

## Article

# Synthesis of New Homopiperazine-1.4-Diium Tetrachloridromercurate (II) Monohydrate ( $C_5H_{14}N_2$ )[ $HgCl_4$ ] $\cdot H_2O$ , Crystal Structure, Hirshfeld Surface, Spectroscopy, Thermal Analysis, Antioxidant Activity, Electric and Dielectric Behavior

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**Abstract:** Using acid–base assays and simple slow evaporation method at ambient temperature, we were successful in producing a novel salt with the chemical formula ( $C_5H_{14}N_2$ )[ $HgCl_4$ ] $\cdot H_2O$ . According to single-crystal X-ray diffraction data, the crystal packing was regulated by H-bonds and by Coulomb interactions (also called electrostatic interactions) between distinct entities, which formed a 3D network. The 2D fingerprint plots and the Hirshfeld surface were utilized to examine the effect of intermolecular interactions. FTIR spectroscopy, PL spectroscopy, thermal analysis, and electrical conductivity experiments were also carried out, and the antioxidant activity was tested.

**Keywords:** photoluminescence; FT-IR; chloromercurate (II); dielectric analysis; antioxidant activity

## 1. Introduction

Several strategies have been used to investigate, synthesize, and describe mercury-based compounds because of their self-assembling nature [1]. The anions in this class of compounds have long been recognized to exhibit a wide range of stoichiometric, geometric, and connectivity properties, due to the full 4f and 5d electron shells, which make them more flexible [2]. These compounds may have different geometries, and their deformed forms and substantial distortions in the ideal polyhedron are readily possible [3–6].  $Hg^{2+}$  ions have a wide range of potential applications in the paper industry, paints, and preservation of mercury (II) compounds. Despite these advantages in terms of potential applications in various fields, the formation of polymers containing  $Hg^{2+}$  ions is disproportionately sparse in comparison to  $Zn^{2+}$  and  $Cd^{2+}$  metals [7–18].

Recently, homopiperazine (heterocyclic amine) has found widespread use in several applications, including as a component of liquids for  $CO_2$  capture [19] and as a component of various organic and organic/inorganic supramolecular ionic salts and transition metal complexes. In these applications, the materials are generally characterized by X-ray

diffractions, we can conclude that there are a large number of X-ray structures involving the dication of homopiperazinium in salts or mixed salts; we note sulfate oxalate manganese [20], cobalt sulfate [21], zinc phosphate [22], and so on. There are also an interesting number of structures in which homopiperazine reacts like bidentate ligand on nickel [23], copper [24], and platinum [25–28]. There are several uses for homopiperazines in medicine, including antimicrobial, antibiotic, antituberculous, antipsychotic, anticonvulsant, depressive, anti-inflammatory, cytotoxic, antimalarial, antiarrhythmic, and antiviral [29–33].

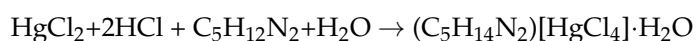
In this article, according to the motivations stated above, we have introduced a novel compound, homopiperazine-1,4-diium tetrachloromercurate (II) monohydrate  $[(\text{HgCl}_4)]^{2-}$ ,  $(\text{C}_5\text{H}_{14}\text{N}_2)^{2+}$ ,  $\text{H}_2\text{O}$ . We will analyze the information given by the single-crystal XRD and by PXRD. We will discuss their spectroscopic properties (FT-IR and PL) and their thermal properties. Moreover, we will study their intermolecular interactions by the analysis of Hirshfeld surfaces. Furthermore, we will determine the electric and dielectric properties to give more information about conduction modes. We ended the study with a test of antioxidant activity.

## 2. Experimental Part

### 2.1. Chemical Preparation

The compound  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  is obtained by acid–base reaction. The homopiperazine amine ( $\text{C}_5\text{H}_{14}\text{N}_2$ ) (0.28 mL, 2 mmol, purity 98%, Sigma-Aldrich, Burlington, MA, USA) dissolved in 20 mL of ethanol was added to a solution containing  $\text{HgCl}_2$  (0.271 g, 1 mmol, 99.5% Fluka, Buchs, Switzerland) dissolved in 15 mL of hydrochloric acid (36–38%, Sigma-Aldrich) (6 M) (molar ratio 1:2) and 15 mL of water. Drop by drop, concentrated hydrochloric acid (HCl) was added to the solution until it was clear. Colorless prismatic crystals of high quality formed after almost three weeks of crystallization in the solution at room temperature.

The reaction scheme is as follows:



The CHN-elemental analysis for the compound  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  is as follows: Anal. calculated C, 12.98; H, 3.48; and N, 6.05%; and experimental: C, 12.67; H, 3.09; and N, 5.98%.

### 2.2. Investigation Methods

Rigaku Mercury CCD2 (Rigaku Corporation, Tokyo, Japan) equipped with  $\text{MoK}_\alpha$  radiation (0.71075) at 298 K was used to determine crystal data of  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$ . The refinement was carried out by the SHELXL version 2018/1 program [34]. Empirical absorption adjustments were calculated on the basis of a multi-scan. ORTEP and DIAMOND software were used to generate the structural graphics [35]. Table 1 contains selected crystallographic data and experimental information. The experimental PXRD patterns of  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  were determined using a powder diffractometer called Advance Bruker D8 with  $\text{Cu}-\lambda(\text{K}_{\alpha 1}) = 1.54060 \text{ \AA}$  radiation (with receiving slit size = 0.1 mm, and sample length = 10 mm) and by the variation of  $2\theta$  from 0 to  $50^\circ$ . The simulated diffractogram is determined directly by Mercury software [36].

The  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  compound's Fourier transform infrared spectrum was acquired using a Nicolet Impact 410 FT-IR spectrophotometer, according to the manufacturer (SpectraLab Scientific Inc., Markham, ON, Canada). A SAFAS FLX-Xenius spectrofluorometer (SAFAS, Monaco, Monaco) was used to conduct photoluminescence experiments at room temperature ( $T = 25^\circ\text{C}$ ), with the intensities of the photoluminescence measurements being corrected for the screening effect.

**Table 1.** The results obtained by the X-ray diffraction analysis on a single crystal.

| Crystal Data                                                          |                                                                                       |
|-----------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Chemical formula                                                      | (C <sub>5</sub> H <sub>14</sub> N <sub>2</sub> )[HgCl <sub>4</sub> ]·H <sub>2</sub> O |
| Molar mass (g·mol <sup>−1</sup> )                                     | 462.59                                                                                |
| Crystal system, space group                                           | Monoclinic, P2 <sub>1</sub> /c                                                        |
| Temperature (K)                                                       | 293                                                                                   |
| a, b, c (Å)                                                           | 6.272 (3), 12.480 (6), 15.984 (9)                                                     |
| β (°)                                                                 | 94.386 (6)                                                                            |
| V (Å <sup>3</sup> )                                                   | 1247.5 (11)                                                                           |
| Z                                                                     | 4                                                                                     |
| Radiation type                                                        | Mo Kα                                                                                 |
| μ (mm <sup>−1</sup> )                                                 | 13.16                                                                                 |
| Crystal size (mm)                                                     | 0.45 × 0.3 × 0.2                                                                      |
| Form, Color                                                           | Prism, colorless                                                                      |
| Data Collection                                                       |                                                                                       |
| Diffractometer                                                        | Rigaku Mercury CCD2                                                                   |
| Absorption correction                                                 | Multi-scan                                                                            |
|                                                                       | 0.048, 0.071                                                                          |
| T <sub>min</sub> , T <sub>max</sub>                                   | h = −8–8                                                                              |
| Limits h, k, l                                                        | k = −16–13                                                                            |
|                                                                       | l = −17–20                                                                            |
| No. of measured, independent, and observed<br>(I > 2σ(I)) reflections | 9371, 2829, 2214                                                                      |
| R <sub>int</sub>                                                      | 0.061                                                                                 |
| (sinθ/λ) <sub>max</sub> (Å <sup>−1</sup> )                            | 0.649                                                                                 |
| Refinement                                                            |                                                                                       |
| R[F <sup>2</sup> > 2σ(F <sup>2</sup> )], wR (F <sup>2</sup> ), S      | 0.035, 0.089, 1.07                                                                    |
| No. of reflections                                                    | 2829                                                                                  |
| No. of parameters                                                     | 119                                                                                   |
| Δρ <sub>min</sub> , Δρ <sub>max</sub> (e·Å <sup>−3</sup> )            | −1.50, 1.47                                                                           |
| CCDC No.                                                              | 2155598                                                                               |

