BIMETALLIC LIQUID CRYSTALLINE FUNCTIONAL MATERIALS

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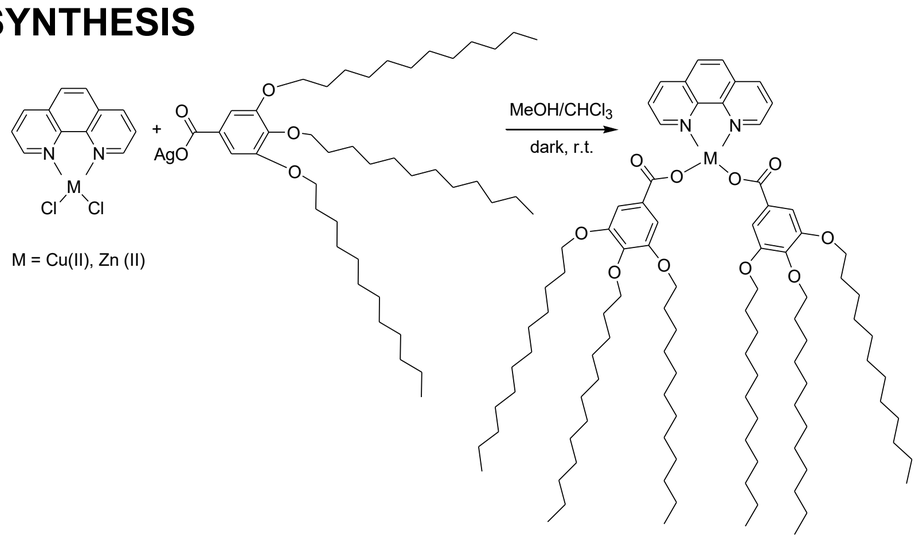
INTRODUCTION

The continued extension of liquid crystal science to additional technologies requires new types of mesomorphic materials that integrate novel structural elements and physical properties [1] due to their applications in sensing, used as backlighting in displays, security inks and so on.[2]
1,10-phenantroline has been extensively used as a metal chelating ligand due to its robust redox stability and ease of coordination with *d*-block metals while lipophilic benzoate was showed to be an excellent monodentate ligand able to induce liquid crystallinity into metal complexes, avoiding several steps required to functionalize the main ligands [2].
On this background, herein we present the synthesis of new heteroleptic liquid crystalline coordination complexes of Cu(II) and Zn(II) metal centre.

SYNTHESIS



CHARACTERISATION

Structural analysis and purity of the Zn(II) and Cu(II) complexes were carried out using:
- Atomic absorption spectroscopy (AAS);
- Fourier-transform infrared spectroscopy (FT-IR);
- Nuclear magnetic resonance spectroscopy (NMR) (^{1}H NMR for the Zn-complex).

Mesomorphic properties were determined by
- Polarized opical microscopy (POM);
- Differential Scanning Calorimetry (DSC).

Their similar structural features suggested the idea of obtaining bimetallic liquid crystalline systems by combining them in different molecular ratio. Three systems (Am $1_{Zn}/1_{Cu}$, Am $3_{Zn}/1_{Cu}$ and Am $1_{Zn}/3_{Cu}$) were obtained by mixing the components dissolved in CH_2Cl_2. The solutions obtained were sonicated 20 minutes and then evaporated at room temperature. The mesomorphic properties of the new materials were investigated by POM and DSC.

