



Synthesis and physico-chemical studies of a novel bis [3,5-diamino-4H-1,2,4-triazol-1-ium] dichloride monohydrate

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ABSTRACT

The title new compound, $(C_2H_6N_5^+)_2 \cdot 2Cl^- \cdot H_2O$, contains two 3,5-diamino-4H-1,2,4-triazol-1-ium cations, two chloride anions and one water molecule. The crystal structure is stabilized by O - H...Cl, N - H...Cl, N - H...O and N - H...N hydrogen bonds, one of them being a three-center interaction. Strong $\pi - \pi$ stacking interactions between neighboring triazolium rings are present, with a centroid - centroid distance of 3.338 (7) Å. The exocyclic N atoms are sp^2 hybridized, as evidenced by bond lengths and angles, in agreement with an enamine-imine tautomerism. A dielectric spectroscopic study of the title compound was performed. The ^{13}C CP-MAS NMR spectrum is in agreement with crystallographic data. The infrared spectrum has been recorded at ambient temperature and interpreted on the basis of literature data. The temperature dependence of the imaginary part of the permittivity constant was analyzed with the Cole - Cole formalism in the temperature range 325 - 375 K.

Indexing terms/Keywords

X-ray diffraction; IR spectroscopy; CP-MAS NMR; DFT calculations; dielectric spectroscopy.

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INTRODUCTION

Chemists and physicists of the solid state have shown an increasing interest in the study of halide anion salts containing organic cations owing to their numerous practical and potential applications in various fields such as supramolecular chemistry [1] and biochemical processes [2]. Among all halide anions, the chloride one has been successfully used to assemble double - helical motifs of various molecules [3]. We report here the synthesis and the crystal structure of a new member of this family, $(C_2H_6N_5^+)_2 \cdot 2Cl^- \cdot H_2O$ (I), which was isolated during our studies of the preparation of new organic hydrochloride compounds [4, 5].

2. Experiment

2.1. Chemical preparation

An aqueous 1M HCl solution and 3,5-diamino-1,2,4-triazole in a 1:1 molar ratio were mixed and dissolved in sufficient ethanol. Crystals of (I) grew as the ethanol evaporated at 293 K over the course of a few days (yield = 65 %).

2.2. Investigation techniques

The characterization of the title compound was carried out by X-ray diffraction, solid state NMR, IR and dielectric spectroscopies and DFT calculations.

2.2.1. X-ray single crystal structural analysis

A suitable crystal was selected and mounted on a Gemini kappa-geometry diffractometer (Agilent Technologies UK Ltd) equipped with an Atlas CCD detector and using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensities were collected at 100 K by means of the CrysAlisPro software [6]. Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysAlisPro software [6]. Analytical absorption correction was applied using the modeled faces of the crystal [7]. The structure was solved by direct methods with SIR97 [8] and the least-square refinement on F^2 was achieved with the CRYSTALS software [9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93 - 0.98, N---H in the range 0.86 - 0.89 and O---H = 0.82 \AA) and $U_{iso}(H)$ (in the range 1.2 - 1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The drawings were made with Diamond [10]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

2.2.2. Physical measurements

The ^{13}C NMR spectrum of the title compound was recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. The chemical shifts are given relative to tetramethylsilane (precision 0.5 ppm). The spectra were recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons. The IR spectrum was recorded in the range 4000 - 400 cm^{-1} with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet. A 7280 DSP Lock-in Amplifier was used in the frequency range 100 Hz - 2 MHz for dielectric measurements. The finely grain samples were pressed into pellets of 8 mm diameter and 1.2 mm thickness using a hydraulic press at 3000 Kg/cm^2 . Contacts were made by coating the surfaces of the sample with silver paste. Measurements were made in the temperature range 325 - 375 K. The temperature regulation was provided by a programmable DC power supply (HP E3632A), a programmable Keithley multimeter (Model 2000) and an oven developed in our laboratory. The temperature was controlled to within $\pm 0.1 \text{ }^\circ\text{C}$. Before performing the measurement, a sufficient time was allowed for thermal stabilization.