A PYRIS 1 TGA apparatus (Perkin Elmer, Waltham, MA, USA) was used to manufacture thermograms in the temperature range 300–680 K with an initial mass of about 11.8 mg utilizing a PYRIS 1 DTA thermogram generator. The electrical measurements of the real  $Z'$  and imaginary  $Z''$  impedance characteristics changed across a temperature range (311–403 K). These measurements were taken with a Hewlett Packard HP 4192A analyzer (Test Equipment Center Inc., Gainesville, FL, USA). To guarantee electrical connections, the pelleted sample's two parallel sides were covered with silver paint. A weak mechanical pressure was used to maintain contact between the platinum wires and the sample, which was regulated by a screw/spring system and transferred through an alumina rod. Furthermore, the anti-free-radical activity of DPPH· was also tested using assays similar to those reported by Brand-Williams et al., with slight changes [37]. Thus, in a volume of 1 mL, different concentrations of the extract to be tested are prepared in methanol, and then 2 mL of the 0.1 mM concentration of DPPH· solution are added. After vigorous stirring, the mixture is incubated for 1 h in the dark, and then the absorbance was determined using a UV–vis spectrophotometer (JASCO-V530) (Jasco photometers & spectrophotometers, Portland, OR, USA) at 515 nm. Parallel to this, a solution containing 1 mL of DPPH· was created as an analytical blank. The anti-free-radical activity was estimated using the percentage inhibition (%I) value obtained by the following formula:

$$\%I = \frac{Abs_0 - Abs_1}{Abs_0} \times 100 \quad (1)$$

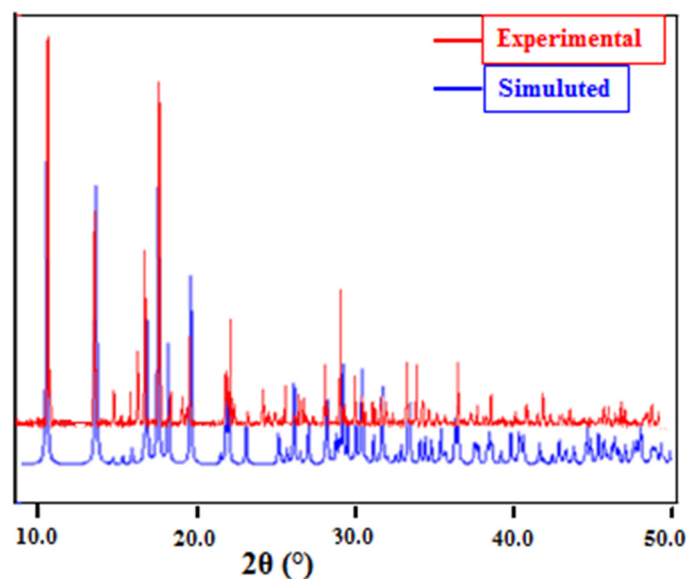
where  $Abs_0$  is absorbance of the analytical blank, and  $Abs_1$  is absorbance of the solution in the presence of extract.

The anti-free-radical activity or  $EC_{50}$  (efficient concentration 50 percent), defined as the quantity of extract required to halve the initial concentration of DPPH $\cdot$ , can be determined using the curve showing the variation of (%I) as a function of the different concentrations of the extract.

### 3. Results and Discussion

#### 3.1. X-ray Diffraction Powder Analysis

The coincidence between the peak positions of the experimental and the simulated powder X-ray diffraction patterns (PXRD), indicated in Figure 1, verify the phase purity of the compound  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ .



**Figure 1.** Experimental powder XRD pattern of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  compared with theoretical PXRD pattern.

#### 3.2. Structure Description of $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$

The asymmetric unit of the title compound consists of one homopiperzine-1,4-dium, one tetrachloridomercurate  $[HgCl_4]^{2-}$ , and one water molecule (Figure 2). Table 1 shows the experimental details of the novel compound. As can be seen in Figure 3, this compound's atomic structure may be defined by the alternation of three entities: organic cations  $(C_5H_{14}N_2)^{2+}$ , inorganic anions  $[HgCl_4]^{2-}$ , and water molecules. The various components of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  are held by a variety of H-bonds and by electrostatic interactions (Table S1). The hydrogen bonds lead to a wide variety of ring motifs  $R_2^1(5)$ ,  $R_2^2(5)$ , and  $R_4^2(8)$  (Figure 4).

In the  $[HgCl_4]^{2-}$  anion, the  $Hg^{2+}$  is surrounded by four chloride atoms (Cl1, Cl2, Cl3, and Cl4). To distinguish between tetrahedral geometry, square plane geometry, and trigonal pyramid geometry, Yang et al. have proposed the parameter " $\tau_4$ ", employing the following relation [38]:

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141} \quad (2)$$

where  $\alpha$  and  $\beta$  are the two highest angles ( $\alpha = 137.77(7)^\circ$  and  $\beta = 106.74(6)^\circ$ ). If  $\tau_4$  tends to 0, the geometry is homologous to the geometry of the square plane; if  $\tau_4$  tends to 1, the geometry is assimilated to tetrahedral geometry; and if  $\tau_4$  is close to 0.85, the geometry is assimilated to trigonal pyramid geometry. In this case,  $\tau_4$  is equal to 0.819 (close to 0.85). Therefore, this value shows the trigonal pyramid geometry of  $[HgCl_4]^{2-}$  anions. Indeed, these results correspond to those observed in comparable compounds [39–44].

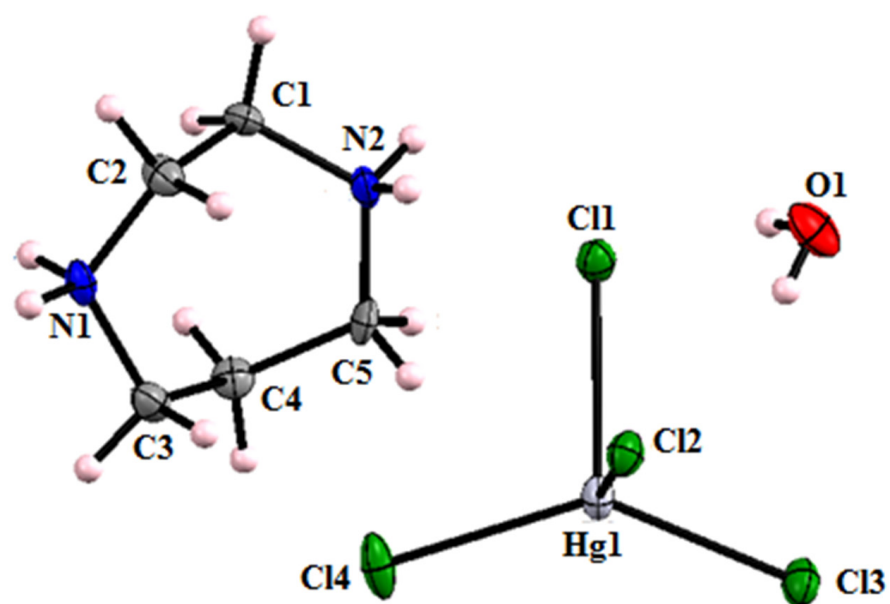


Figure 2. The asymmetric unit of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ .

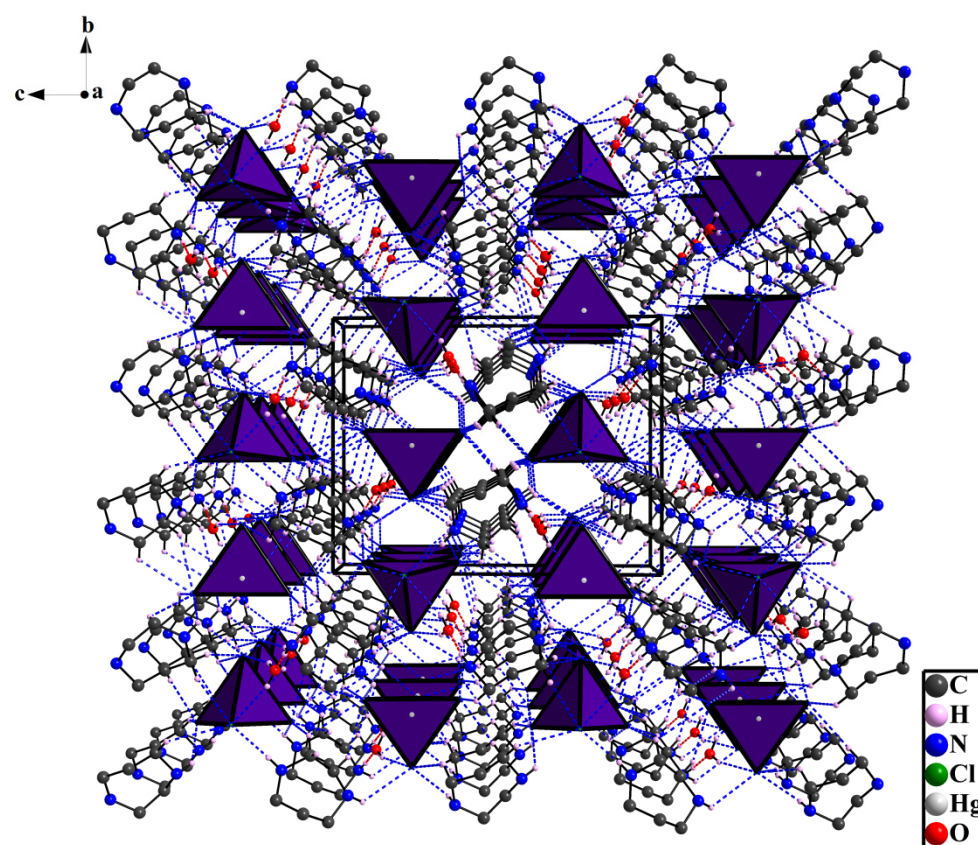
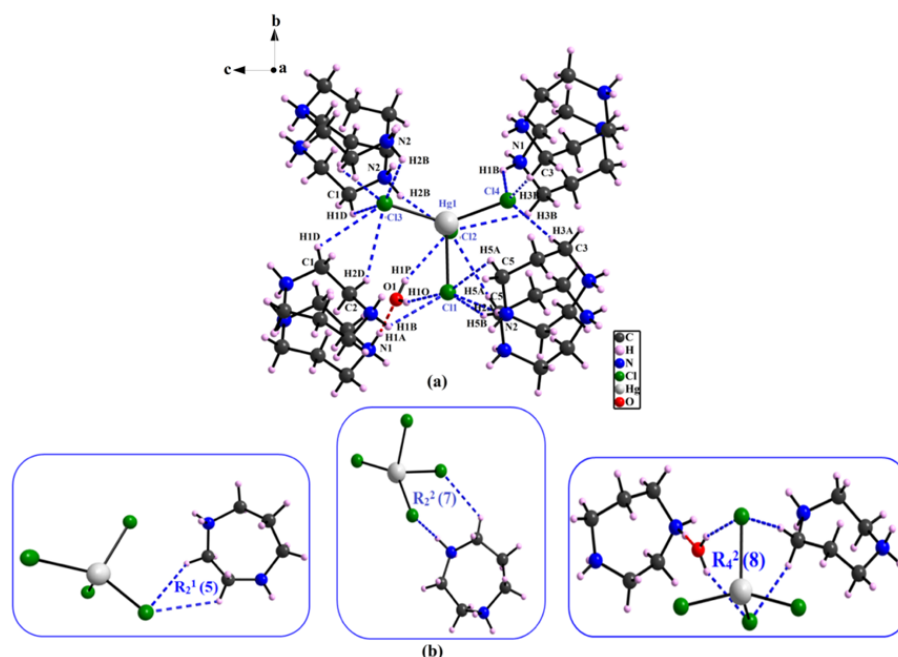


Figure 3. Perspective view of the  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  compound (the red and blue lines represent hydrogen bonds).



