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Crystal structure, electrical study and dielectric behavior of a new centrosymmetric hybrid material

Soumaya Chaouachi*, Besma Hamdi, Ridha Zouari

Laboratoire des Sciences des Matériaux et de l'Environnement, Faculté des Sciences de SFAX, University of SFAX, PB 1171, 3000 SFAX, Tunisie

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ABSTRACT

The new organic–inorganic material $[C_9H_8NO]_2CoCl_4$ crystallizes at room temperature in the monoclinic system and C2/c space group. The atomic arrangement can be described as an alternation of organic–inorganic layers along the *b*-direction. The material cohesion of the compound is assured by hydrogen bonds C—H···Cl and N—H···Cl established between the anions and cations, N—H···O hydrogen bonds and $\pi - \pi$ stacking interactions established between almost parallels cations. Thermal analysis discloses a phase transition at the temperature 347 K, a detailed dielectric study was reported and shows a good agreement with thermal measurements. The electrical and the dielectric properties of the title compound have been investigated by means of impedance spectroscopy measurements over a wide range of frequencies and temperatures, 209 Hz–5 MHz and 298–423 K, respectively. The analysis of Nyquist plots has revealed the contribution of three electrically active regions corresponding to the bulk mechanism, distribution of grain boundaries and electrode processes, the dielectric relaxation is described by a non–Debye model. The study of the dielectric constants (ε'), (ε") and loss tangent tan (δ) with frequency exhibits a distribution of relaxation times.

Contents

1. Introduction

In recent years, The prospect of creating new functional materials with tunable properties gives a strong motivation on the research of open framework materials, namely, organic–

* Corresponding author.
E-mail address: soumayachaouachi23@yahoo.fr (S. Chaouachi).

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inorganic hybrid materials. The $[C_9H_8NO]_2CoCl_4$ compound belongs to the organic–inorganic crystal family with the general formula A_2MX_4, where A is organic cation, M is a transitions divalent metal ion, X is Cl or Br a halogen. The materials based upon substituted complex ammoniums with halogenated metals such as Hg, Cd, Zn, Co and Cu etc. present very interesting physical properties [1–7]. The thermal analyses of complexes have been utilized as an analytical tool or technique for studying their thermal decomposition behavior, it thus gives information on the optimum temperature range for the resulting products to attain a constant weight [8,9]. For the investigation of their electrical and dielectric properties these systems are considered heterogeneous and many relations have been proposed describing their behavior in terms of conductivity and permittivity. These materials show good results due to their electronic properties and extended structure, with strong interaction between the atoms, ions or molecules which occur throughout the lattice system [10,11]. In fact, this technique is a powerful method that allows the study of the dynamics of organic cation in a wide temperature and frequency range. The electrical and dielectric properties demonstrated by organic–inorganic hybrids materials are vital in a large number of applications, for the investigation of the dielectric processes occurring in organic–inorganic hybrids compound [12,13]. The experimental study of the A.C. conductivity is an important source to characterize the electrical properties and to understand the nature of the conduction in materials, the researchers have shown that electrical-conductivity properties of organic semiconducting materials strongly depend on their chemical structures [14–16]. The dielectric properties of usual interest are the real (ε') and imaginary (ε") components of the complex permittivity $\varepsilon^* = \varepsilon'(x) + i\,\varepsilon''(x)$. The permittivity of a material reflects the transport processes and molecular relaxation of the material which depends on many parameters such as temperature, time and composition.

The present paper is devoted to the synthesis, structural characterization by X–ray diffraction, differential scanning calorimetry (DSC) and dielectric measurements of the bis (8–Hydroxyquinolinium) tetrachlorocobaltate(II). The purpose of this work falls under this context is more particularly, our analysis pertains to the comprehension of the dielectric properties in the $[C_9H_8NO]_2CoCl_4$ hybrid compound, by using the impedance measurements, the real and imaginary parts of the electric modulus (M' and M"). and this study undertakes the investigation of the frequency and temperature dependences of the dielectric parameters such as (ε'), (ε"), tan (δ).