2.2.3. DFT calculations

The infrared spectrum was calculated with the Gaussian 09 software by using different starting molecules: only one organic cation, the organic cation and the chlorine atom linked to it and all the atoms of the asymmetric unit. The positions of the protons were optimized in all cases by using the B3LYP/6-31++G** method and finally the infrared spectra was calculated. In all cases at least one imaginary frequency (close to zero) was obtained and finally a calculation was made with only one organic cation and a full optimization before determination of the frequencies. In that case no imaginary frequency was obtained and a comparison of the frequencies at wavenumbers higher than 400 cm^{-1} showed that quite the same results (in terms of position, intensity and nature of vibration) were obtained than with the other systems for the vibrations having a sufficient intensity (naturally in the case of the system containing all the atoms of the asymmetric unit the bands were dedoubled). Finally the spectrum was drawn by broadening the peaks with a lorentzian.



Table 1. Experimental details

Crystal data	
Chemical formula	2(C ₂ H ₆ N ₅)·H ₂ O·2(Cl)
<i>M_r</i>	289.15
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0785 (5), 24.680 (2), 8.1521 (6)
β (°)	93.656 (7)
<i>V</i> (Å ³)	1220.47 (17)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	0.54
Crystal size (mm)	0.41 × 0.38 × 0.25
Data collection	
Diffractometer	Xcalibur, Atlas, Gemini ultra diffractometer
Absorption correction	Multi-scan <i>CrysAlis PRO</i>
<i>T_{min}</i> , <i>T_{max}</i>	0.930, 1.000
No. of measured, independent and observed [<i>I</i> > 2.0σ(<i>I</i>)] reflections	7662, 2980, 2505
<i>R_{int}</i>	0.034
(sin θ/λ) _{max} (Å ⁻¹)	0.697
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.053, 1.05
No. of reflections	2980
No. of parameters	155
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.49, - 0.42

3. Results and discussion

3.1. Structure description

The main geometrical features of the different chemical entities of the coordination compound (C₂H₆N₅)₂, 2Cl⁻·H₂O are reported in Tables 2 and 3.

As shown in Fig. 1, the asymmetric unit of the crystal structure of the title compound contains two 3,5-diamino-4H-1,2,4-triazol-1-ium cations, two chloride anions and one water molecule. The organic cations containing the N(4), N(5), N(7), N(9) and N(10) nitrogen atoms are interconnected via N(7) - H(71)···N(4)ⁱⁱⁱ hydrogen bonds to form organic chains running along the *c*-axis direction at *y* = (2*n* + 1) / 4 (Fig. 2, Table 1). The organic cations containing the N(11), N(13), N(14), N(16) and N(17) nitrogen atoms are associated via N(11) - H(111)···N(13)^{vii} hydrogen bonds leading to the formation of dimers characterized by strong π - π stacking interactions between neighboring triazolium rings, with a centroid - centroid distance of 3.338 (7) Å [11] (Fig. 3). These dimers, the Cl⁻ anions and the water molecules are located between the organic chains through a set of hydrogen bonds. Fig. 2 and Table 1 show that the Cl⁻(1) anion is acceptor of six hydrogen bonds, while the Cl⁻(2) anion is involved in four hydrogen bonds. The water molecule is donor in two O -



H...Cl hydrogen bonds and acceptor in two N - H...O hydrogen bonds. The organic cations are interconnected via N - H...N hydrogen bonds. Among all the hydrogen bonds of the network, one is bifurcated N(5) - H... (Cl(1), O(3)).

Examination of the organic moiety geometrical features (Table 2) shows that the exocyclic N(9) - C(8), N(10) - C(6), N(11) - C(12) and N(17) - C(15) bond lengths of 1.344 (2), 1.330 (2), 1.353 (2) and 1.323 (2) Å, respectively, are approximately equal to a typical C=N double bond, indicating that the nitrogen atoms N(9), N(10), N(11) and N(17) are sp^2 hybridized. This assumption is well confirmed by the sum of the angles, close to 360° around these four atoms [12]. This suggests that the starting reagent exists as a mixture of imine - enamine tautomers.

