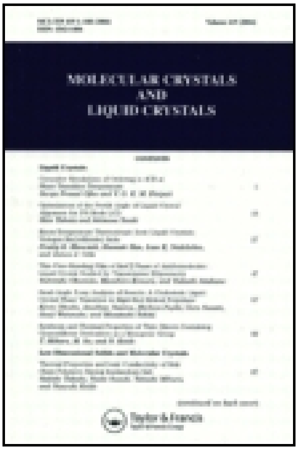

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Structural Characterization of the Mesophases Exhibited by Dicopper and Diruthenium Trialkyloxybenzoates

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Structural Characterization of the Mesophases Exhibited by Dicopper and Diruthenium Trialkyloxybenzoates

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Binuclear Copper and Ruthenium complexes derived from long-chain 3,4,5-tiralkyloxybenzoates (noted as B3OCn), namely $Ru_2(B3OCn)_4Cl$ and $Cu_2(B3OCn)_4$ with n = 10, 12, 14, 16 and 18, were synthesized. The structure of their mesophases was characterized by X-ray diffraction. Both series exhibit low-temperature liquid crystalline phases and, in particular, room temperature mesophases for the lower homologues of the ruthenium series. The mesophases exhibited by $Ru_2(B3OCn)_4Cl$ were found to be hexagonal columnar (Col_H) in nature, whereas the structure of the mesophases of the copper derivatives depends on the aliphatic chain length, being Col_H for n = 10, 12, 14 and cubic for the longer homologues.

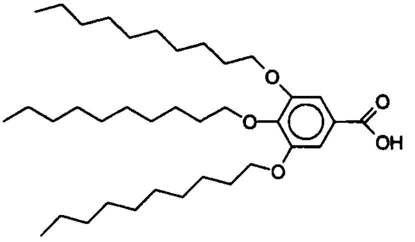
Keywords: metallomesogens; ruthenium carboxylates; room temperature liquid crystals; copper carboxylates; cubic mesophases; hexagonal columnar mesophases

INTRODUCTION

In previous studies, it was shown that the crystal (K) to liquid crystal (LC) transition temperatures of mixed-valent diruthenium tetracarboxylates, $Ru_2(RCO_2)_4Cl$ can be lowered using combinations of equatorial carboxylates

RCO_2^- and axial anions X^- that ensure an appropriate filling of the intermolecular space.[1],[2] For example, the use of 3,4-dialkyloxybenzoates (B2OCn) allowed to obtain mesogenic $Ru_2(B2OCn)_4Cl$ compounds ($T_{K \rightarrow LC} \cong$ 150°C) in contrast to the non-mesogenic $Ru_2(RCO_2)_4Cl$ analogues, where R is a linear and saturated aliphatic chain. A further improvement was achieved with the synthesis of $Ru_2(B3OCn)_4Cl$ which revealed to exhibit a stable enantiotropic mesophase from 42 to 240°C.[3] In that work, it was also suggested that the use of this kind of equatorial ligands would be helpful in promoting the appearance of liquid crystalline phases in some polymeric systems. Indeed, divalent carboxylates polymerized by axial binding of pyrazine (pz), $M_2(RCO_2)_4pz$ (M = Cu or Ru) did not exhibit thermotropic behavior when R was a linear aliphatic chain.[4]

In order to get a deeper insight into the advantages of using bulky equatorial carboxylates, two different series of bimetallic compounds derived from 3,4,5-trialkyloxybenzoates (B3OCn) were synthesized, namely the $Ru_2(B3OCn)_4Cl$ and $Cu_2(B3OCn)_4$ series. The first one was studied in order to test the validity of the strategy and to obtain low transition temperature metallomesogens. The second one was studied as a starting point, in order to compare, in a second step, their mesomorphic behavior with that of the polymeric pyrazine derivatives.



B3OCn

n = 10, 12, 14, 16, 18

EXPERIMENTAL

Measurements:

A Leitz DMRX Microscope equipped with a polarizing optics and a Leitz 1350 heating stage was used for optical microscopy (OM) studies. Thermodynamic values of the phase transitions were measured with a Shimadzu DSC-50 calorimeter. X-ray diffraction experiments were carried out on powder samples in Lindemann capillaries. Diffraction patterns were recorded either photographically or using an INEL CPS-120 curved positionsensitive detector, with a radiation from an INEL X-ray generator. Also photographic detection was performed using a Guinier focusing camera equipped with a bent quartz monochromator (Cu Kα_1 radiation).

