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ORIGINAL ARTICLE

Experimental and theoretical investigations of the molecular structure, the spectroscopic properties and TD-DFT analysis of a new semiconductor hybrid based iron(III)

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Abstract In this work, a new hybrid material $(C_5H_6N_2Cl)_2[FeCl_4].Cl$ abbreviated $(CAP)_2[FeCl_4].Cl$ was prepared using room temperature slow evaporation technique. The X-ray diffraction analysis revealed that the compound is crystallized in the centrosymmetric space group $P2_1/c$ of the monoclinic system. The crystallographic network consists of an Fe(III) ion located on an inversion center and coordinated by four chlorine, isolated Cl^- and two $(CAP)^+$ protonated cations linked by N–H...Cl and C–H...Cl hydrogen bonds to form a zero-dimensional network. Hirshfeld surface analysis was used to analyze intermolecular interactions present in the crystal structure. The vibrational properties were inspected by means of Infra-Red absorption and Raman diffusion spectroscopy techniques. In addition, theoretical calculations based on the DFT/B3LYP/LanL2DZ method and the time-dependent density functional theory (TD–DFT) were performed in order to gain more information and help in the examination of over-all properties of the title compound. Good and interesting experimental findings were presented and good consistency was found with the calculated results.

1. Introduction

The research in hybrid compounds in the last years was focused on using the range of interactions found within organic and inorganic worlds in order to create, design and engineering new materials. The hybrid materials have won great scientific and technological attention due to their interesting and significant properties in many domains such as optoelectronics, biology, catalytic and magnetic functionalities

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[1–5]. The general formula in this family is R_2 $[MX_4]$ where M = transition metal, X = Cl, Br..., and R is an organic cation. A wide variety of these complexes is known where the R-group is a protonated alkyl amine [6,7], or heterocyclic such as pyridine [8,9]. An important feature of hybrid materials is their structural tunability. As a matter of fact, some structural differences are observed if the counter ions of the inorganic parts are monoprotonated or diprotonated amines. The crystallographic orientation and the thickness of the inorganic sheets may vary according to the choice of the appropriate organic cations. The dimensionality and shape of the functional crystals have a significant impact on the physical and chemical properties of the hybrid materials [10]. In other words, from the research carried out on the iron complexes, the iron chloride proved many connection forms by corner, edges or faces forming zero (0-D), one (1-D), two (2-D) or three dimensional (3-D) networks attached to the organic cations by hydrogen bonds. The presence of intermolecular hydrogen bonds in molecular packing is dedicated to the stability of the complex.

Over the past decades, intermolecular interactions and crystalline stacking have been widely studied by the Hirshfeld surface analysis. The use of this application has been noticeably growing up recently in the field of crystallography. This is because this analysis allowed the identification of individual types of intermolecular contacts and visualization of the fidelity of the crystal structure [11]. The 3–D Hirshfeld surfaces reflect intermolecular interactions in a novel visual manner as triangulation surfaces. Here, the associated 2–D fingerprint plots' [12] area provides the percentage of each intermolecular interaction explores quantitatively the types of intermolecular contacts experienced by molecules and displays this information in a convenient color plot.

Vibrational spectroscopy is an efficient tool for the characterization of crystalline materials. It is effectively used to identify functional groups and determine the molecular structure of synthesized crystals. It can also provide deeper knowledge about the relationships between molecular architecture and charge transfer of new efficient materials of technological application. On the other hand, literature survey revealed that the Density Functional Theory (DFT) has become a powerful tool in the investigation of structural, vibrational and optical properties [13,14]. The combination of infrared and Raman spectroscopies with quantum chemical computations have been used as effective tools in the vibrational analysis of molecular systems [15,16].

In the light of the optical properties investigation of this kind of materials has been the focus of substantial current research studies. Thus, we investigated the frontier molecular orbitals' (FMOs) calculations together with the charge transfers found in interactions that take place within the molecules to explain the bands observed in the predicted UV–Vis spectrum. Our previous published papers have been focused on the development of optical properties of new hybrid material $[Cu(CAP)_2Cl_2]$ and $(8\text{–}HQ)_2[FeCl_4]\cdot Cl$ [17,18]. As an extension of our searches work in exploring new properties concerning hybrid materials and illustrating their use in the range of applications of semiconductor materials that have been presented in the literature. In fact, the importance of these materials is their physical properties such as magnetism, conductivity, luminescence with interesting applications.

This work develops the role of hydrogen bonds and isolated halogen present in the crystal packing architecture and explores the optical properties' investigation of the $(CAP)_2[FeCl_4]\cdot Cl$ synthesized by slow evaporation. We performed X-ray diffraction, FT-IR, FT-Raman and UV–Vis spectroscopy which provided us with information about the complete crystal structure at room temperature. The intermolecular interactions in this compound via Hirshfeld surface analysis were also studied. Moreover, the optimized geometry, vibrational study and optical absorption spectra of the title compound were investigated using DFT theory and then compared to experimental data. Finally, the electronic properties were calculated with time dependent density functional theory (TD–DFT).

2. Experimental

2.1. Preparation

The single crystal of $(CAP)_2[FeCl_4]\cdot Cl$ was prepared by slow evaporation of aqueous solution containing anhydrous CAP (0.25 g) powder dissolved in HCl (37%) added to a solution of $FeCl_3$ (0.684 g) in a minimum volume of H_2O. The resulting solution was well stirred then kept at room temperature. After two weeks, orange prismatic crystals were obtained by slow evaporation at room temperature. A single crystal suitable for X-ray diffraction analysis was selected and studied.

The reactions' sequence for the synthesis is shown in the following equation:

$$2(C_5H_6N_2C1) + FeC1_3 \xrightarrow{HCl} (C_5H_6N_2C1)_2[F_eC1_4].C1$$

2.2. Crystal chemistry

Copper and chlorine atoms were chemically analyzed in order to confirm the formula determined by structural refinement [19]. Density was measured at room temperature using pycnometer. The measured density (Dm = 1.5 (3) g cm^{-3}) was very close to the calculated value (Dx = 1.6 g cm^{-3}).

2.3. X-ray data collection

A single crystal was selected in order to perform structural analysis by X-ray diffraction. Single-crystal X-ray data were carefully selected under a polarizing microscope and glued to a cactus needle mounted on a four-circle Bruker Kappa Apex II CCD area detector diffractometer equipped with graphite monochromatic MoKα radiation (λ = 0.71073 Å) for data collection at T = 293 K. The crystal compound has a prismatic form with a size of about (0.38 × 0.36 × 0.22) mm^3. The empirical absorption corrections were based on multiscan. The crystal structure was solved using the WINGX software [20]. The chlorine and iron atoms were fixed using the Patterson with the SHELXS program of the SHELXTL package and the organic moieties were found from successive Fourier calculations using SHELXL-2014 [21]. Anisotropy thermal displacement parameter refinement was used for all non-hydrogen atoms. All hydrogen atoms were geometrically fixed.

The crystal data, collected reflections, and parameters of the final refinement are reported in Table 1. The structural