**Figure 4.** (a) The intermolecular H-bonds between the organic cation (homopiperazinium) and chlorine anion ( $\text{Cl}^-$ ), between the organic cation and  $\text{H}_2\text{O}$  molecule, and between the water molecule and chlorine anion; (b) the different ring motifs in  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$ .

The organic cations  $[\text{C}_5\text{H}_{14}\text{N}_2]^{2+}$  are intercalated between the inorganic entities to ensure the balance charge of  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$ . The geometrical properties of the organic cations  $[\text{C}_5\text{H}_{14}\text{N}_2]^{2+}$ , summarized in Table S2, are consistent with those reported in the literature [45]. Each cation establishes thirteen hydrogen bonds among them. Two are bifurcated:  $\text{N1-H1B} \dots (\text{Cl1}^{\text{iii}}, \text{Cl4}^{\text{vi}})$  and  $\text{N2-H2B} \dots (\text{Cl2}^{\text{ii}}, \text{Cl3}^{\text{i}})$  (For symmetry codes, see Table S1). The conformation of the  $[\text{C}_5\text{H}_{14}\text{N}_2]^{2+}$  ring may be defined in terms of Cremer and Pople puckering coordinates [46], and it was shown that  $Q = 0.7906 \text{ \AA}$ ,  $q_2 = 0.4355 \text{ \AA}$ ,  $q_3 = -0.6599$ ,  $\theta = 33.43^\circ$ , and  $\varphi = 50.93^\circ$ , identical to the most stable chair conformation. This result can be confirmed by the asymmetrical parameters.

Table S2 gathers the values of the distances and angles of the different entities constituting the structure of the title compound.

### 3.3. Hirshfeld Surface Analysis

Using CrystalExplorer software [47], we can determine the nature of the intermolecular interactions present in  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  using 3D Hirshfeld surface analysis (HS), while the 2D fingerprint traces quantitatively reveal the contributions of interactions in the crystalline edifice. The Hirshfeld surfaces (HS) around the asymmetric unit are portrayed in Figure 5, presenting the surfaces that were mapped over  $d_{\text{norm}}$  (Figure 5a), curvedness (Figure 5b), and shape index (Figure 5c) surfaces. Dark-red dots found in the  $d_{\text{norm}}$  view represent the contacts of the H-bonds:  $\text{H} \dots \text{Cl}$  and  $\text{H} \dots \text{O}$  (Figure 6).

The value 59.6% is attributed to the dominant contacts, which are  $\text{H} \dots \text{Cl}/\text{Cl} \dots \text{H}$ , corresponding to the interactions  $\text{C-H} \dots \text{Cl}$ ,  $\text{N-H} \dots \text{Cl}$ , and  $\text{O-H} \dots \text{Cl}$  (Figure 7a). They are illustrated by a pair of sharp spikes characteristics in the 2D fingerprint plot. Furthermore, because of the abundance of chlorine and hydrogen on the molecular surface, these connections are the most common contacts: in this case, the  $S_{\text{Cl}}$  is 32.35%, and the  $S_{\text{H}}$  is 61.6%, with an enrichment rate larger than the unity  $E_{\text{HCl}} = 1.495$  (Table 2). The  $\text{H} \dots \text{H}$  contacts occupy 27.2% of the total surface, due to the abundance of hydrogen at the molecular surface with  $E_{\text{HH}} = 0.719$ . The  $\text{H} \dots \text{H}$  contacts are illustrated by a large spot located in the middle of the 2D fingerprint (Figure 7b). The percentage 8.1% is reserved for the third interactions in the  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$ , which are  $\text{H} \dots \text{O}/\text{O} \dots \text{H}$  contacts with an enrichment rate greater than the unit  $E_{\text{HO}} = 1.623$  (Figure 7c). They refer to  $\text{N-H} \dots \text{O}$

hydrogen bonds type.  $\text{Hg} \dots \text{Cl}/\text{Cl} \dots \text{Hg}$  contacts contribute 2.5% of the total surface (Figure 7d). The percentages 1.3% and 1.1% are assigned, respectively, to the  $\text{Cl} \dots \text{Cl}$  contacts and to the  $\text{Hg} \dots \text{H}/\text{H} \dots \text{Hg}$  interactions (Figure 7e,f). Additionally, Figure 8 illustrates the produced crystal's void region. The voids in the crystalline substance were observed by generating an isosurface of the electron density (0.002 a.u.). The volume of the empty surface per unit cell is about  $72.91 \text{ \AA}^3$ , and its surface area is  $295.82 \text{ \AA}^2$ . The crystal unit lattice has a void percentage around 5.844%.

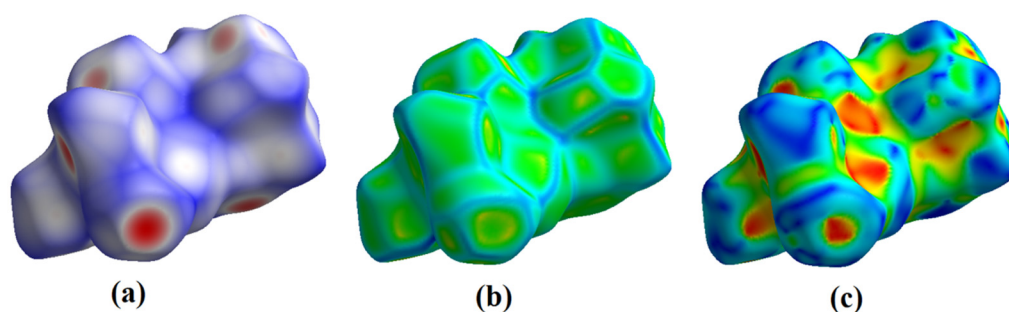


Figure 5. HS mapped over  $d_{\text{norm}}$  (a), curvedness (b), and shape index (c) surfaces.

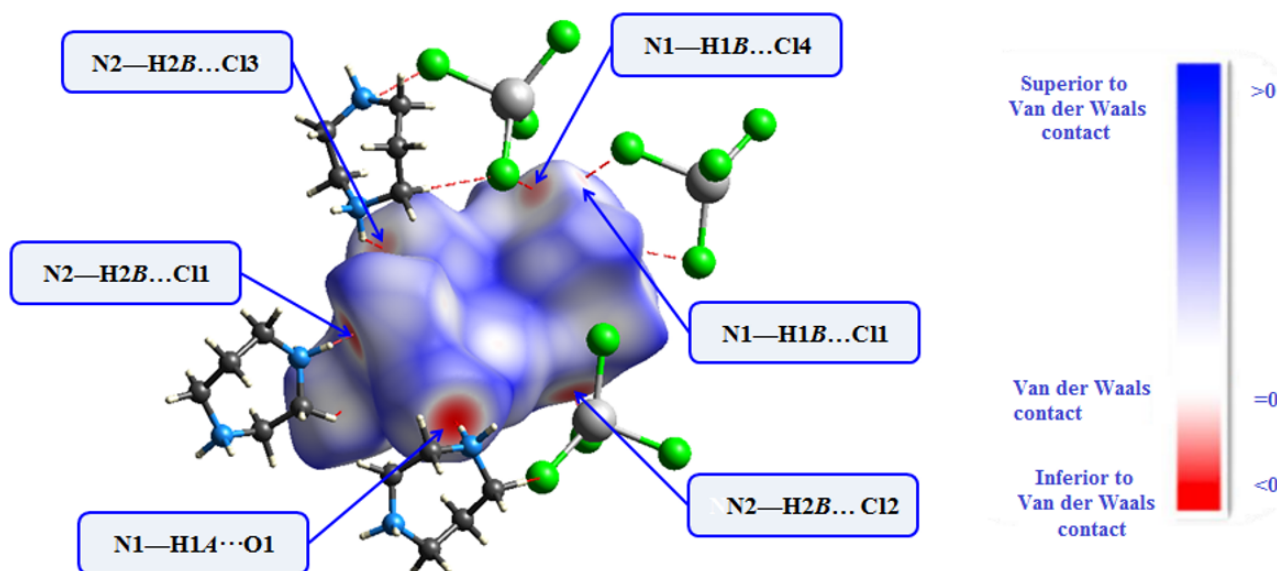
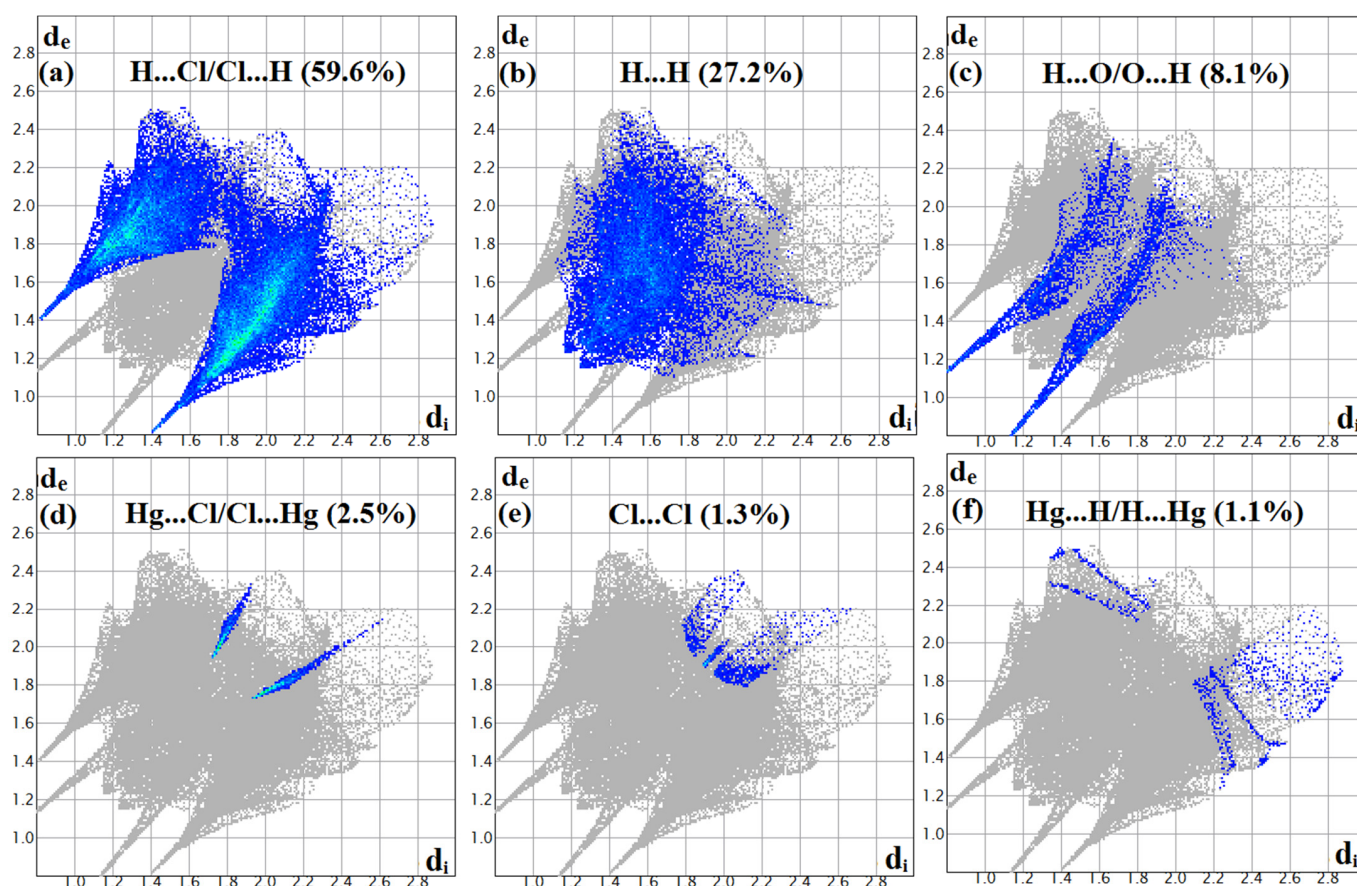


