

# STRUCTURAL QUESTIONS ON CRYSTALLINE, COLUMNAR AND CUBIC PHASES OF MESOGENIC BIMETALLIC CARBOXYLATES ANSWERED BY SINGLE-CRYSTAL CRYSTALLOGRAPHY

María Ana Castro<sup>1</sup>, Marcia Rusjan<sup>1</sup>, Ricardo Baggio<sup>2</sup>, Daniel Vega<sup>2</sup>, Oscar Piro<sup>3</sup>, Andrés Zelcer<sup>1</sup>, Zulema D. Chaia<sup>1</sup>, Rosana Gómez<sup>4</sup>, Augusto Fagnola<sup>4</sup>, María de los Angeles Persello<sup>4</sup>, Benoît Heinrich,<sup>5</sup> Bertrand Donnio<sup>5</sup>, Daniel Guillon<sup>5</sup>, Fabio.D. Cukiernik<sup>4,1</sup>

- 1) INQUIMAE – Dto. Qca. Inorgánica, Analítica y Qca. Física – Facultad Cs. Exactas y Naturales – Univ. Buenos Aires – Pab. II – Cdad. Universitaria (C1428EHA) Núñez, Capital Federal, Argentina. // 2) Dto. Física – Comisión Nacional de Energía Atómica - Av. Gral. Paz 1499 (1650) San Martín, Prov. Buenos Aires, Argentina. // 3) IFLP & Dto. Física – Facultad Cs. Exactas – Univ. Nac. La Plata CC67 (1900) La Plata, Prov. Buenos Aires, Argentina. // 4) Instituto de Ciencias - Univ. Nac. Gral. Sarmiento – J. M. Gutiérrez 1150 (B1613GSX) Los Polvorines, Prov. Buenos Aires, Argentina. // 5) Inst Physique et Chimie des Matériaux de Strasbourg – Groupe des Matériaux Organiques – CNRS-Univ. Louis Pasteur (UMR 7504) – 23, rue du Loess, 67034, BP43, Strasbourg Cedex 2, France.

Single crystal crystallography of mesogens or related non-mesogenic analogues have been used in the past in order to provide structural information useful for suggesting suitable models of molecular structure and intermolecular organization in the mesophase [1]. These studies allowed to know molecular lengths (correlated to characteristic distances in N, S or Col mesophases [2]), molecular conformations or intermolecular interactions (monomeric vs dimeric alternatives, aggregation behavior [3]), interatomic distances and angles (used sometimes as reference for EXAFS studies [4]), etc. We report herein three recent crystallographic studies we performed on bimetallic carboxylates, and explain the way these results have help us to understand some structural features of such mesogenic compounds, either by validating the models previously suggested or by showing completely different pictures.

Case 1) Coordination polymers based on diruthenium tri(alkoxy)benzoates of general formula  $[\text{Ru}_2(3,4,5\text{-}(\text{C}_n\text{H}_{2n+1}\text{O})_3\text{C}_6\text{H}_2\text{CO}_2)_4\text{Cl}]_x$  exhibit  $\text{Col}_H$  mesophases even below room temperature [5,6]. We proposed a model [6-8], depicted in figure 1a, aimed to describe the supramolecular organization in the mesophase based on information coming from both local probes (RR, SQUID, EXAFS, IR) and “macro-structural” determinations (XRD, dilatometry). One of its central aspects is the “zig-zag” conformation of the polymeric “ $\text{Ru}_2\text{-Cl-Ru}_2\text{-Cl}$ ” strands, with a Ru-Cl-Ru angle estimated as  $112 - 120^\circ$ . We succeeded now to crystallize and solve the structure of the  $n = 2$  homologue (non mesogenic); it confirms (figure 1b) the zig-zag nature of the polymeric strands, and exhibits a Ru-Cl-Ru angle of  $116^\circ$ .

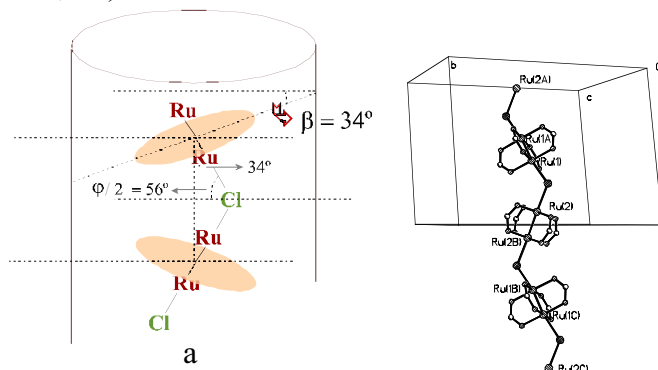
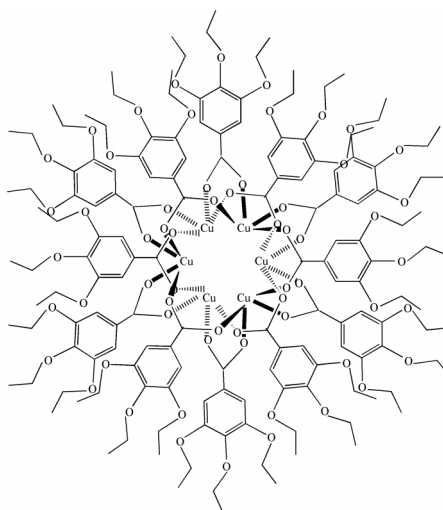


Figure 1 b

Case 2) Compounds of general formula  $[\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_3)_4\text{Y}]_x$  ( $\text{Y}^-$  = long chain axial anion: octylsulfonate, dodecylsulfate or aliphatic carboxylate) exhibit lamellar crystalline phases [9] where the bimetallic centers are separated by two layers of aliphatic chains. Interlamellar distances, as measured by powder XRD experiments, suggest some degree of interpenetration of these two layers for all the cases in which the lengths of equatorial carboxylates and axial anions differ, and no interpenetration when their lengths are similar. The crystalline structure of a mid-chain derivative confirmed this hypothesis.

Case 3) Long-chain copper tri(alkoxy)benzoates exhibited columnar or cubic mesophases, depending upon the aliphatic chain length (and thermal history!) [5,6]. Some controversies took place in the past about the micellar or bicontinuous nature of the cubic phase. The model we suggested a few years ago [6], based on some magnetic and EXAFS evidences, involved the formation of mononuclear species, geometrically similar to the well known phasmids. However, the crystalline structure of the non-mesogenic  $n = 2$  homolog (figure 2) revealed the presence of completely unexpected hexameric units of formula  $[\text{Cu}_6(\text{O}_2\text{CC}_6\text{H}_2(\text{OC}_2\text{H}_5)_3)_{12}]$  and globular geometry, supporting a micellar model for the cubic mesophases of long chain derivatives.



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