Table 2. Selected geometric parameters (Å, °)

N4 - N5	1.400 (2)	N11 - C12	1.353 (2)
N4 - C8	1.319 (2)	C12 - N13	1.310 (2)
N5 - C6	1.322 (2)	C12 - N16	1.385 (2)
C6 - N7	1.356 (2)	N13 - N14	1.402 (2)
C6 - N10	1.330 (2)	N14 - C15	1.323 (2)
N7 - C8	1.373 (2)	C15 - N16	1.353 (2)
C8 - N9	1.344 (2)	C15 - N17	1.323 (2)
N5 - N4 - C8	103.33 (15)	N13 - C12 - N16	111.61 (17)
N4 - N5 - C6	111.51 (15)	C12 - N13 - N14	103.36 (15)
N5 - C6 - N7	106.76 (16)	N13 - N14 - C15	111.78 (16)
N5 - C6 - N10	127.61 (18)	N14 - C15 - N16	106.56 (16)
N7 - C6 - N10	125.58 (17)	N14 - C15 - N17	126.55 (18)
C6 - N7 - C8	106.76 (15)	N16 - C15 - N17	126.88 (18)
N7 - C8 - N4	111.62 (16)	C12 - N16 - C15	106.66 (15)
N7 - C8 - N9	123.14 (17)	C15 - N17 - H171	121.7
N4 - C8 - N9	125.24 (18)	C15 - N17 - H172	119.1
N11 - C12 - N13	125.97 (18)	H171 - N17 - H172	118.9
N11 - C12 - N16	122.35 (17)		

Table 3. Selected hydrogen-bond interactions

<i>D</i> - H... <i>A</i>	<i>D</i> - H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> - H... <i>A</i>
O3 - H31...Cl2 ⁱ	0.82	2.32	3.127 (2)	170
O3 - H32...Cl1 ⁱⁱ	0.80	2.35	3.150 (1)	178
N5 - H51...Cl1	0.85	2.79	3.408 (4)	130
N5 - H51...O3	0.86	2.14	2.857 (3)	141
N7 - H71...N4 ⁱⁱⁱ	0.85	2.06	2.832 (3)	150
N9 - H91...Cl1 ^{iv}	0.85	2.48	3.322 (4)	170
N9 - H92...Cl2 ^v	0.86	2.44	3.296 (1)	171
N10 - H101...Cl2 ^{vi}	0.83	2.67	3.247 (1)	128
N10 - H102...Cl1	0.85	2.36	3.158 (1)	155
N11 - H111...N13 ^{vii}	0.86	2.24	3.068 (3)	163
N14 - H141...O3 ^{viii}	0.85	2.0	2.803 (3)	153
N16 - H161...Cl2	0.85	2.32	3.162 (4)	173
N17 - H171...Cl1 ⁱⁱ	0.84	2.52	3.246 (7)	145
N17 - H172...Cl1 ^{viii}	0.85	2.41	3.244 (2)	167

Symmetry codes : (i) $x, y, z-1$; (ii) $x-1, y, z$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x-1/2, -y+1/2, z+1/2$; (v) $x-1/2, -y+1/2, z-1/2$; (vi) $x+1, y, z$; (vii) $-x+3, -y+1, -z+2$; (viii) $-x+2, -y+1, -z+1$.

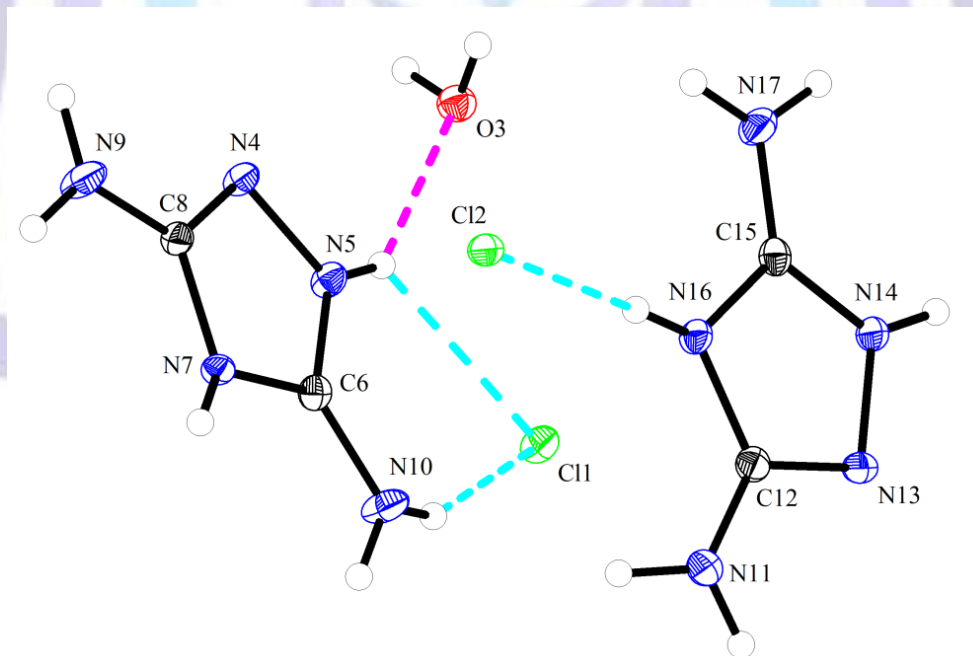


Figure. 1 A view of the title compound, showing 50% probability displacement ellipsoids and spheres for the H atoms. Hydrogen bonds are shown as broken lines.