Figure 6. H-Bonds present in the  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4] \cdot \text{H}_2\text{O}$  compound.

Table 2.  $E_{\text{XY}}$ (enrichment reports) of  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4] \cdot \text{H}_2\text{O}$ .

| Atoms     | Hg  | Cl    | O    | H    |
|-----------|-----|-------|------|------|
| % Surface | 1.8 | 32.35 | 4.05 | 61.6 |
| Hg        |     | 2.15  |      | 0.50 |
| Cl        |     | 0.12  |      | 1.49 |
| O         |     |       |      | 1.62 |
| H         |     |       |      | 0.72 |



**Figure 7.** Relative contributions of various intermolecular interactions to the Hirshfeld surface area of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ : (a)  $H \dots Cl/Cl \dots H$  contacts; (b)  $H \dots H$  contacts; (c)  $H \dots O/O \dots H$  contacts; (d)  $Hg \dots Cl/Cl \dots Hg$  contacts; (e)  $Cl \dots Cl$  contacts; (f)  $Hg \dots H/H \dots Hg$  contacts.

### 3.4. Vibrational Study

Figure 9 shows the IR spectrum of the crystal  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ . We will determine the different functional groups using published research of similar materials possessing the same organic cation [48–52]. In Table S3, we propose an attempt to designate this compound's most representative vibrational modes.

The bands located at  $3522$  and  $3433\text{ cm}^{-1}$  correspond to the valence vibrations of the water molecule. In the region of wavenumbers between  $3200$  and  $2700\text{ cm}^{-1}$ , there are four broad bands. The first two bands detected at  $3127$  and  $3012\text{ cm}^{-1}$  are assigned to the asymmetric and symmetric N–H bond stretching, respectively. The remaining two bands observed at  $2840$  and  $2776\text{ cm}^{-1}$  are attributed to the asymmetric and symmetric C–H stretching, respectively. The thin band at  $1625\text{ cm}^{-1}$  corresponds to  $NH_2$  in-plane deformation vibration. On the other hand, the intense band appearing at  $1572\text{ cm}^{-1}$  corresponds to the  $\delta(C-N-H)$  asymmetric bending. The band located at  $1456\text{ cm}^{-1}$  is attributed to  $\delta(CH_2)$ . The two low-intensity bands at  $1225$  and  $1125\text{ cm}^{-1}$  correspond to the C–N stretching. The band at  $1068\text{ cm}^{-1}$  is assigned to C–C stretching. The rocking vibration band,  $\rho(NH_2)$ , is located at  $979\text{ cm}^{-1}$ . The two bands at  $883$  and at  $829\text{ cm}^{-1}$  correspond to  $\delta(C-C-C)$  ring bending vibrations, while the band seen at  $531\text{ cm}^{-1}$  is attributed to the deformation vibrations  $\delta(C-N-C)$  and to the deformation vibrations  $\delta(C-C-N)$ .

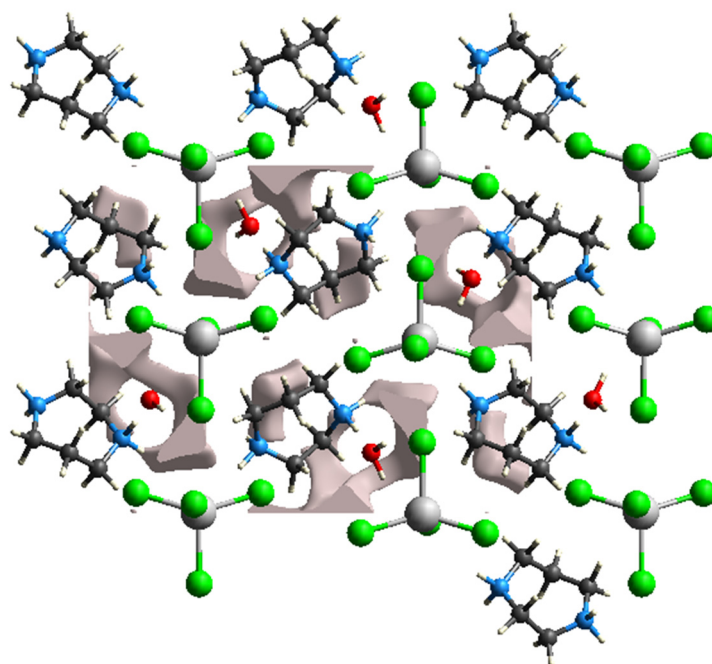


Figure 8. The crystal voids: 0.002 a.u. electron-density isosurfaces.

