *et al.*, 1980; Cotton *et al.*, 1988; Barral *et al.*, 1997). The longest chain [$Ru_2(O_2CR)_4X$] compound for which the molecular structure is known is the non-mesogenic pentanoate derivative [$Ru_2\{O_2C(CH_2)_3CH_3\}_4Cl$] (Cukiernik, Luneau *et al.*, 1998). We have now determined the structure of the title ruthenium decanoate derivative with octanesulfonate as the axial anion, [$Ru_2\{O_2C(CH_2)_8CH_3\}_4\{O_3S(CH_2)_7CH_3\}$], (I). This compound is particularly interesting, as it undergoes a transition to a thermotropic hexagonal columnar LC phase at 458 K. We are confident that the crystal structure information we report here will be useful when interpreting the structure of the mesophase of the whole [$Ru_2\{O_2C(CH_2)_n$-$CH_3\}_4\{O_3S(CH_2)_7CH_3\}$] series of compounds, with n = 8–16.


(I)
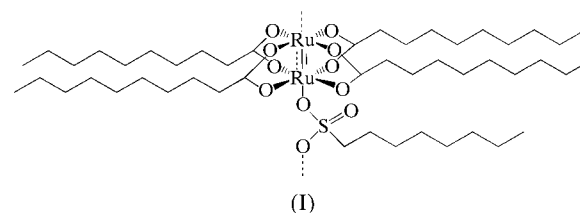
In compound (I), an $\{Ru_2\}^{5+}$ metallic centre is bridged by four carboxylate equatorial ligands; the axial positions are occupied by the octanesulfonate anion. The unit cell contains two independent dinuclear complexes, each located at a crystallographic inversion centre. The Ru atoms are in an environment of approximately C_{4v} symmetry, while the dinuclear structure exhibits approximate D_{4h} symmetry.

The Ru—O equatorial bond distances are in the range 2.019 (3)–2.034 (3) Å. The average O—C—O bond angle of the carboxylate ligands is 123.1 (3)°, and the $O_i-Ru_j-Ru'_j$ angles (i = 11, 12, 13, 14, 21, 22, 23 or 24, and j = 1 or 2) are nearly 90°. Thus, the pseudo-octahedral environment of the Ru atoms is not significantly distorted, indicating that the dinuclear structure is achieved with little stress around the metal centres.

The Ru—Ru' distance is 2.271 (3) Å (averaged for the two independent dinuclear units), a typical value for mixed-valence diruthenium carboxylates axially coordinated by O atoms (Aquino, 1998). Four alkyl chains from carboxylate ligands are oriented towards the periphery of the polar centre in a zigzag conformation; two are completely extended, while the others rotate around the β-C atom (C12 and C32) in order to align with the former chains. The alkyl chain of the sulfonate ligand also aligns in an extended conformation parallel to the carboxylic acid alkyl chains.

The alkylsulfonate moiety acts as a bidentate ligand bridging two independent dinuclear units (Fig. 1). The three S—O distances are consistent with double bonds, although the S—
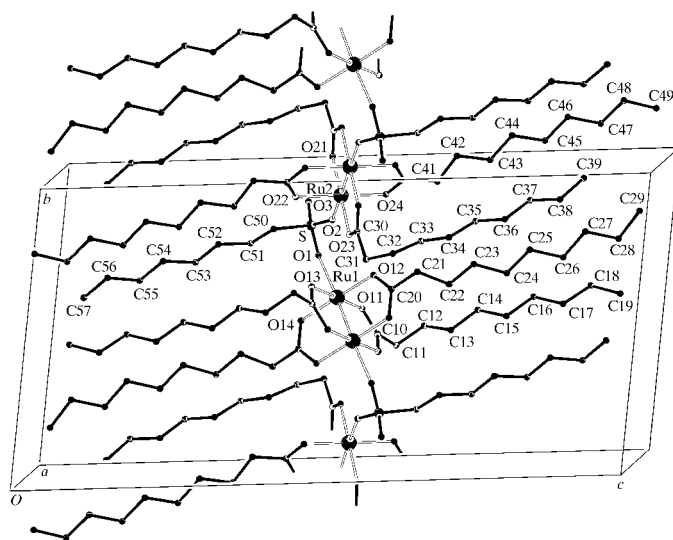
Figure 1
The crystal packing of (I) viewed down the *a* axis, showing the non-H atom labelling. Only the most populated (61% occupancy) of the two conformations of the C1*n* chain is shown for clarity.

