



Spectroscopic studies and density functional theory investigations of a cobalt phthalocyanine derivative



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HIGHLIGHTS

- The α and β phases of a cobalt derivative have been studied by spectroscopic methods.
- Its complex structure arises from the presence of crystalline and molecular phases.
- Theoretical calculations predict novel deformations on the bond Co-anthraquinone.

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ABSTRACT

Colloidal solutions at room temperature were used to obtain various polymorphic forms of a $[\text{PcCoCN}]_n$ and double potassium salt from 1,8-dihydroxyanthraquinone derivative. Nanocrystals in the form α and β were characterized using IR and UV–Vis spectroscopy techniques. Likewise in this context, an energy doublet in the absorption spectra of the monoclinic form at 1.8 and 2 eV was observed. The complex structure inherent to the spectra of the CoPc derivative is attributed to the simultaneous presence of both crystalline and molecular phases in the samples. The optical absorption of the compound was also investigated in order to evaluate changes in the electronic structure of these metal organic nanostructures. The absorption spectra of the CoPc derivative recorded in the UV–Vis region manifested two absorption bands, namely the Q- and B- bands. DFT calculations of this structure help to establish the source of the spectroscopic behavior and also lead to a particular phenomenon not known previously in this kind of complex, because the optimized structure of the cobalt complex manifests a very strange deformation of the bond between the anthraquinone derivative and the cobalt atom; the origin of this deformation is also discussed.

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Introduction

Phthalocyanine (Pc) is a porphyrin derivative, characterized by high symmetry, planarity and electron delocalization [1]. Pc and their metallic derivatives are currently one of the most important organic compounds due to their ultrafast response times, ease processing and large optical non linearities [2,3]. Metallophthalocyanines (MPcs) show very intense optical absorption values in the visible region. Thus, they are considered likely candidates for optical amplification in the 600–700-nm region, which makes them potentially useful for nonlinear optical applications [4]. Pc and its numerous metallic complexes have been widely used because of their wide-spread applications in the field of solid state technology [5], e.g., optoelectronics, organic nanophotonics and photocopy industry [5–7].

MPcs are plane aromatic macrocycles that constitute four isoindol units joined at their 1 and 3 positions by nitrogen atoms. Their structure consists of 42 π electrons, which extend over 32 carbon atoms and 8 nitrogen atoms. However, electronic delocalization takes place mainly over the inner ring system, in such a way that the phthalocyanine is formally considered as an aromatic system made up of 16 atoms and 18 π electrons. As the central cavity of the phthalocyanine molecule contains hydrogen atoms, these can be replaced by more than 70 different atomic elements, giving them great versatility. MPcs are unique two-dimensional π -conjugated macrocyclic materials, which offer numerous possibilities for molecular engineering and show very effective thermal and chemical stability [5]. Likewise, the Pcs are arranged in crystalline formations, depending on the stacking order of the aromatic rings. Due to the force of the π bonds, they can be accommodated in different structures; this also depends on the substitutes they have. The main crystalline formations of Pcs are alpha (α) and beta (β) [8]. The difference between these

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two types refers to the angle that exists between the symmetry axis and the stacking direction (see Fig. 1 for CuPc). Alpha crystals have a 26.5° angle, while beta crystals have a 45.8° angle. Nanocrystals have been synthesized in a supersaturated solution of a Pc containing a crystallizing liquid that does not dissolve the Pc [2,3]. Akimov et al. [7,9] have obtained MgPc nanocrystals after adding some water to a saturated solution of MgPc in acetone. Rangel-Rojo et al. [10] have pioneered fabrication of Pc nanocrystals from vanadyl-phthalocyanines. MPcs are characterized by polymorphism, as they contain molecular, dimeric and more aggregated associates with either crystalline or amorphous phases [9]. The absorption spectra of different polymorphs from certain phthalocyanine compounds manifest significant differences between them [8,11]. The type of crystallization determines their physical properties.

In this study, we analyze and compare the optical absorption spectra of different aggregate forms of cobalt(II) phthalocyanine derivative $C_{47}H_{22}N_9O_4KCo$, in the simple and binary mixtures of solvents. The first component of the mixture must dissolve the cobalt compound and must provide a solution that is close to saturation. The other components were chosen for not dissolving the MPc derivative, but could be mixed with the first solvent. Diffraction (XRD) was carried out over the compound to search for crystallinity. We also report the important optical parameters related to the principal optical transitions in the UV-Vis region, as well as the surface properties studied by scanning electron microscopy (SEM) and transmission electron microscopy (HRTEM), furthermore DFT calculations were carried out in order to discover the origin of the spectroscopic particularities, however they also provide a very interesting feature concerning the bonding of one of the substituents.