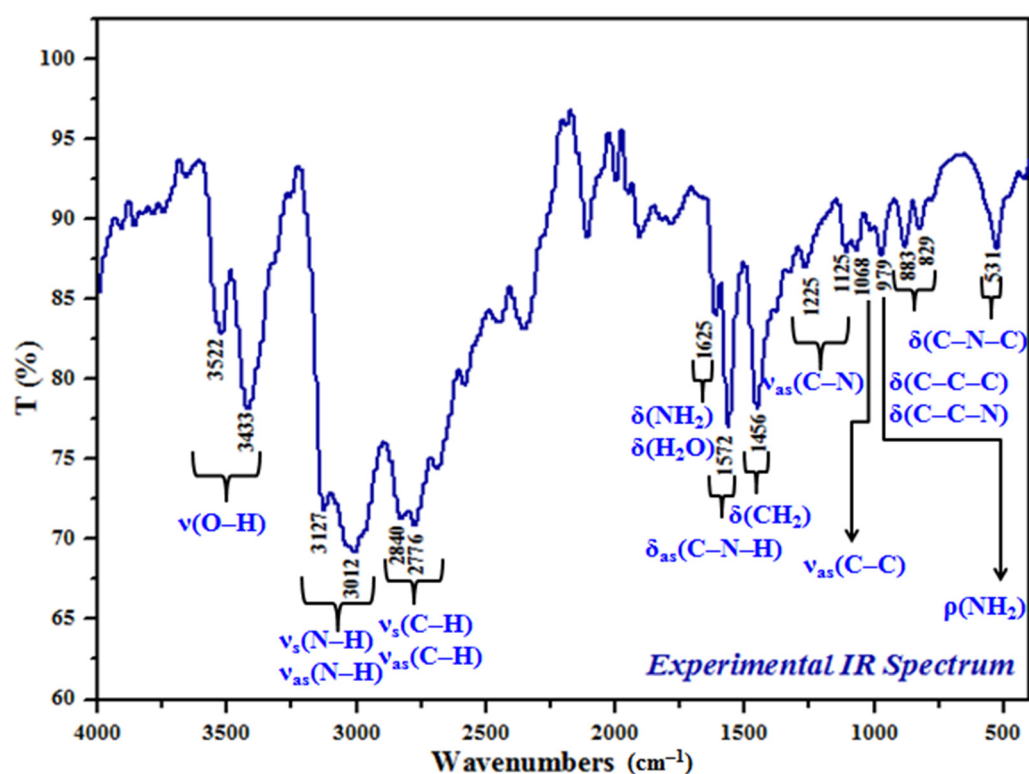


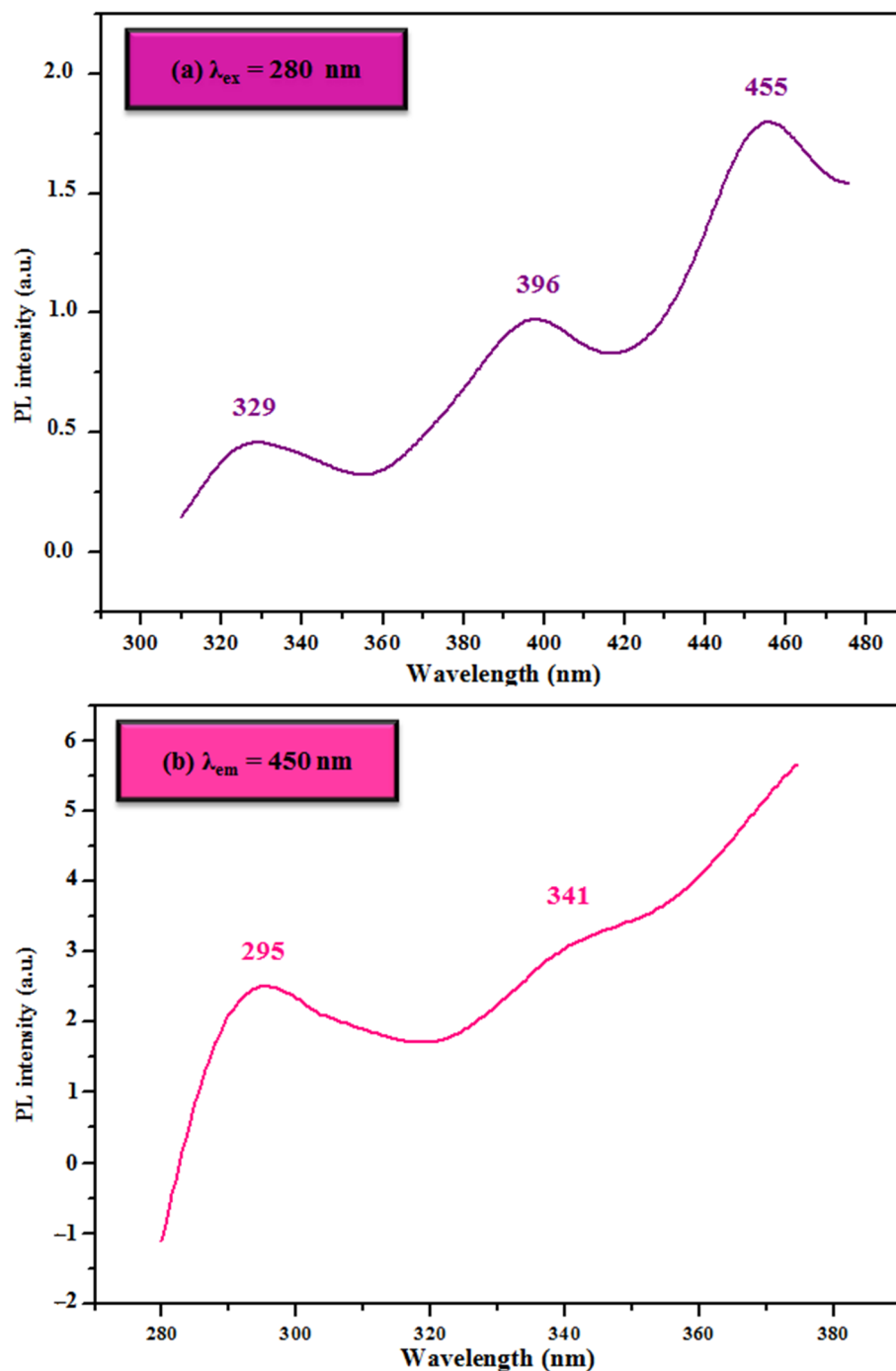
Figure 9. IR absorption spectrum of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ .

### 3.5. Fluorescence Properties

We performed photoluminescence (PL) measurements to determine the transmission mode of the light radiation emitted by the compound following excitation. This method is used to examine the optical emission properties of materials.

The excitation and emission spectra of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  are shown in Figure 10 at ambient temperature and in the solid state. The excitation spectrum is recorded for a wavelength of the order of 280 nm, and three bands are observed, of which the most intense

is detected around 455 nm. The emission spectrum is constituted by two bands; the first band is observed at 295 nm, and the second band is detected at 341 nm (the most intense). These two bands may mainly arise from ligand-metal charge transfer (LMCT) [53,54].



**Figure 10.** PL spectrum of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ .

### 3.6. Thermal Behavior

Figure 11 highlights the results obtained by the thermal analysis of the compound  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ . According to the TGA-DTA curve, four peaks were detected in the DTA curve, and three mass losses in the TGA curve. The first peak at 370 K corresponds to the elimination of the water molecule, with a loss of mass of 3.605% (experimentally) vs. 3.8% (theoretically). The second and the third peaks are observed at 510 ( $\Delta H = 415.279 \text{ J} \cdot \text{g}^{-1}$ ) and at 539 K, and they correspond to the departure of the organic part  $(C_5H_{14}N_2)^{2+}$  and

four chlorine atoms, with a mass loss theoretically equal to 52.739% and experimentally to 53%. The fourth peak, located at 615 K ( $\Delta H = 495.741 \text{ J}\cdot\text{g}^{-1}$ ), corresponds to the Hg atom's escape, with a mass loss of 43% (experimentally)/43.3% (theoretically). The black residue (10%) obtained at the end of the analysis is formed by a mixture of mercury oxide and carbon.

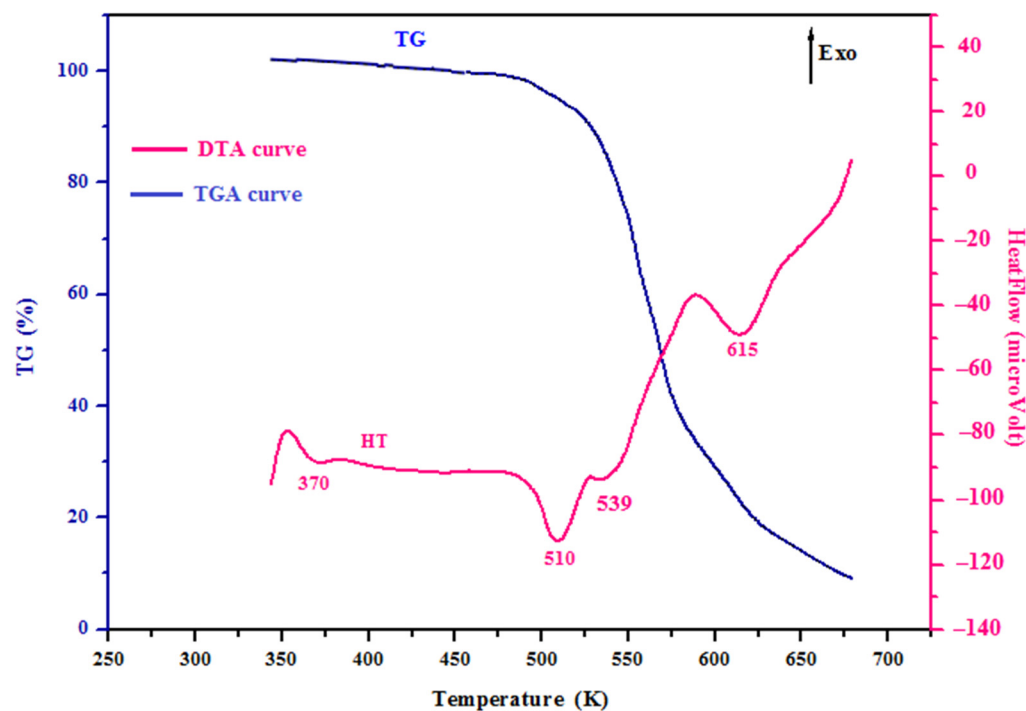


Figure 11. TGA-DTA curves for  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$ .

### 3.7. Dielectric Constant Investigation

We suggest investigating the electric transport capabilities of the compounds created in order to explore probable ionic conduction. To investigate the conductivity of the compound, we generated a pellet with geometric factor  $g = e/s = 0.197 \text{ cm}^{-1}$ .

Electrical conductivity measurements provide insight into the behavior of charge carriers in a dielectric conductivity field, as well as their mobility and conduction processes. Crystals have greater temperature conductivity due to inherent flaws created by thermal fluctuations, as proven for the Hg complex [55], where the activation energy  $E_a$  was approximately 0.72 eV.

#### 3.7.1. The Dielectric Constants ( $\epsilon'$ and $\epsilon''$ ) Versus $\ln(f)$

The spectra in Figure 12 reveal the link between dielectric constants ( $\epsilon'$  and  $\epsilon''$ ) and frequencies. At low frequencies, these spectra exhibit dielectric dispersion, where all polarization processes contribute. In general, the polarization process is divided into four parts: electron polarization (or atomic polarization), orientation polarization (also known as dipolar polarization), ion polarization, and interfacial polarization (also called space charge polarization). However, as frequency increases, the influence of various bias mechanisms decreases. Several studies [56,57] have identified this sort of behavior, which may be explained by the polarization process. Observations of the dielectric behavior of simple salts have been made in a similar manner [58,59].