O3 bond is significantly shorter than the other two. This can be ascribed to a slight softening of the S—O bonds involved in coordination to the Ru centres (S—O1 and S—O2), arising from π back-donation.

Due to the bridging nature of the octanesulfonate axial anion, the bimetallic centres polymerize in an infinite chain nearly parallel to the *b* axis. An intermolecular distance along the polymeric structure of 6.76 (1) Å can be calculated, being the distance between two neighbouring dinuclear centres. The corresponding Ru—Ru axes are nearly perpendicular to each other [91.94 (4)°]. However, all the aliphatic chains (both carboxylic and sulfonic) of each such polymeric structure are parallel, without interdigitation.

In the global structure, polar chains composed of dinuclear centres and sulfonate axial ligands are separated by non-polar double layers of alkyl chains. An interlayer separation of 26.623 (3) Å can be inferred from the distance between adjacent *ab* faces. There is no interdigitation between adjacent layers.

Experimental

[Ru₂{O₂C(CH₂)₈CH₃}₄Cl] was synthesized following a method already reported for other homologues of this series (Cukiernik, Ibn-Elhaj *et al.*, 1998). Compound (I) was obtained by a metathesis reaction. A methanol suspension of [Ag{O₃S(CH₂)₇CH₃}] (150 mg) was added slowly to [Ru₂{O₂C(CH₂)₈CH₃}₄Cl] (418 mg) dissolved in methanol. The reaction was protected from light and refluxed for 3 h under nitrogen. The AgCl by-product was filtered off while still hot and the solvent was evaporated under vacuum. The pale-brown solid obtained was dissolved in CH₂Cl₂, the solution was filtered on a 0.2 µm porous membrane and, after addition of heptane, the CH₂Cl₂ was evaporated under vacuum. After a couple of hours, a pale-brown solid was filtered off, and then washed by suspension in ethylic ether and distilled water. Brown crystals of (I) were obtained by slow

Crystal data

[Ru₂(C₁₀H₁₉O₂)₄(C₈H₁₇O₃S)]	$Z = 2$
$M_r = 1080.43$	$D_x = 1.321$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.0020$ (1) Å	Cell parameters from 8725
$b = 13.3040$ (4) Å	reflections
$c = 26.7230$ (6) Å	$\theta = 1.0$–27.5°
$\alpha = 83.427$ (2)°	$\mu = 0.65$ mm^{-1}
$\beta = 85.045$ (1)°	$T = 120$ (2) K
$\gamma = 74.051$ (1)°	Thin plate, red
$V = 2712.9$ (1) Å³	$0.40 \times 0.18 \times 0.06$ mm

Table 1
Selected geometric parameters (Å, °).

