

# NANO-ENCAPSULATION OF COORDINATION POLYMERS. STEP 1: MASTERING THE BUILDING BLOCKS

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## Introduction

One-dimensional coordination systems, or coordination polymers, are the object of innumerable studies due to their wide range of applications. They are advantageous over the monomeric species due to the common cooperativity between metal centers. The present work focuses on copper complexes, of which some multinuclear species exhibit properties which are absent in the mononuclear ones. An example is magnetism, observed in copper 1D, 2D or 3D frameworks [1]. A few copper oligomers have also been described as suitable molecular wires [2].

As part of our ongoing research efforts, we aim to modify the properties of coordination complexes by encapsulation, or, more specifically, threading of the polymer with cyclodextrins which are nano-sized sugar rings with typically six to eight glucose units. Cyclodextrins are able to self include organic or metallo-organic hydrophobic molecules of suitable size and geometry [3], thus being expected to dock on aromatic bridging ligands of coordination polymers.

Aiming at the preparation of the polymer  $[\{\text{Cu}(\text{hfac})_2(\text{bis}-(N\text{-oxide})\text{-}4,4'\text{-bipyridine})\}@\beta\text{-CD}]_n$ , preliminary studies on the interactions between the building blocks must be carried. The present work presents reports on the synthesis optimization for the mononuclear complex  $[\text{Cu}(\text{hfac})_2(\text{ppno})_2]$  in which  $\text{hfac} = 1,1,1,5,5,5\text{-hexafluoroacetylacetonate}$  and  $\text{ppno} = 4\text{-}(\text{phenyl})\text{pyridine-}N\text{-oxide}$ , and its inclusion into beta-cyclodextrin ( $\beta\text{-CD}$ , 7 glucose units).

## Experimental

### Materials

$\beta\text{-CD}$  was kindly donated by Wacker Chemie.  $[\text{Cu}(\text{hfac})_2]$  was prepared according to literature procedures [4] and ppno was obtained from Sigma.

### Apparatus and procedures

Microanalyses for CHN were carried out at the Chemistry Dept. of the University of Aveiro.

Powder XRD data were collected at ambient temperature on an X'Pert MPD Philips diffractometer ( $\text{CuK}\alpha$  X-radiation) with a curved graphite monochromator. FT-IR spectra (KBr pellets) were recorded on a Unicam Mattson Mod 7000 apparatus.

Preparation of  $[\text{Cu}(\text{hfac})_2\text{ppno}]$ : to an acetone solution (10 mL) of  $[\text{Cu}(\text{hfac})_2]$  (100.0 mg, 209  $\mu\text{mol}$ ) ppno was added (71.7 mg, 419  $\mu\text{mol}$ ) and the mixture was stirred for 30 min at 30 °C. Recrystallization from ethanol/water afforded a blend of two solids, which were washed with hexane to remove unbound ppno and separated by ether extraction to isolate compound **1** from the ether-soluble phase.

Elem. anal. for  $\text{C}_{32}\text{H}_{20}\text{O}_6\text{N}_2\text{F}_{12}\text{Cu} = \text{C}, 46.87; \text{N}, 3.416; \text{H}, 2.458$ ; found: C, 46.42; N, 3.558; H, 2.480.

Preparation of **1**@ $\beta\text{-CD}$ : to a solution of  $\beta\text{-CD}$  (65.8 mg, 50  $\mu\text{mol}$ ) in water (4mL) was added a second solution of **1** (32.4 mg, 25  $\mu\text{mol}$ ) in ethanol (4mL), and the mixture stirred for 3h at 30°C. Solvent removal by freeze-drying yielded a pale-green solid.

Elem. anal. for  $2(\text{C}_{42}\text{H}_{70}\text{O}_{35})\cdot(\text{C}_{32}\text{H}_{20}\text{O}_6\text{N}_2\text{F}_{12}\text{Cu}), 26(\text{H}_2\text{O}) = \text{C}, 41.63; \text{N}, 0.837; \text{H}, 6.820$ ; found: C, 41.17; N, 0.917; H, 5.405.

## Results and discussion

Reaction of  $[\text{Cu}(\text{hfac})_2]$  with ppno led to the isolation of a green solid which was washed and separated into two products. Compound **1**, soluble in ethyl ether, was decanted and subsequently dried. The ether-insoluble phase (**2**) was also isolated and dried. Powder X-ray diffraction showed that they are distinct (Fig. 1). Microanalysis revealed that the C, H and N composition of **1** matches that calculated for  $[\text{Cu}(\text{hfac})_2(\text{ppno})_2]$ , a mononuclear complex composed of mixture of the *cis* and *trans* forms [5]. Compound **2** has a higher carbon percentage, so it may be a second type of a binuclear complex [6].