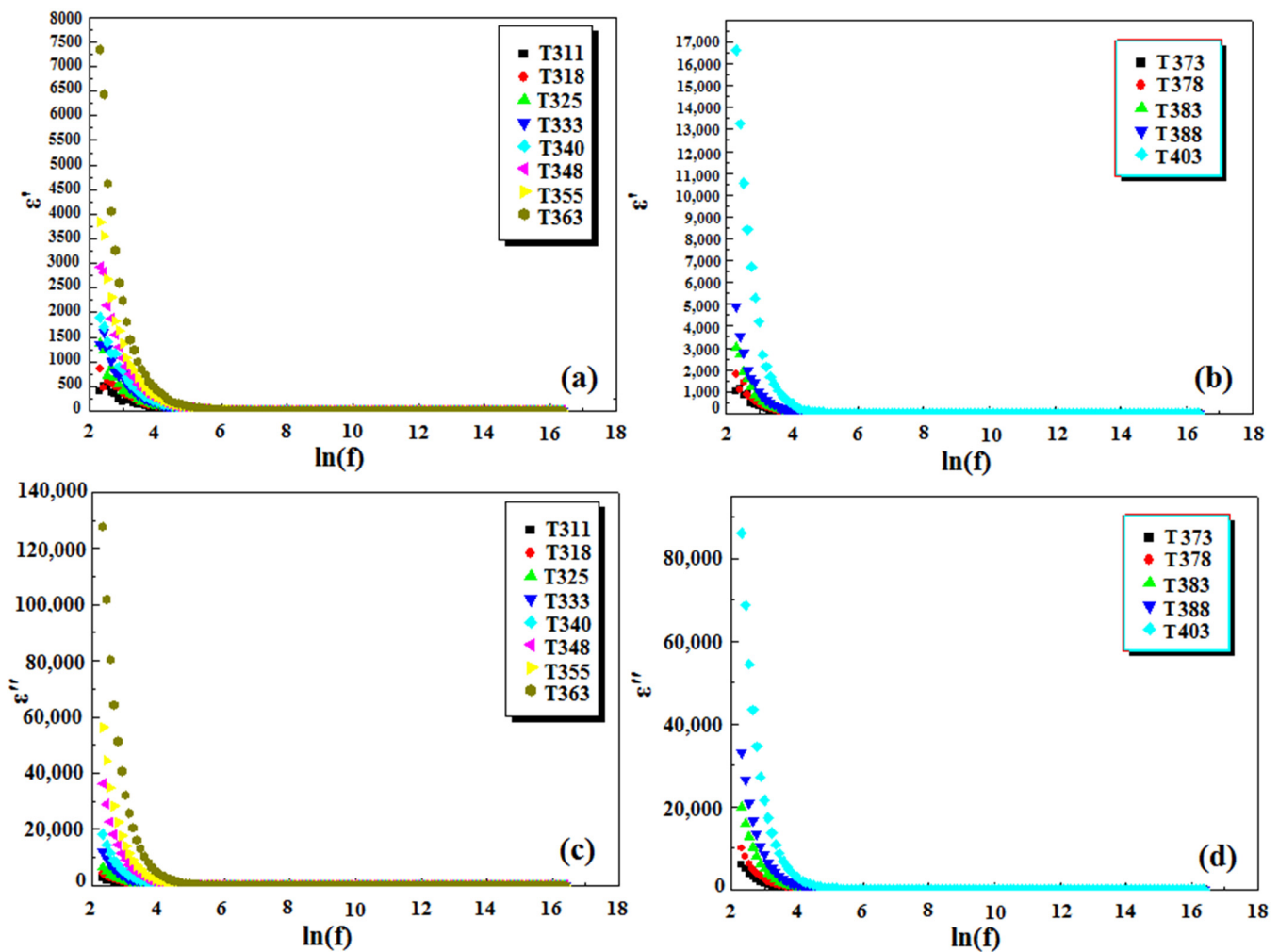


Figure 12. (a,b)  $\epsilon'$  as a function of  $\ln(f)$ ; (c,d)  $\epsilon''$  as function of  $\ln(f)$ .

### 3.7.2. Impedance Spectroscopy

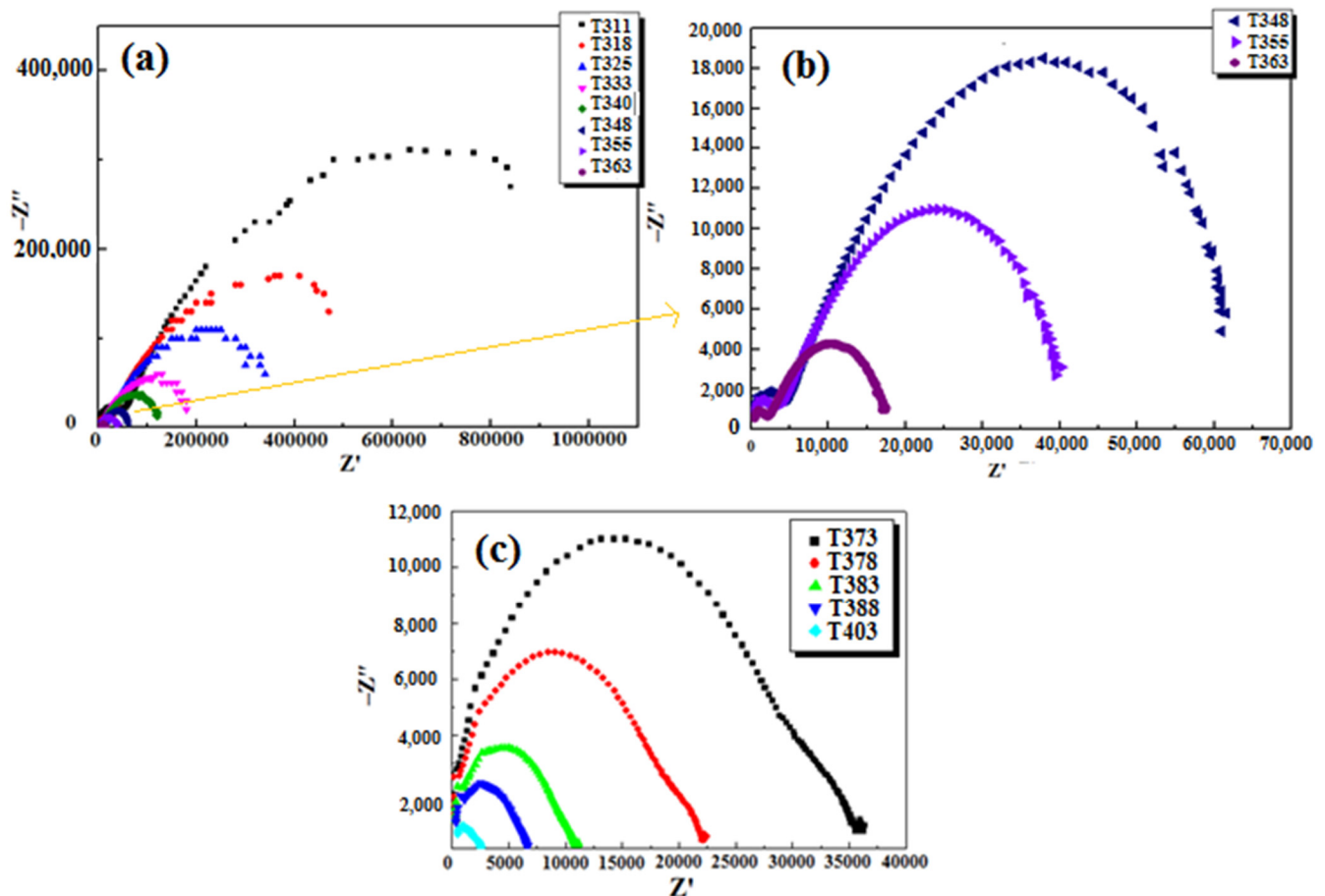
The impedance spectroscopy technique is used to examine and discriminate between the contributions of the material electrode contact and the grain and grain boundary. Semicircular arcs at high frequencies are ascribed to grain contributions, whereas semicircular arcs at low frequencies are assigned to grain boundaries [60]. The impedance spectrum of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  is shown in Figure 13 between 311 and 403 K. We noted that the conduction is reduced by those of the grain boundaries at temperatures below 363 K (Figure 13a,b); on the other hand, at temperatures above 373 K, the conduction is reduced by the grains (Figure 13c). Nyquist diagram is another name for this graph. These lines, which are quite complicated, form semicircular arcs. There is a certain frequency associated with each of the experiment's data points. The diameter of the semicircle denotes the electrical resistivity of the product at the specified temperature, and the greatest resistivity value corresponds to the relaxation frequency  $\omega = 1/RC$ . Using impedance curves, it is possible to show that the radius of the semicircle decreases as the temperature rises. This is in accordance with the Cole–Cole rule [61]. The impedance  $Z$  may well be measured and expressed in the following ways as a function of resistance  $R$  and capacitance  $C$ :

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega) \quad (3)$$

$$\text{With; } Z'(\omega) = \frac{R}{1 + \omega^2 R^2 C^2} \quad (4)$$

$$Z''(\omega) = \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (5)$$

$Z'(\omega)$  and  $Z''(\omega)$  represent the real and imaginary components of the impedance created by the above equations, respectively [62]. The impedance data were matched to the equivalence of the R and C parallel systems [63].