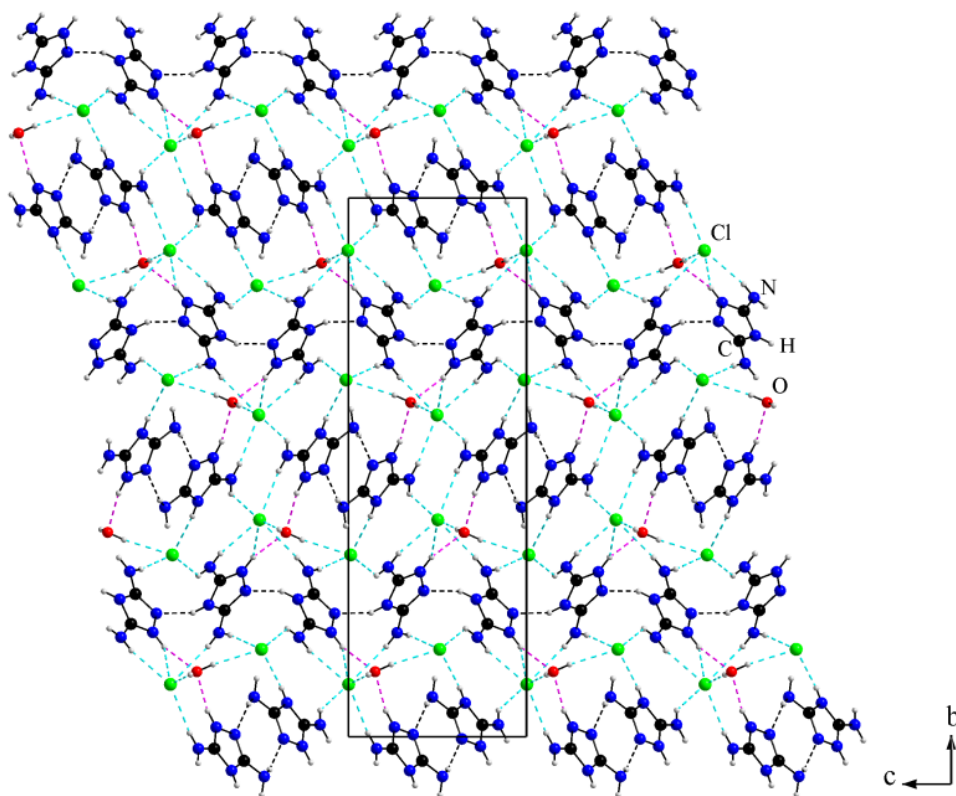


Figure. 2 The packing diagram of the compound viewed down the *a*-axis. Hydrogen bonds are shown as broken lines.