The mononuclear  $[\text{Cu}(\text{hfac})_2(\text{ppno})_2]$  complex (**1**) was used as guest for inclusion into  $\beta\text{-CD}$ , carried out by co-dissolution in water/ethanol at 30°C; the solid adduct was isolated by freeze-drying.

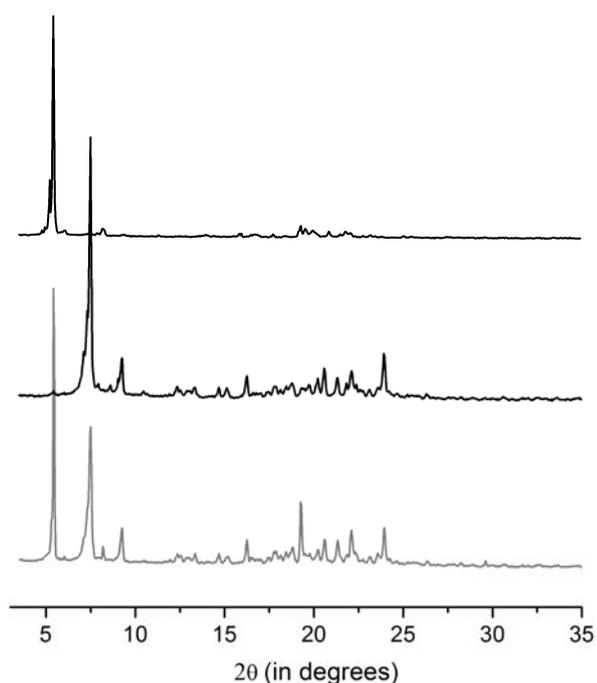


Fig. 1 Powder diffractograms of: (*bottom*) green solid product as obtained from the reaction, (*middle*) product **1** and (*top*) product **2**.

Microanalysis of **1**@ $\beta$ -CD (see Experimental section for details) shows the expected 2:1 stoichiometry ( $\beta$ -CD-to-guest), in agreement with the initial proportions used in the reaction.

In addition, the powder X-ray diffractogram in Fig. 2 shows an overall envelope different from the simple superimposition of the patterns of its components, thus pointing to the formation of a true inclusion compound,  $[\text{Cu}(\text{hfac})_2(\text{ppno})_2]@ \beta\text{-CD}$ , as expected. The low crystallinity of the material, however, does not permit to elucidate the details on the type of host packing in this adduct.

## Conclusion

The results briefly presented in this work show that a careful optimization of the reaction conditions allows the isolation of the mononuclear  $[\text{Cu}(\text{hfac})_2(\text{ppno})_2]$  (**1**) which can be successfully included into  $\beta$ -CD, forming a 2:1 host-to guest solid adduct. The experimental method here presented will allow the future preparation of  $\beta$ -CD-bearing  $[\text{Cu}(\text{hfac})_2]$  polymers using *bis*(N-oxide)-4,4'-bipyridine as the bridging guest ligand.

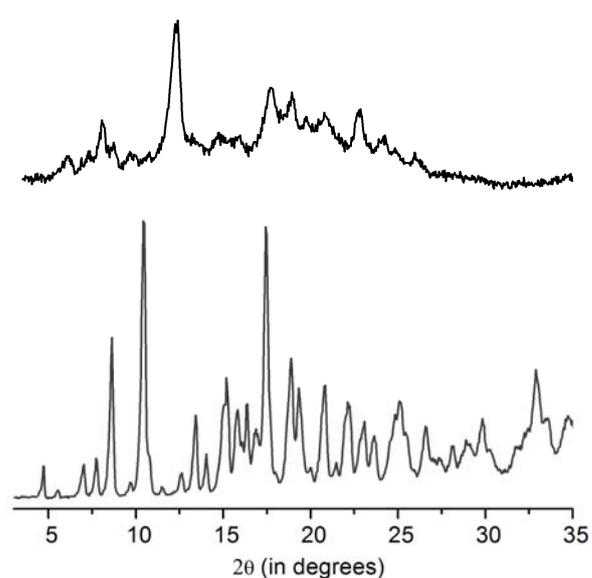


Fig. 2 Powder diffractograms of: (*bottom*) pristine  $\beta$ -CD hydrate and (*top*) adduct **1**@ $\beta$ -CD.

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