Synthesis:

$Ru_2(B3OCn)_4Cl$ and $Cu_2(B3OCn)_4$: Two starting materials, namely $Ru_2(CH_3(CH_2)_2COO)_4Cl$ and $Cu_2(CH_3COO)_4$ were used to obtain the studied compounds. The chemical route is based on the substitution of the acetate or butyrate ligand by the appropriate trialkyloxybenzoic acid derivative. This was achieved by slow addition of the starting compound into a stirred solution of B3OCn in an appropriate solvent. The products were purified by recrystallization and characterized by infrared spectroscopy and elemental analysis. Details on the synthetic procedures will be given elsewhere.[5]

RESULTS AND DISCUSSION

Ruthenium Compounds

The X-ray diffraction studies performed as a function of temperature on the ruthenium $Ru_2(B3OCn)_4Cl$ compounds confirmed the mesomorphic behavior found by DSC and OM studies,[5] and lead to the determination of the structural parameters of the LC phases detected.

The five compounds present similar diffraction patterns above 60°C with sharp peaks in the respective ratio: 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{9}$, $\sqrt{12}$, $\sqrt{13}$. Figure 1 shows a typical diffraction pattern obtained at 90°C for $Ru_2(B3OC18)_4Cl$. Such a series of reflections is typical of a well developed two-dimensional hexagonal lattice of a columnar mesophase. The corresponding values of the parameters of the hexagonal phases are listed in Table I.

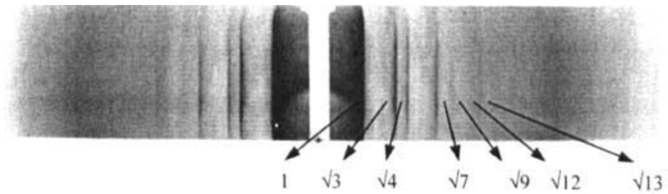


FIGURE 1. X-ray diffraction pattern registered at 90°C obtained with $Ru_2(B3OC18)_4Cl$.

TABLE I. Hexagonal lattice parameter *a* (Å) at 90°C for the compounds of the series $Ru_2(B3OCn)_4Cl$, and corresponding area, *S* (Å^2), of the hexagonal unit cell area.

n	a	S
10	26.8	622
12	29.5	754
14	32.0	887
18	35.7	1104

In the wide angle region of the diffraction pattern, a diffuse band is observed at about 4.5 Å corresponding to the usual intermolecular distance between the disorganized alkyl chains. More interestingly, another diffuse but less broad signal at about 6.1 Å is present in all the patterns. This signal can be tentatively assigned to a repeating distance between the dimers: Ru=Ru-Cl-. For fully extended polymeric linear chain, the sum of the Ru-Ru and Ru-Cl typical distances would lead to an intracolumnar periodicity of 7.3-7.4 Å.[6] The smaller value found in the present work can be due to a smaller Ru-Cl-Ru angle which can be estimated to be about 120°. Typical values range from 180° to 118°, the latter being detected in $Ru_2(O_2CC_6H_4\text{-}pOCH_3)_4Cl$,[7] a compound closely related to those studied here.

It is interesting to remark that S varies linearly with the length of the peripheral chains (Figure 2).

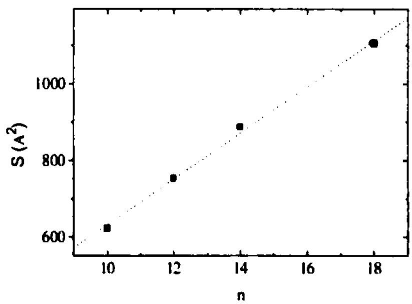


FIGURE 2. Variation of the unit cell area, S, with the number of carbon atoms in peripheral chains, in the hexagonal mesophase of $Ru_2(B3OCn)_4Cl$.

The slope of this linear variation leads to a value of the periodicity along the columnar axis of about 5.7 Å (indeed, h can be obtained through the expression : $h = 12 \times V_{CH2} / (dS/dn)$, where V_{CH2} is the volume of one methylene group taken as 28.3 Å^3 at 90°C[8]). This value is in a reasonable agreement with that of 6.1 Å directly measured on the X-ray patterns, and confirms that the Ru-Cl-Ru angle should be near 120° between two neighboring Ru binuclear complexes.

The temperature range of stability of the mesophase for each compound of the series $Ru_2(B3OCn)_4Cl$, as determined by DSC, Optical Microscopy and X-ray diffraction can then be summarized as follows. The n = 10 and 12 derivatives exhibit a columnar hexagonal mesophase at room temperature, whereas the n = 14, 16 an 18 derivatives show a transition from a crystalline phase to a columnar hexagonal mesophase at 26, 43 and 58°C respectively. For all of them the mesophase is stable up to 220-270°C, when decomposition takes place.