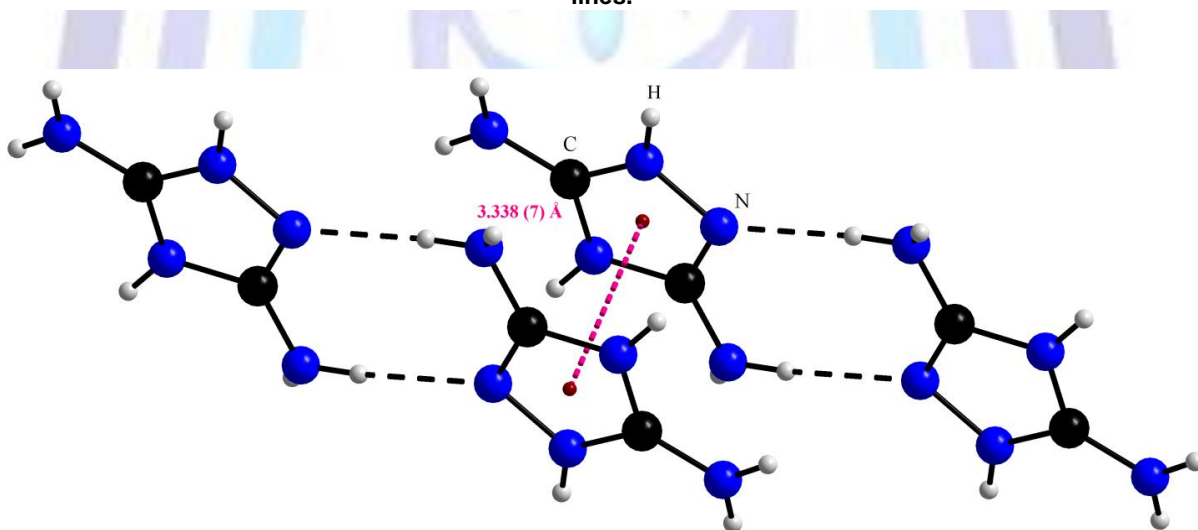


Figure. 3 π - π stacking interactions between neighboring triazolium rings in the title compound. Hydrogen bonds are shown as broken lines.

3.2 NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of $(\text{C}_2\text{H}_6\text{N}_5^+)_2 \cdot 2\text{Cl}^- \cdot \text{H}_2\text{O}$ is shown in Fig. 4. It exhibits only one broad and quite asymmetric resonance signal at ca. 150 ppm corresponding to the four crystallographically independent aromatic carbon atoms. The peaks of these carbon atoms are overlapping probably due to their relatively similar chemical environments.

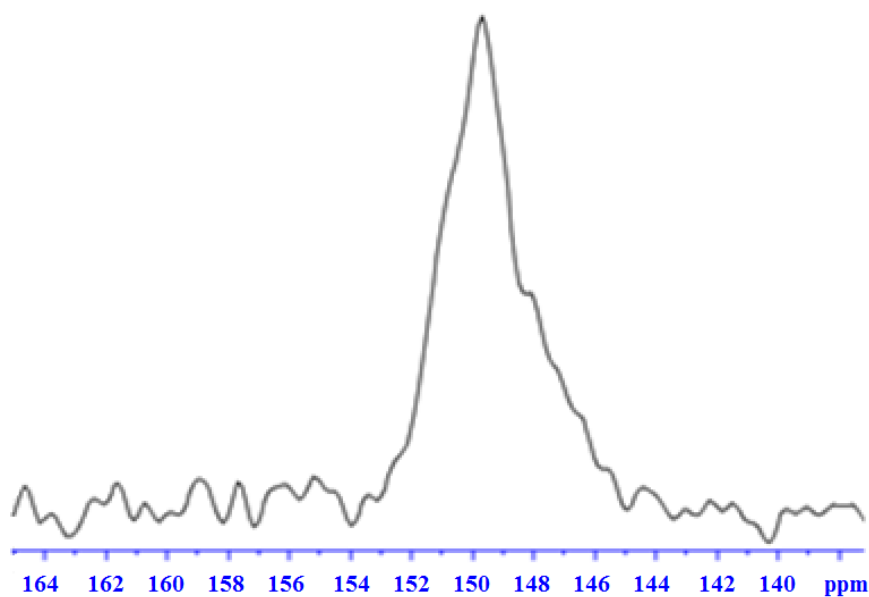


Figure. 4 ^{13}C CP-MAS NMR spectrum of $(\text{C}_2\text{H}_6\text{N}_5^+)_2, 2\text{Cl}^-\cdot\text{H}_2\text{O}$.

3.3 IR absorption spectroscopy

FTIR spectroscopy was used to verify the functional groups present in the crystal and their vibrational behavior in the solid state. Hydrogen bonding interactions are able to affect both frequency as well as intensity and width of the vibrations. The IR spectrum of the title crystalline compound is shown in Fig. 5. The characteristic vibrational modes of these compounds can be compared to those of similar materials [13 - 15]. In the high frequency region, the observed bands between 3600 and 3100 cm^{-1} can be assigned to the OH stretching mode and to the asymmetric and symmetric stretching modes of the NH_2 group, respectively [16]. The peaks situated between 2918 and 2670 cm^{-1} correspond to non-fundamental NH stretching modes and to the CH stretching modes [17]. The bands observed at 1700 , 1510 and 1460 cm^{-1} are assigned to the $\delta(\text{OH})$, to the asymmetric $\delta_{\text{as}}(\text{NH}_2)$ and symmetric $\delta_{\text{s}}(\text{NH}_2)$ bending modes, respectively, and to C-C, C-N and N-N stretching vibrations [18, 19]. The bands between 1000 and 600 cm^{-1} are assigned to the out of plane bending modes $\nu(\text{C}_{\text{ary}}\text{-H})$, $\nu(\text{C}_{\text{ary}}\text{-C})$ and $\nu(\text{N-H})$ [20].