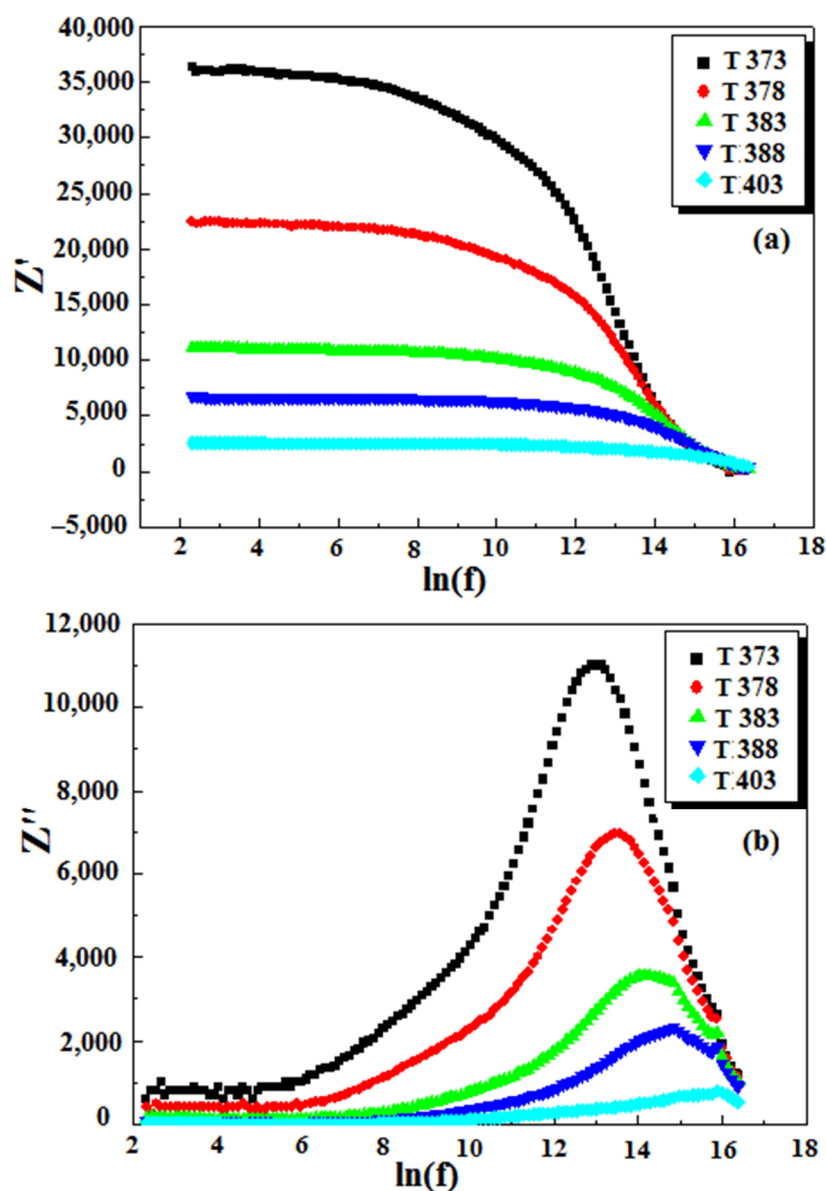


**Figure 13.** (a)— $Z''$  versus  $Z'$  of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  at the range of 311–363 K; (b) Illustrative representation of  $-Z''$  versus  $Z'$  of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  at 363, 355 and 348 K; (c)— $Z''$  versus  $Z'$  of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  at the range of 373–403 K.

The impedance analysis of this complex enables us to have a better understanding of the observed dielectric dispersion phenomena. The real component  $Z'$  and the imaginary part  $Z''$  have a frequency dependency, which illustrates the complex impedance of this sample at different temperatures (Figure 14).

In Figure 14a, we can notice that in the zone where the frequencies are high,  $Z'$  becomes independent of them, and this is manifested by the merging of the curves. Furthermore, the rise in frequencies and temperatures causes a decrease in the magnitude of  $Z'$ , but it causes an increase in the conductivity of the material. This observation might be explained by the release of space charge, which results in a decrease in the material's barrier properties as the temperature increases [64].

$Z'$  increases with frequency and reaches a maximum before quickly decreasing, as seen in Figure 14b. The value of the maxima of  $Z''$  falls gradually as frequency and temperature increase, finally merging into the high-frequency area. This might be a sign of the material's polarization effects accumulating at low frequencies and high temperatures [65].

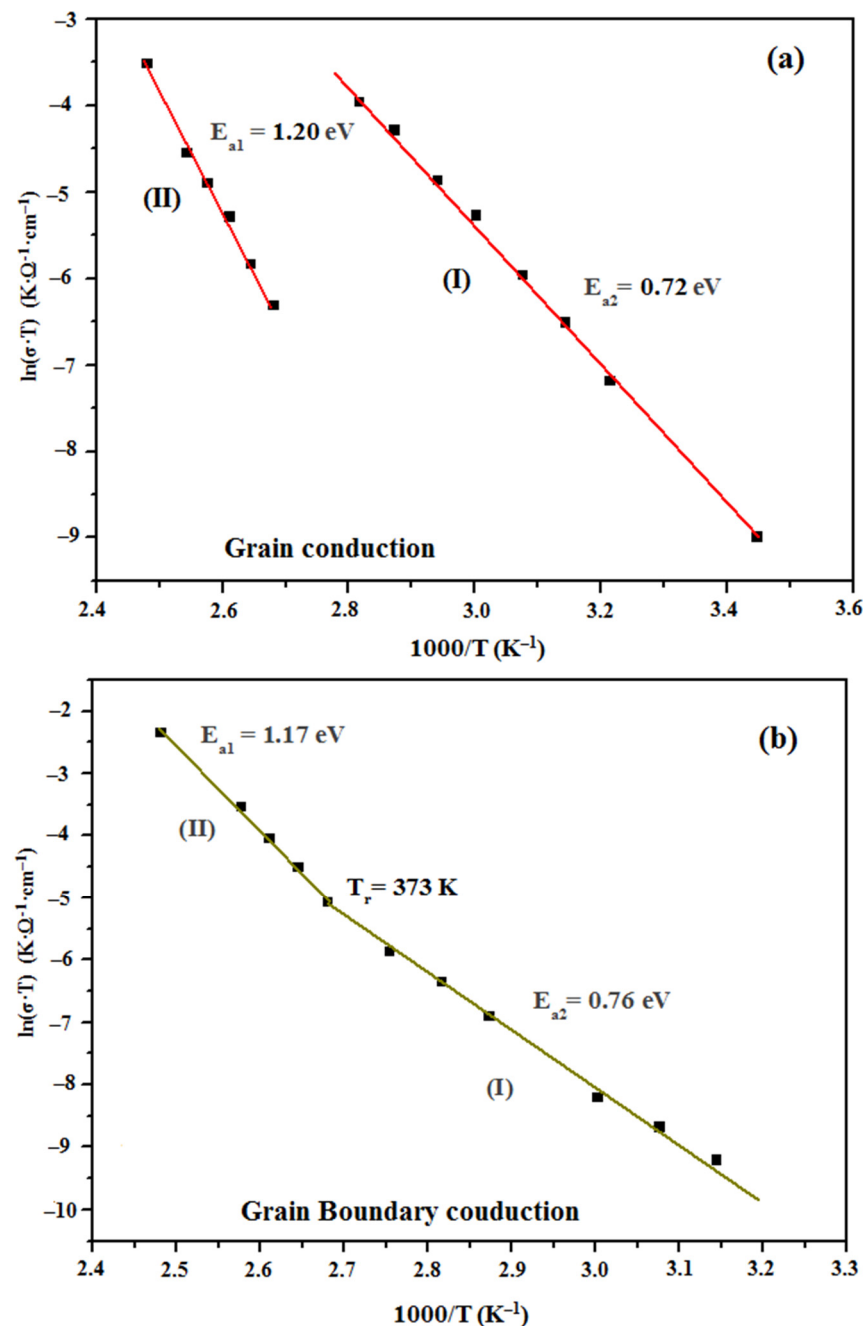


**Figure 14.** (a)  $Z'$  (real part of impedance) versus  $\ln(f)$  in the range of 373–403 K of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ ; (b)  $Z''$  (imaginary part of impedance) versus  $\ln(f)$  in the range of 373–403 K of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ .

### 3.7.3. Electric Conductivity

Based on the Arrhenius modeling equation, Figure 15 depicts the development of electrical conductivity (grain and grain boundary) as a function of temperature:  $\sigma \cdot T = A \exp(-E_a / K_B \cdot T)$  [66] (where  $E_a$  represents the activation energy,  $A$  is the pre-exponential factor,  $K$  is the Boltzmann constant, and  $T$  is the temperature in Kelvin). The curves of Figure 15a,b show a breakout towards 373 K. Indeed, the curves are made up of two parts, (I) and (II). The first part (I) is located in the region of temperatures below 363 K, while the second part (II) is placed in the region of temperatures above 373 K. The conductivity follows Arrhenius' law in both parts. According to the curves in Figure 15, there is a modification in the slope of the linear curve at  $T = 373$  K. The change in the slope can be explained by a modification of the conduction mechanisms, which causes the departure of the water molecule (dehydration) because our compound contains  $H_2O$ . This phenomenon is observed in other materials [67]. We think that the conduction is of proton origin. Protons of the synthesized material come from the organic part and from the water molecules. After

dehydration, conducting proton density decreases, inducing the sudden decrease of the conductivity observed at 373 K. This result was confirmed in the TGA-DTA part. The activation energies deduced for both conduction are very close:  $E_{a1} = 1.20$  eV and  $E_{a2} = 0.72$  eV (grain conduction), and  $E_{a1} = 1.17$  eV and  $E_{a2} = 0.76$  eV (grain boundary conduction).



**Figure 15.** (a)  $\ln(\sigma \cdot T)$  versus  $1000/T$  for  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  in the grain conduction; (b)  $\ln(\sigma \cdot T)$  versus  $1000/T$  for  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  in the grain boundary conduction. Such as the first part (I) is located in the region of temperatures below 363 K, while the second part (II) is placed in the region of temperatures above 373 K.