Copper Compounds

The copper series exhibit a different behavior with the presence of two distinct mesophases as the length of the side chains increases. The high temperature patterns for the compounds in which n = 10, 12, 14 are characteristic of a hexagonal columnar mesophase as can be seen for n = 12 in Figure 3; ten peaks corresponding with a two-dimensional hexagonal arrangement of columns were found in this case. Despite the large number of reflections contained in the small angle region, the structure presents only a two-dimensional long range correlation, as unambiguously shown by the presence of one unique diffuse band at about 4.5 Å in the wide angle region.

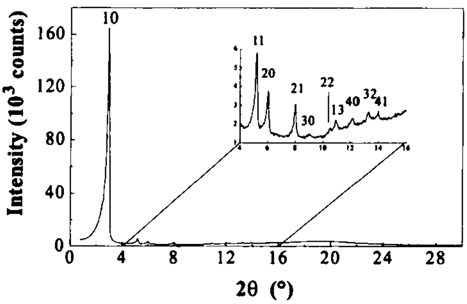


FIGURE 3. X-ray diffraction pattern registered at 120°C for $Cu_2(B3OC12)_4$.

For the last two members of the series (n = 16, 18), the diffraction peaks are in the ratio: $1:\sqrt{2}:\sqrt{3}:\sqrt{4}:\sqrt{5}:\sqrt{6}:\sqrt{7}:\sqrt{8}$, which apparently can only be consistent with a body centered cubic structure (the cubic nature of the mesomorphic phase is confirmed by the isotropic texture observed by polarized microscopy). It was not possible on the only basis of the powder X-ray diffraction data to distinguish between the following possible space groups: I23, $I2_13$, Im3, Ia3, I432, I43m, Im3m. An example of a pattern obtained for this cubic phase is shown in Figure 4, for the n=16 derivative.

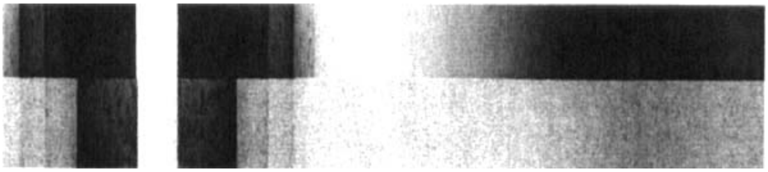


FIGURE 4. X-ray diffraction pattern registered at 90°C for $Cu_2(B3OC16)_4$ in the cubic phase.

The values of the structural parameters thus determined are summarized in the following table:

TABLE II. Structural parameters of the compounds of the series $Cu_2(B3OCn)_4$ at 85°C: ***a*** is the intercolumnar distance for n = 10, 12 and 14 and the cubic cell parameter for n = 16 and 18; V_m is the molecular volume; ***S*** is the hexagonal unit cell area; ***h*** is the periodicity along the columnar axis; V_c is the volume of the cubic cell and N_c is the number of molecules in the cubic cell. **K**, **LC** and **I** stand for crystal, liquid crystal and isotropic respectively.

n	K-LC (°C)	LC-I (°C)	Phase	a (Å)	V_m ($Å^3$)	S ($Å^2$)	h (Å)	V_c ($Å^3$)	N_c
10	75	131	Col_{hex}	30.9	4399	826	5.3		
12	80	130	Col_{hex}	33.2	5077	955	5.3		
14	80	130	Col_{hex}	35.4	5756	1084	5.3		
16	85	112	Cubic	39.8	6435			63 044	9.8
18	85	113	Cubic	42.1	7113			74 610	10.5

The partial molecular volume of the columnar core, V_0, corresponding mainly to the polar heads of the carboxylates, has been calculated from the data of the literature [9]. V_m is then obtained by adding to V_0 the volume of the adequate number of methylene groups for each derivative, $V_{CH2} \cong 28.3$ $Å^3$ at

85°C. Knowing the hexagonal parameter, it is then possible to deduce S and h in the hexagonal mesophase; knowing the cubic parameter, it is straight forward to deduce V_c and N_c.

It is worth to point out that the value of h found in the columnar mesophase (5.2-5.4 Å) is significantly larger than that found in the same mesophase with linear copper(II) carboxylates (4.6Å) [9]. This suggests a tilt of the polar binuclear complex cores of about 30° with respect to the columnar axis.