Experimental details

Cobalt (II) phthalocyanine derivative ($C_{47}H_{22}N_9O_4KCo$) was obtained using the procedure reported previously [12] by adding the bidentate ligand: double potassium salt from 1,8-dihydroxanthraquinone ($C_{14}H_6O_4K_2$) to the complex $(\mu\text{-cyano})(\text{phthalocyaninato})Co(III)$ or $[PcCoCN]_n$. Initially the solubility of these compounds was evaluated in various polar and non-polar solvents. Fig. 2 shows the molecular structure for cobalt phthalocyanine derivative.

Add 0.11 g (0.19 mmol) of $(\mu\text{-cyano})(\text{phthalocyaninato})cobalt(III)$, $[PcCoCN]_n$ to 0.22 g (0.7 mmol) of double potassium salt from 1,8-dihydroxanthraquinone and dissolve it in 20 ml of methanol (pH = 6). The resulting mixture was maintained under reflux for about 3 days until a precipitate was obtained. Next, the product was filtered, washed with absolute methanol and then vacuum-dried. The product was purified from 1:1 methanol-water. The resulting purple powder was dried under high vacuum. IR (KBr, cm^{-1}) ν_{max} : 1615 (C–H); 1508 (C–C); 1123 (C=N); 1083 (C–O); 2152 (CN) [12].

$C_{47}H_{22}N_9O_4KCo$ nanoparticles were prepared in colloidal solutions. According to Akimov et al. [7,9], the first component of the mixture must dissolve the CoPc derivative in a molecular form, whereas the second component is chosen because it does not dissolve the compounds but can be mixed with the first solvent in arbitrary proportions. The addition of the second component to the saturated molecular solution of $C_{47}H_{22}N_9O_4KCo$ has two consequences: simple dilution of the solution and reduction of the limiting solubility of the compound, to the point where the solution reaches supersaturation and the compound precipitates. The solubility of CoPc was evaluated and the following solvents were chosen: acetone, diethylamine and chloroform, which maximize the

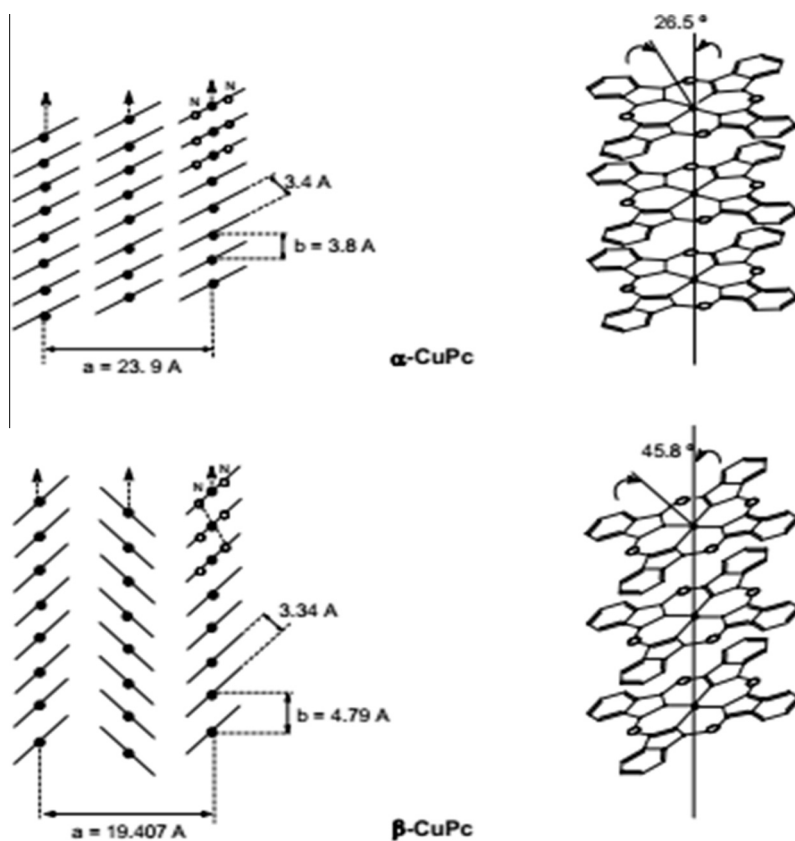


Fig. 1. Crystalline formations of CuPc: alpha (α) and beta (β).

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