2. Experimental

The synthesis of $[C_9H_8NO]_2CoCl_4$ was obtained by dissolving (0.2 g, 1.36 mmol) of 8-hydroxyquinoline powder (C_9H_7NO) and (0.656 g, 2.76 mmol) of Cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$) in concentrated HCl (37%) solution in a molar ratio 2:1. The resulting solution was then kept at room temperature. After two weeks, green prism crystals appeared. The reaction sequence for the synthesis is shown in the following equation:

$$C_9H_7NO + CoCl_2{\cdot}6H_2O \xrightarrow{HCL} [C_9H_8NO]_2CoCl_4 + 6H_2O$$

The sample was characterized by X-ray structural analysis was performed on a single crystal selected with an optical microscope. Differential scanning calorimetry (DSC) measurements were recorded on a NETZSCH apparatus (Model 204 Phoenix) at a heating rate of 5 K min^{-1} at the temperature range from 300 to 430 K, using a polycrystalline sample in a flowing nitrogen atmosphere. Afterwards, the electrical measurements were performed using a two gold electrode configuration. In fact, the $[C_9H_8NO]_2CoCl_4$ sample was pressed on pellet disks of about 8 mm in diameter and 2 mm in thickness using 3t/cm^2 uniaxial pressure. These measurements were made over a wide range of temperatures 293–423 K and frequencies 209 Hz–5 MHz with the TEGAM 3550 ALF automatic bridge monitored by a microcomputer.

3. Results and discussion

3.1. X-ray structure determination and description

The intensity data were collected on a Bruker APEX (II) CCD four circle diffractometer, with graphite monochromatic Mo Ka radiation (0.71073 Å) at room temperature. Atomic scattering factors were taken from the International Tables for X-ray crystallography [17]. A total of 9370 reflections were collected using the ω–2θ scan technique of which 1325 have $I > 2\sigma$ (I) and were used for the structure determination. Then the structure was solved by the Patterson method using SHELXS–86 [18] and refined by SHELXL–97 [19] programs, which readily established the heavy atoms positions and facilitated the identification of the light atoms from different Fourier maps. The details of the main crystal data are summarized in Table 1. The crystal structures and packing interactions are depicted using ORTEP-III [20] and DIAMOND [21] respectively.

The bis (8–hydroxyquinolinium) tetrachlorocobaltate (II) compound crystallizes in the monoclinic system (C2/c space group) with the following unit cell dimensions: a = 15.234(6) Å, b = 8.136 (4) Å, c = 16.730(5) Å, β=91.386(14) °, V = 2073.0(14) Å^3 and Z = 4. The asymmetric unit of the title compound consists of one crystallographically independent organic cation, denoted

Table 1
Summary of crystal data, X-ray diffraction intensity measurements and Refinement parameters for $[C_9H_8NO]_2\ CoCl_4$.

Crystal data	
Formula	$(C_9H_8NO)_2{\cdot}CoCl4$
Formula weight(g mol^{-1})	493.06
Crystal system/space group	Monoclinic, C2/c
Cell dimensions	
a (Å)	15.234(6)
b (Å)	8.136(4)
c (Å)	16.730(5)
B (°)	91.386(14)
V (Å^3)	2073.0(14)
Z	4
Data collection	
Dx (mg m^{-3})	1.580
μ (mm^{-1})	1.36
Crystal size (mm)	0.36 × 0.29 × 0.23
Range	
h	−18 → 18
K	−10 → 10
l	−18 → 20
F(000)	996
Absorption correction	Multi-scan
θ range for data collection	2.2–26.4
reflections with $I > 2\sigma(I)$	1325
No. Of independant reflection	2124
Variables parameters	124
Refinement	
R [$F2 > 2\sigma(F2)$]	0.037
wR(F2)	0.088
Rint	0.051
GooF S	1.06
T (K)	293
Tmin, Tmax	0.629, 0.732
Δρmax; Δρmin (e Å^{-3})	0.28, −0.34
$w = 1/[\sigma 2(F_o^2) + (0.0281P)^2 + 0.361P]$	where $P = (F_o^2 + 2F_c^2)/3$
Refinement	F^2