UNIVERSITY OF BUCHAREST

FACULTY OF CHEMISTRY

DOCTORAL SCHOOL IN CHEMISTRY

DOCTORAL THESIS SUMMARY

Emissive Liquid Crystalline Materials based on d^{10} Metal complexes.

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Summary

Liquid crystals are an exciting class of materials because they behave as both solids and liquids, and this has made them very useful in a wide range of applications, the most common being in the display of devices, sensors, photonics and even in drug delivery systems, among many others. Incorporating an abundant and relatively affordable metal like copper into an organic liquid crystal could induce or enhance the resulting material's liquid crystalline, electronic, optical, magnetic and thermal properties.

This thesis examines the behaviour of luminescent liquid crystals based on copper(I) complexes with Benzoyl thiourea. The first chapter introduces the topic and provides an insight into the various studies that have already been carried out on liquid crystalline materials based on copper(I) complexes. Even though the study of copper(I) complexes concerning their liquid crystalline property is quite limited, metallomesogens prepared with different structural components and ligands from groups such as azamacrocycles, alkythiolates, ethers, isocyanides, phenanthroline, Schiff bases, pyrazolates, phosphine, biquinoline, and benzoylthiourea have been reported. A special section also discusses the emission properties of copper(I) metallomesogens.

Chapters 2-5 contain original studies carried out during my PhD studies. The compounds reported were generally characterized structurally by NMR (^{1}H, ^{13}C and ^{31}P), ESI-MS, XRD and IR studies, and their mesomorphic properties were investigated via a combination of polarising optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction studies. The stability of the compounds was also investigated using Thermogravimetry analysis (TGA). In the 2nd chapter, the compounds reported were copper(I) metallomesogens of the type $\mathbf{Cu(L^{n})_{2}X}$, where X = Cl, Br, or I, with the classical benzoyl thiourea ligands having long alkoxy chains on either terminal of the compounds. The prepared compounds (Ligands and complexes) had varying mesomorphic properties, displaying Nematic and Smectic mesophases. Generally, it was observed that the chain length, type and position of substituents, and the type of attached halide ion influence the compounds' thermal, liquid crystalline and photophysical properties. The studied resulting complexes displayed emission in the solid state but were non-emissive in DCM solution. The QY and average phosphorescent lifetimes ranged from 0.4% to 1.7% and 1.7µs to 5.4µs, respectively. I also identified from a representative sample; Cu$\mathbf{(L^{3})_{2}Cl}$ the existence of mechanochromic behaviour which exhibited a red shift (from 544 to 550nm) upon grinding of the crystalline solid. This emission was further red-shifted to 590nm when the sample was cooled into a

glassy state from its liquid crystalline phase, thereby indicating the existence of a thermochromic luminescence behaviour. In addition, I demonstrated the effect of temperature on the photoluminescence spectra, which revealed a consistent decrease in emission intensity with increasing temperature both on heating and on cooling. This behaviour indicates the strong sensitivity of the compound's emissive properties to both mechanical and thermal stimuli.

In chapter 3, a novel set of liquid crystals based on copper(I) complexes with a cyano or fluoro group attached at the *para* position of an aromatic ring in a benzoyl thiourea ligand was prepared and studied for their liquid crystalline properties. Studies have shown that by incorporating electron-withdrawing fluoro or cyano groups into the structural unit of a LC compound, one can enhance their thermal stability, phase transition temperatures, and optical properties. The prepared **$Cu(BTU)_2X$** compounds, which were analogous in structure to those in chapter 2 displayed a SmA mesophase depending on the type of the attached terminal group (F or CN), number of alkoxy chains (one or two) and the nature of the halide ion coordinated to the metal center (Cl, Br or I). The complexes in chapter 3 had comparable emission properties with those discussed in the 2nd chapter.

Even though most of the liquid crystalline compounds are neutral, a good number of them are ionic. In the study discussed in chapter 4, I presented novel ionic liquid crystals based on copper(I) complexes with benzoyl thiourea ligands having either tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) as the counterions. The structural studies via XRD show that copper is in coordination with four benzoyl thiourea compounds through the sulphur atom in a monodentate manner, resulting in a distorted tetrahedral geometry. A study of the thermotropic liquid crystalline property revealed a SmA phase for all the studied complexes, including modification of nematic and SmC mesophases in some of the ligands into SmA. As expected, complexation of the uncoordinated ligands to copper(I) stabilised the mesophases at wider temperature ranges, with the PF_6^- analogues generally shifting the mesophase to isotropic liquid transition temperatures to lower values. All the studied complexes exhibited very low enthalpies. The thermal stabilities were moderate (> 170 °C); $BF_4^- > PF_6^-$. Interestingly, even though we have seen from the literature that neutral copper(I) complexes are generally more emissive than their ionic counterparts, I found in this work an ionic complex **$[Cu(L^7)_4]PF_6$** prepared from a ligand having a peripheral cyano group and double alkoxy substitution on either side of the BTU displaying the highest emission (QY = 3.1%) among all the compounds presented in this thesis. It is worth noting that the sulphur-coordinated compounds (like those of my BTU Cu(I) complexes) have generally been shown to be less emissive than those in phosphorus or nitrogen-coordinated Cu(I) complexes. The reduced efficiency in sulphur-coordinated systems has often been associated with structural distortions or non-radiative decay pathways influenced by ligand flexibility or solvent interactions in the case of solutions.

In the final chapter, I investigated the gelation properties of some of the BTUs discussed in preceding chapters. The compounds did form interesting physical gels with the LC mixture, E7. The gels were characterized by DSC, POM, and rheological measurements. Dielectric spectroscopy measurement was performed for a representative sample and a fast relaxation time of of 3.77×10^{-8} s (37.7 ns) was obtained. Furthermore, novel chiral BTUs were also prepared, alongside their corresponding copper (I) complexes and their helical twisting powers were investigated. The results revealed an improved HTP values for the complexes in comparison to the uncoordinated chiral ligands.