RESULTS

DSC

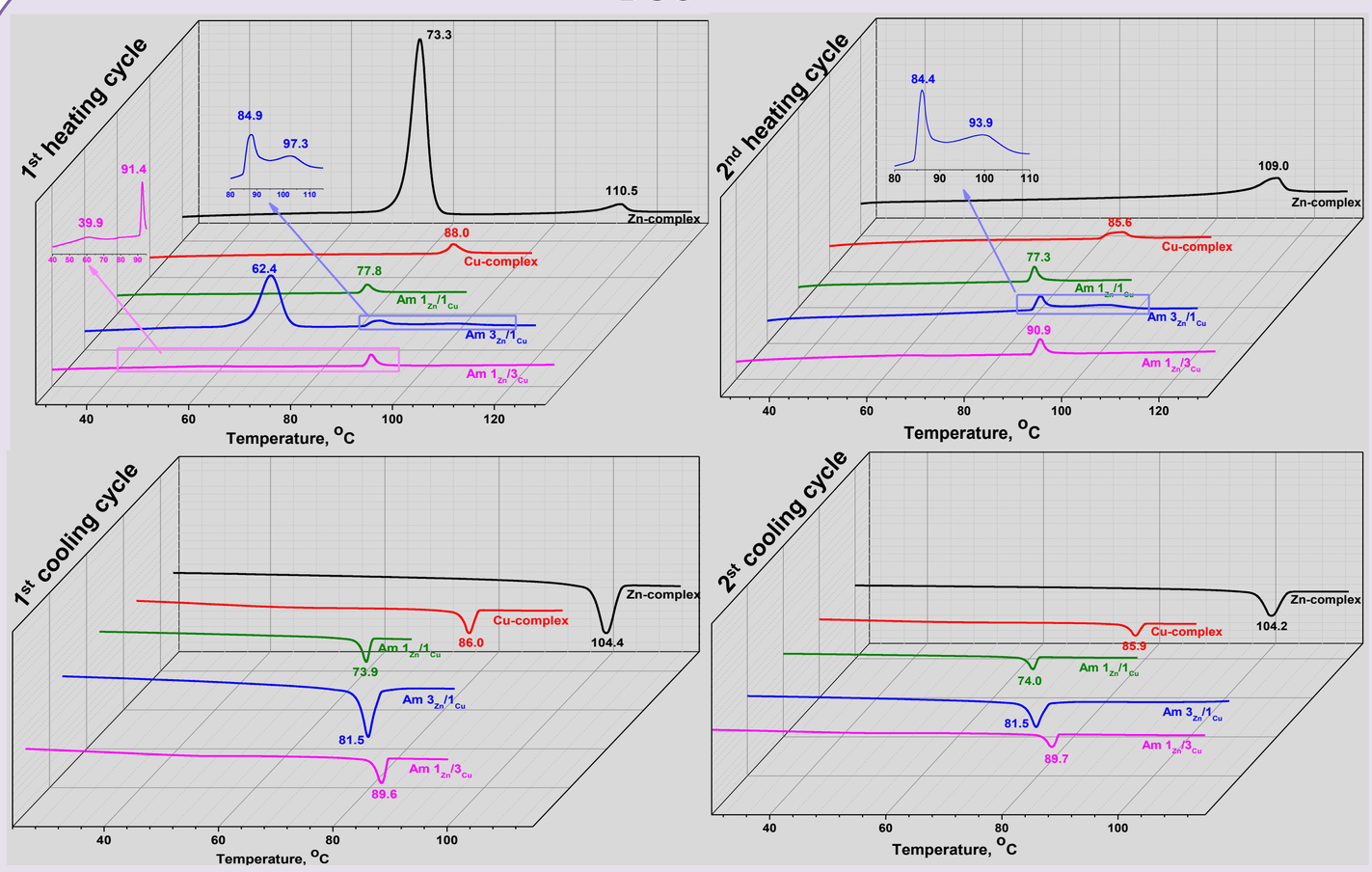


Figure 1. DSC traces for Zn-complex, Cu-complex, Am $1_{Zn}/1_{Cu}$, Am $3_{Zn}/1_{Cu}$, Am $1_{Zn}/3_{Cu}$