As for the cubic phase, it is interesting to note that, among all the space groups possible from the experimental data, the Im3m space group has been previously found in some lyotropic and thermotropic liquid crystals phases,[10, 11] the corresponding cubic phase being located between a lamellar and a columnar mesophase. More recently, a micellar cubic phase of symmetry Im3m has been found to appears besides a hexagonal mesophase in a water surfactant system [12]. The transition from the columnar to the cubic phase has been proposed to occur through peristaltic undulations of the columnar cores. Such a mechanism could be in agreement with our results, as such undulations are equivalent to a tilt of the elementary units with respect to the columnar axis. Since, other micellar cubic phases have been found in amphiphilic polyhydroxy derivatives.[13] In the case of the present study, more work is needed to understand, from the molecular point of view, how the binuclear molecules are ordered in a supramolecular structure giving a cubic phase, with the possible existence of some micellar arrangement.

CONCLUSION

The structural characterization of the mesophases exhibited by the compounds of the series $Ru_2(B3OCn)_4Cl$ confirms the occurrence of a columnar hexagonal arrangement. Particularly interesting is the fact that the two first members of this series (n = 10, 12) present a room temperature mesophase, which could be potentially useful from the point of view of future applications of these compounds.

The copper compounds exhibit two different structures depending upon the length of the aliphatic peripheral chains. Columnar hexagonal mesophases were observed for the short chain members of the series (as it was typically found for a large number of other copper carboxylates derivatives studied so far[14]). But a body centered cubic mesophase was determined for the long chain ones. The space group of these cubic phases cannot still be completely ascertained with the experiments reported in this paper, and a more complete characterization is now underway. On the other hand, the fact that two different structures are present in the same series of compounds let us presume that there should be some correlation (epitaxial relationships) between both structures waiting for more investigations.

Acknowledgments

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References

[1] F.D. Cukiernik, M. Ibn-Elhaj, P. Maldivi, A.M. Giroud-Godquin, J.C. Marchon, A. Skoulios, *Liq. Cryst.*, **9**, 903 (1991).

[2] F.D. Cukiernik, M. Ibn-Elhaj, Z.D. Chaia, J.-C. Marchon, A.-M. Giroud-Godquin, D. Guillon, A. Skoulios, P. Maldivi, *Chem. Mater.*, **10**, 83–91 (1998).

[3] Zulema D. Chaia, Fabio D. Cukiernik, *Fifth International Symposium on Metallomesogens,* Neuchâtel, 1997. (Oral communication).

[4] L. Bonnet, F.D. Cukiernik, A.M. Giroud-Godquin, J.C. Marchon, M. Ibn-Elhaj, D. Guillon, A. Skoulios, *Chem. Mater.*, **6**, 31 (1994). G.S. Attard, P.R. Cullum, *Liq. Cryst.*, **8**, 299 (1990).

[5] Z. Chaia, B. Heinrch, D. Guillon, O. Poizat, F.D. Cukiernik, *manuscript in preparation.*

[6] For a collection of structural parameters see: a) F.D. Cukiernik, *PhD Thesis,* University of Grenoble (1993) b) M. A. S. Aquino, *Coord. Chem. Rev.*, **170**, 141 (1998).

[7] B.K. Das, A.R. Chakravarty, *Polyhedron,* **10**, 491 (1991).

[8] D. Guillon, A. Skoulios, J. J. Benattar, *J. Physique,* **47**, 133 (1986).

[9] H. Abied, D. Guillon, A. Skoulios, H. Dexpert, A.M. Giroud-Godquin, J.C. Marchon, *J. de Physique* **49**, 345 (1988); M. Ibn-Elhaj, D. Guillon, A. Skoulios, A.M. Giroud-Godquin, P. Maldivi, *Liq. Cryst.* **11**, 731 (1992).

[10] V. Luzzati, P. Mariani, T. Gulik-Krzywicki, "Physics of amphiphilic layers", Les Houches 1987 (Springer Verlag, Berlin).

[11] Y. Hendrikx, B. Pansu, *J. Phys. II Fr.*, **6**, 33 (1996).

[12] P. Sakya, J.M. Saddon, R.H. Templer, R.J. Mirkin, G.J.T. Tiddy, *Langmuir* **13**, 3706 (1997).

[13] K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *J. Mat. Chem.* **8**, 529 (1998).

[14] H. Abied, D. Guillon, A. Skoulios, P. Weber, A.M. Giroud-Godquin, J.C. Marchon, *Liq Cryst.* **2**, 269 (1987).