Ru1—O12	2.023 (3)	Ru2—O23	2.035 (3)
Ru1—O14	2.028 (3)	Ru2—O22	2.034 (3)
Ru1—O13	2.020 (3)	Ru2—O2	2.233 (3)
Ru1—O11	2.029 (3)	Ru2—Ru2ⁱⁱ	2.2732 (6)
Ru1—O1	2.228 (3)	O21—C30ⁱⁱ	1.278 (5)
Ru1—Ru1ⁱ	2.2680 (6)	O22—C40ⁱⁱ	1.275 (5)
O11—C10	1.284 (5)	O23—C30	1.282 (5)
C10—O13ⁱ	1.265 (5)	C30—O21ⁱⁱ	1.278 (5)
C10—C11	1.504 (8)	C30—C31	1.491 (6)
C10—C11′	1.505 (9)	C40—O22ⁱⁱ	1.275 (5)
O12—C20	1.262 (5)	C40—C41	1.486 (5)
C20—O14ⁱ	1.275 (5)	S—O3	1.430 (4)
C20—C21	1.502 (5)	S—O1	1.467 (3)
O13—C10ⁱ	1.265 (5)	S—O2	1.471 (3)
O14—C20ⁱ	1.275 (5)	S—C50	1.785 (5)
Ru2—O24	2.019 (3)	C50—C51	1.507 (6)
Ru2—O21	2.021 (3)	C51—C52	1.519 (6)
O12—Ru1—O14	178.8 (1)	O24—Ru2—O22	178.6 (1)
O12—Ru1—O13	90.8 (1)	O21—Ru2—O22	88.7 (1)
O14—Ru1—O13	89.9 (1)	O23—Ru2—O22	91.4 (1)
O12—Ru1—O11	89.8 (1)	O24—Ru2—O2	89.3 (1)
O14—Ru1—O11	89.5 (1)	O21—Ru2—O2	85.5 (1)
O13—Ru1—O11	179.0 (1)	O23—Ru2—O2	95.2 (1)
O12—Ru1—O1	93.1 (1)	O22—Ru2—O2	91.9 (1)
O14—Ru1—O1	87.8 (1)	O24—Ru2—Ru2ⁱⁱ	89.59 (8)
O13—Ru1—O1	87.7 (1)	O21—Ru2—Ru2ⁱⁱ	89.01 (8)
O11—Ru1—O1	93.1 (1)	O23—Ru2—Ru2ⁱⁱ	90.28 (8)
O12—Ru1—Ru1ⁱ	89.10 (8)	O22—Ru2—Ru2ⁱⁱ	89.36 (8)
O14—Ru1—Ru1ⁱ	90.00 (8)	O2—Ru2—Ru2ⁱⁱ	174.33 (9)
O13—Ru1—Ru1ⁱ	89.38 (9)	C30ⁱⁱ—O21—Ru2	119.9 (3)
O11—Ru1—Ru1ⁱ	89.83 (9)	C40ⁱⁱ—O22—Ru2	118.7 (3)
O1—Ru1—Ru1ⁱ	176.36 (7)	C30—O23—Ru2	117.9 (2)
C10—O11—Ru1	118.2 (2)	O21ⁱⁱ—C30—O23	122.9 (4)
O13ⁱ—C10—O11	123.0 (3)	O21ⁱⁱ—C30—C31	117.7 (4)
O13ⁱ—C10—C11	114.4 (8)	C40—O24—Ru2	119.3 (3)
O11—C10—C11	122.5 (8)	O22ⁱⁱ—C40—O24	123.0 (4)
O13ⁱ—C10—C11′	127 (1)	O22ⁱⁱ—C40—C41	119.0 (4)
O11—C10—C11′	110 (1)	O24—C40—C41	117.9 (4)
C20—O12—Ru1	119.3 (2)	O3—S—O1	112.5 (2)
O12—C20—O14ⁱ	123.6 (4)	O3—S—O2	116.4 (2)
O12—C20—C21	118.6 (4)	O1—S—O2	108.32 (18)
O14ⁱ—C20—C21	117.8 (4)	O3—S—C50	105.8 (3)
C10ⁱ—O13—Ru1	119.5 (3)	O1—S—C50	106.7 (2)
C20ⁱ—O14—Ru1	117.9 (3)	O2—S—C50	106.5 (2)
O24—Ru2—O21	92.3 (1)	S—O1—Ru1	129.6 (2)
O24—Ru2—O23	87.6 (1)	S—O2—Ru2	147.4 (2)
O21—Ru2—O23	179.3 (1)	C51—C50—S	113.8 (4)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$.

metal-organic compounds

Data collection

Nonius KappaCCD area-detector diffractometer	11 539 independent reflections
	8728 reflections with $I > 2\sigma(I)$
CCD scans	$R_{int} = 0.084$
Absorption correction: numerical (Spek, 1990)	$\theta_{max} = 27.5°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.782$, $T_{max} = 0.965$	$k = -17 \rightarrow 17$
31 736 measured reflections	$l = -34 \rightarrow 30$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0748P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 2.5168P]$
$wR(F^2) = 0.155$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.124$
11 539 reflections	$\Delta\rho_{max} = 1.04$ e Å^{-3}
647 parameters	$\Delta\rho_{min} = -1.67$ e Å^{-3}
H-atom parameters constrained	

The C11–C19 carboxylate chain is disordered. During the refinement, the corresponding occupancies were allowed to vary so as to sum to 1.0 and the C—C bond distances were restrained to a target value of 1.51 (1) Å. Several H atoms were located in a Fourier difference map. However, they were positioned stereochemically and refined with a riding model. The methyl H atoms were treated in the refinement as rigid bodies and allowed to rotate around the corresponding C—C bond so as to maximize the sum of the observed electron density at the three calculated H-atom positions. As expected, all methyl groups converged to staggered conformations.

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1217). Services for accessing these data are described at the back of the journal.

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