POM

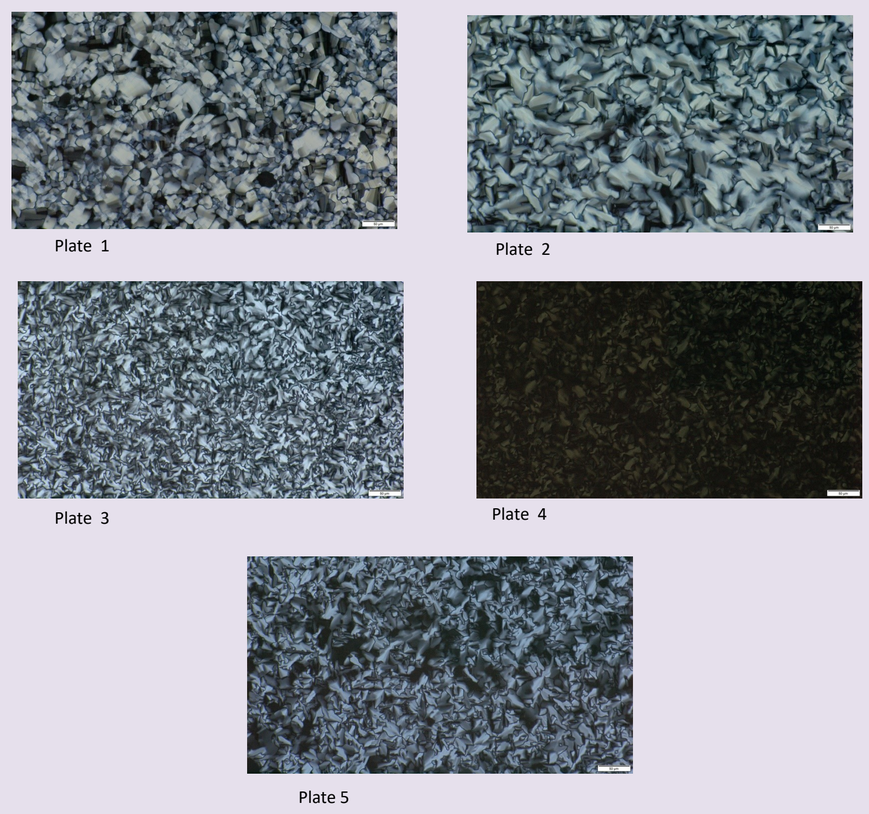


Figure 2. Polarised light optical photomicrograph of the textures exhibited by Zn-complex at 109°C on cooling (Plate 1); by Cu-complex at 90 °C on cooling (Plate 2); Am $1_{Zn}/1_{Cu}$ at 77°C (Plate 3).; Am $3_{Zn}/1_{Cu}$ at 60 °C on cooling (Plate 4); Am $1_{Zn}/3_{Cu}$ at 70 °C on cooling (Plate 5).

DISCUSSIONS

Zn-Complex is obtained as a white solid. It shows mesomorphic properties between 73°C and 110°C. On cooling the LC phase is frozen at r.t.
Cu-complex is obtained as a room temperature liquid crystal.
From POM textures both complexes arrange into columnar mesophases.
- two new liquid crystalline materials were obtained: **Am $1_{Zn}/1_{Cu}$** and **Am $1_{Zn}/3_{Cu}$** with new and highly reproducible thermal behavior as demonstrated by repeated heating-cooling DSC scans and different textures developed on POM.
- The thermal behavior of **Am $3_{Zn}/1_{Cu}$** suggests a non unitary mixture of the two compounds, being a superposition of the DSC thermograms of the initial components. Moreover, on POM a low birefringent texture is observed. All these observations implies the failure of obtaining a new homogeneous materials in this case.

CONCLUSIONS AND PERSPECTIVES

Two new heteroleptic coordination complexes of Cu(II) and Zn(II) were obtained and their liquid crystalline properties were investigated combining POM and DSC measurements. Despite of their similar structural features, different mesomorphic behavior was observed. The Cu(II) complex is liquid crystal at room temperature until 86.0 ºC, whereas the Zn(II) complex is liquid crystal at relatively low temperature (73 - 110ºC).
At a first glance, the successful obtainment of new materials seems to depend on a greater ratio of Cu-complex in the material composition. This is probably due to a greater flexibility of the Cu(II) ion in the tetrahedral coordination, facilitating the accommodation of the more rigid Zn(II) complex.
The new materials will further be investigated structurally by advanced diffractometric techniques in order to understand their self assembly into new mesomorphic systems.
This strategy permits in a straightforward way to obtain liquid crystalline bimetallic materials very interesting for applicative purposes.

REFERENCES

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