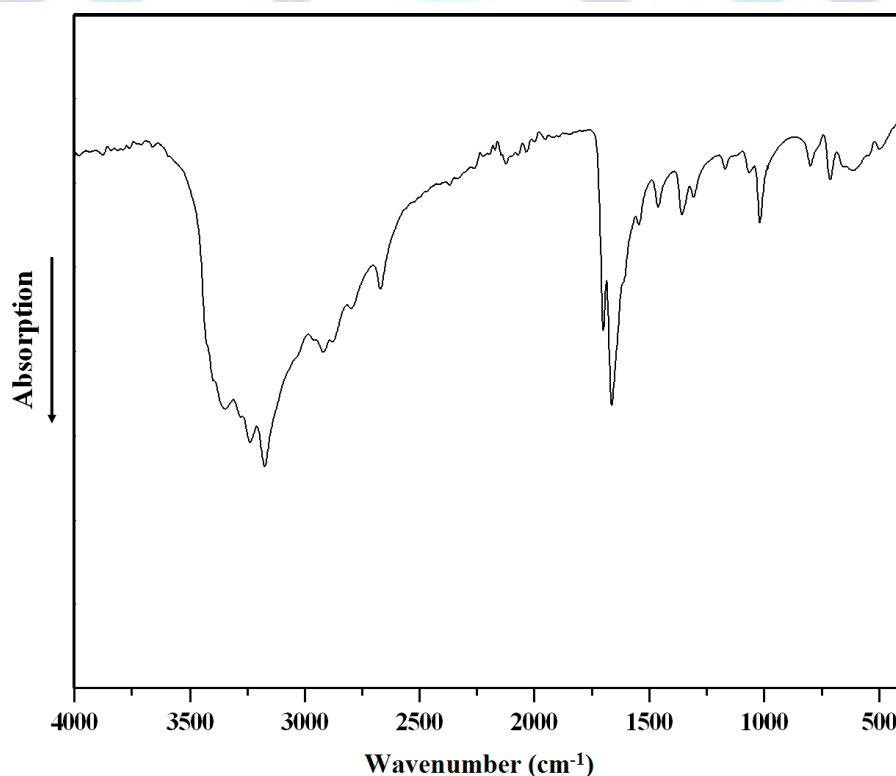


Figure. 5 IR absorption spectrum of the title compound.



3.4 DFT calculations

The DFT calculations show that all observed vibrations are due to the organic cation and to the water molecule. However the vibrations of water lead to intensities much smaller than those of the organic cation as shown when performing the calculations on a system containing all atoms of the asymmetric unit. Even if the calculation led to some slightly imaginary frequencies (ca. -50 cm^{-1} which can be explained by a small variation, within the experimental errors, of the position of one atom) it is this calculation which was taken into account for the comparison. The corresponding spectrum is shown on Figure 6 while the comparison between experimental and theoretical values is shown on Figure 7. Clearly there is a good agreement between the experimental and theoretical values if the scale factor is taken into account. The attributions which can then be deduced from these calculations are the same than those given above.