#### 3.7.4. Electrical Modulus

The purpose of the modulus (M)spectroscopy graph is to discern components that have the same resistance but have a different capacitance. Another fascinating feature of

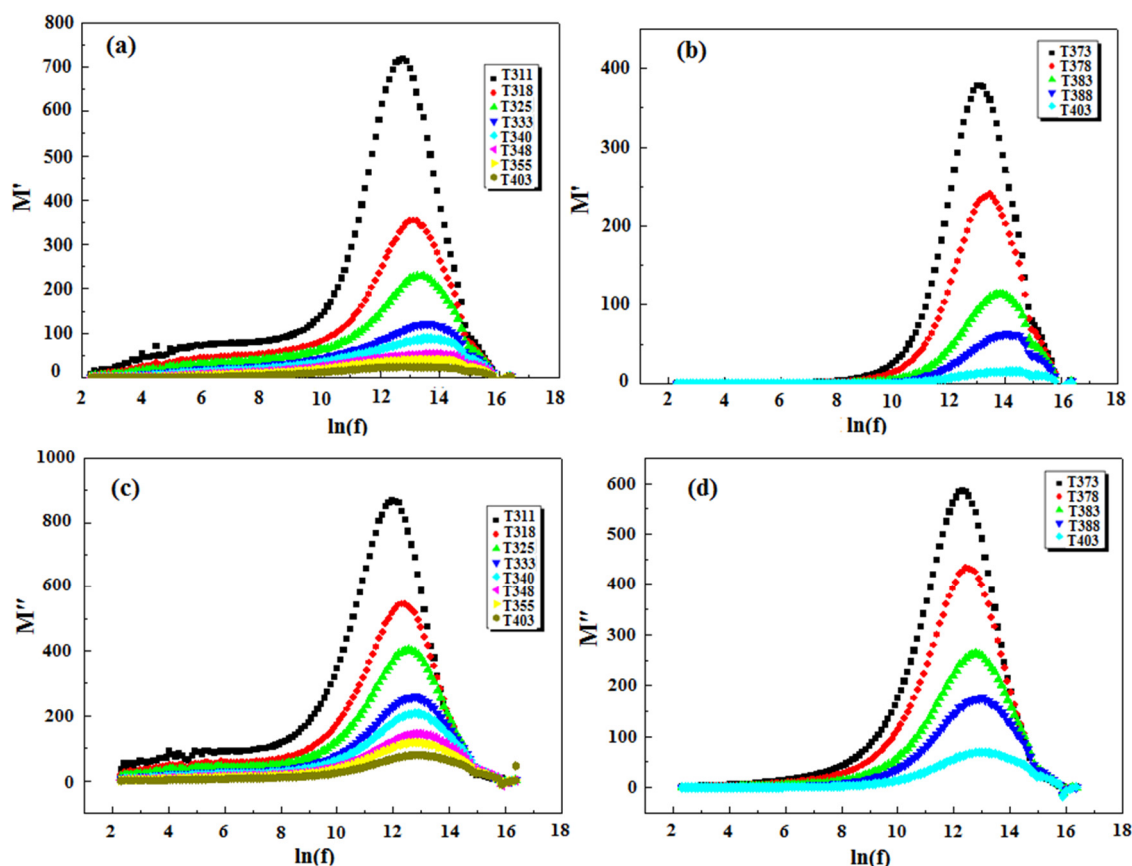
M formalism is the absence of the electrode influence. The following formula was used to calculate the complex electric modulus ( $M^*$ ):

$$M^*(\omega) = \frac{1}{\varepsilon^*} = M' + jM'' \quad (6)$$

where  $M' = \Omega C_0 Z''$ ,  $M'' = \Omega C_0 Z'$ ,  $\omega$  represent the angular frequency ( $2\pi f$ ) and  $\varepsilon^*$  is called the complex permittivity formalism, and  $C_0 = \varepsilon_0(A/t)$  represents the geometrical capacitance such that

- $\varepsilon_0$  represents the permittivity of free space;
- $A$  is the area of the electrode surface;
- $T$  expresses the thickness.

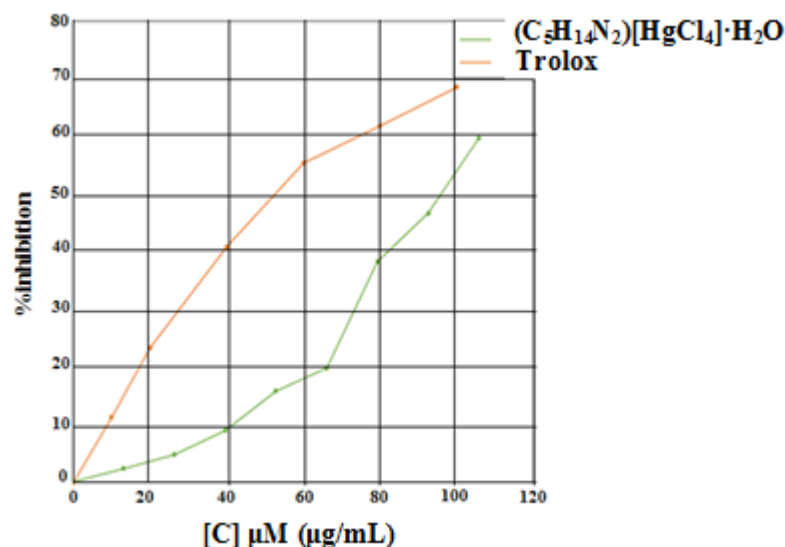
The fluctuation of the real component  $M'$  of the electrical modulus  $M'$  is seen in Figure 16a,b. The low values of  $M'$  are reported at all temperatures and in the low-frequency zone. When the frequency is raised, the value of  $M'$  grows as well, until it hits a maximum, indicating a maximum in dielectric losses. Such findings might be linked to a lack of restoring force guiding charge carrier motion under the influence of generated electric fields. This demonstrates that the electrode effect in the material has been eliminated [68]. In Figure 16c,d, at various temperatures and frequencies, the fluctuation of the imaginary part of the electrical modulus  $M''$  is shown as a function of  $\ln(f)$ , implying a connection between the movements of the mobile ions [69]. At temperatures between 311 and 403 K, a well-recognized relaxation process has been established. As the temperature rises, the relaxation peaks move to higher frequencies. The modulus spectrum's appearance shows that the material has a hopping electrical conduction process.



**Figure 16.** (a,b) Variation of  $M'$  (real part of the electrical modulus) versus  $\ln(f)$  of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  at various temperatures; (c,d) variation of  $M''$  (imaginary part of the electrical modulus) versus  $\ln(f)$  of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$  at various temperatures.

### 3.8. Discussion of Antioxidant Activity

The different concentrations of the 70% ethanolic extract (0,10,15,20,25,30,35, and 40  $\mu\text{g/mL}$ ) acted in a dose-dependent manner at various doses, with 0, 0.96, 1.95, 3.68, 6.52, 8.19, 15.85, 19.36, and 24.78% inhibition. In Figure 17, it is shown that the percentage inhibition of the free radical DPPH $\cdot$  (2,2-diphenyl-1-picrylhydrazyl) has the same pattern for the extract used. It has been observed that the percentage inhibition increases with the concentration of the 70% ethanolic extract, and it is generally lower when compared to that of the synthetic antioxidant DPPH $\cdot$ , which shows a higher antioxidant activity of the inhibition percentage.



**Figure 17.** Inhibition (%) as a function of concentrations of  $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{HgCl}_4]\cdot\text{H}_2\text{O}$  and of Trolox.

The study of the antioxidant activity of the extract from *Staviarebaudiana* using the DPPH $\cdot$  free-radical-scavenging method showed that the 70% ethanolic extract has significant antioxidant activity. This activity remains significantly lower than that of DPPH $\cdot$ , but it is a crude extract, containing a large number of different compounds. It is therefore very likely that it contains compounds which, once purified, may exhibit activity comparable to that of DPPH $\cdot$ .

The antioxidant capacity is expressed in Trolox equivalent (TEAC), which gives a value of  $\text{EC}_{50} = 18.19 \pm 0.04 \mu\text{M}$  ( $\mu\text{g/mL}$ ); it corresponds to the concentration of Trolox that gives a value of  $\text{EC}_{50}$  (Trolox) =  $19.642 \mu\text{M}$  ( $\mu\text{g/mL}$ ) having the same activity as the substance to be tested at one concentration. The result is given in  $\mu\text{M}$  ( $\mu\text{g/mL}$ ) of Trolox equivalent per g of product with a value of  $1.863 \mu\text{mol}$  Trolox/mg of extract (scavenger effect of the DPPH $\cdot$  radical).

The inhibitory activity of the different extracts [70] on a methanolic solution of DPPH $\cdot$  measured at 515 nm, was used to assess their anti-free-radical activity. This effect is explained by the transfer of single electrons from the DPPH $\cdot$ 's exterior orbital to the antioxidant, which would totally react with the radical after reaching a certain concentration. When the concentration is increased, the antioxidant is explained by the existence of multiple bioactive molecules, which is followed by the saturation of the radical's electronic layers.

## 4. Conclusions

The compound homopiperazine-1,4-diium tetrachloridomercurate (II) monohydrate crystallized in the monoclinic system, according to a single XRD. Four types of hydrogen bonds and electrostatic interactions connect the various entities that make up the crystal packing. The different types of intermolecular interactions are demonstrated by Hirshfeld surface. The homogeneity of the single crystal was confirmed by the XRD powder

analysis result. The compound's several types of functional groups were revealed by IR spectroscopy. Thermal studies (TGA-DTA) were used to determine the complex's thermal stability. At room temperature and in the solid form, luminescence research reveals an interesting fluorescence feature. Temperature and frequency were used to depict dielectric characteristics in the 311–403 K range. The Arrhenius law governs the relaxation time and electrical conductivity. The conductivity of this material has been examined as a function of frequency in the temperature range 311–403 K, where the conduction process ascribed to the ion-hopping mechanism. The test for antioxidant activity demonstrates that the produced compound exhibits antioxidant activity.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12040486/s1>, Table S1: The different H-Bonds present in  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ ; Table S2: The different distances and angles of every part in  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ ; Table S3: The main bands detected in the infrared spectrum of  $(C_5H_{14}N_2)[HgCl_4] \cdot H_2O$ : Wavenumbers values and their modes of vibration.

**Author Contributions:** Software, K.H.A. and W.F.; validation, M.H.M.; formal analysis, A.O.; investigation, A.A.A.; resources, M.A.B.; writing—original draft preparation, C.A.; supervision, C.B.N. and M.H.M.; project administration, K.M.A. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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