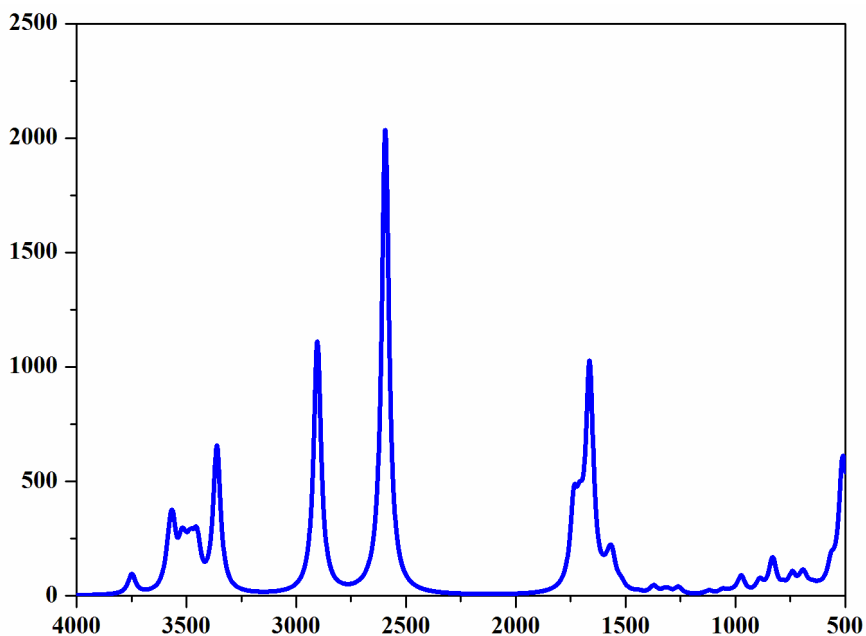


Figure. 6 Calculated IR absorption spectrum in the 500 - 4000 cm^{-1} range.

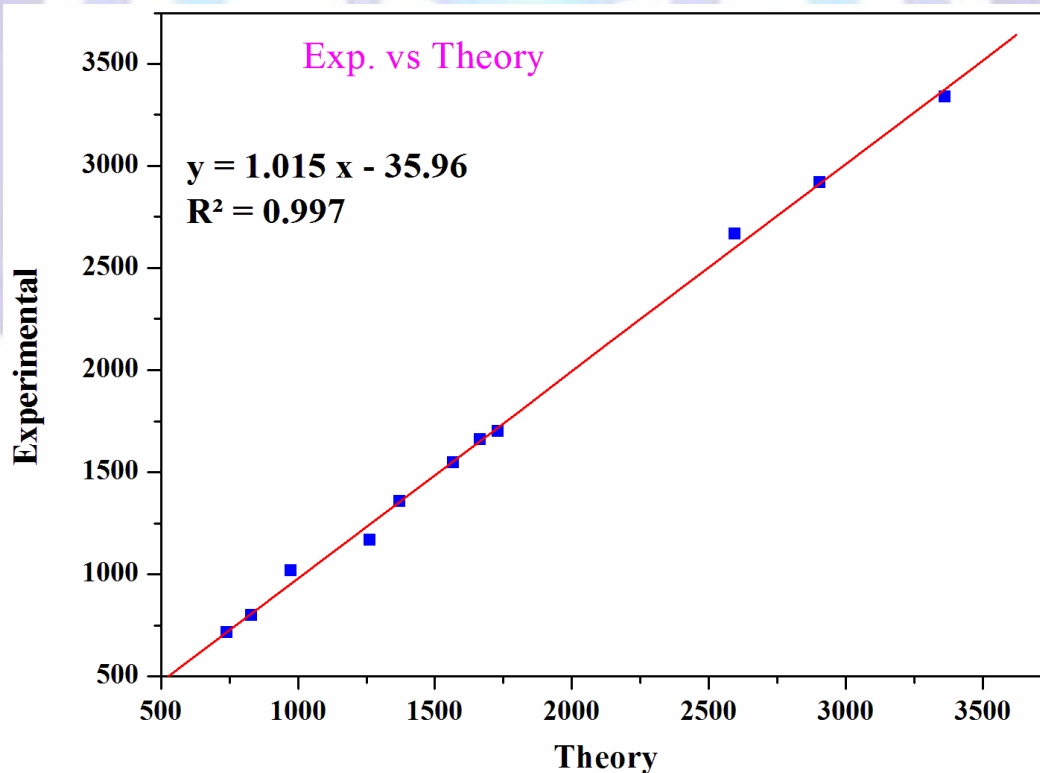


Figure. 7 Comparison between experimental and calculated IR frequencies.



3.5 Dielectric spectroscopy

The frequency dependent complex permittivity of the studied compound ($\epsilon^*(\omega) = \epsilon' - i\epsilon''$) was described analytically by the generalized Cole - Cole model [21]. For the first relaxation process one can write:

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$

Where ϵ_∞ is the high frequency permittivity, ϵ_s is the low frequency permittivity, τ and α are the relaxation times and the distribution parameters ($0 < \alpha < 1$), respectively. For a single Debye type relaxation, the distribution parameter α is equal to zero.

The frequency dependence of the imaginary part of the dielectric permittivity is shown on Figure. 8. A considerable deviation from the Debye-type behavior at low frequencies is observed which can be attributed to the DC conductivity.

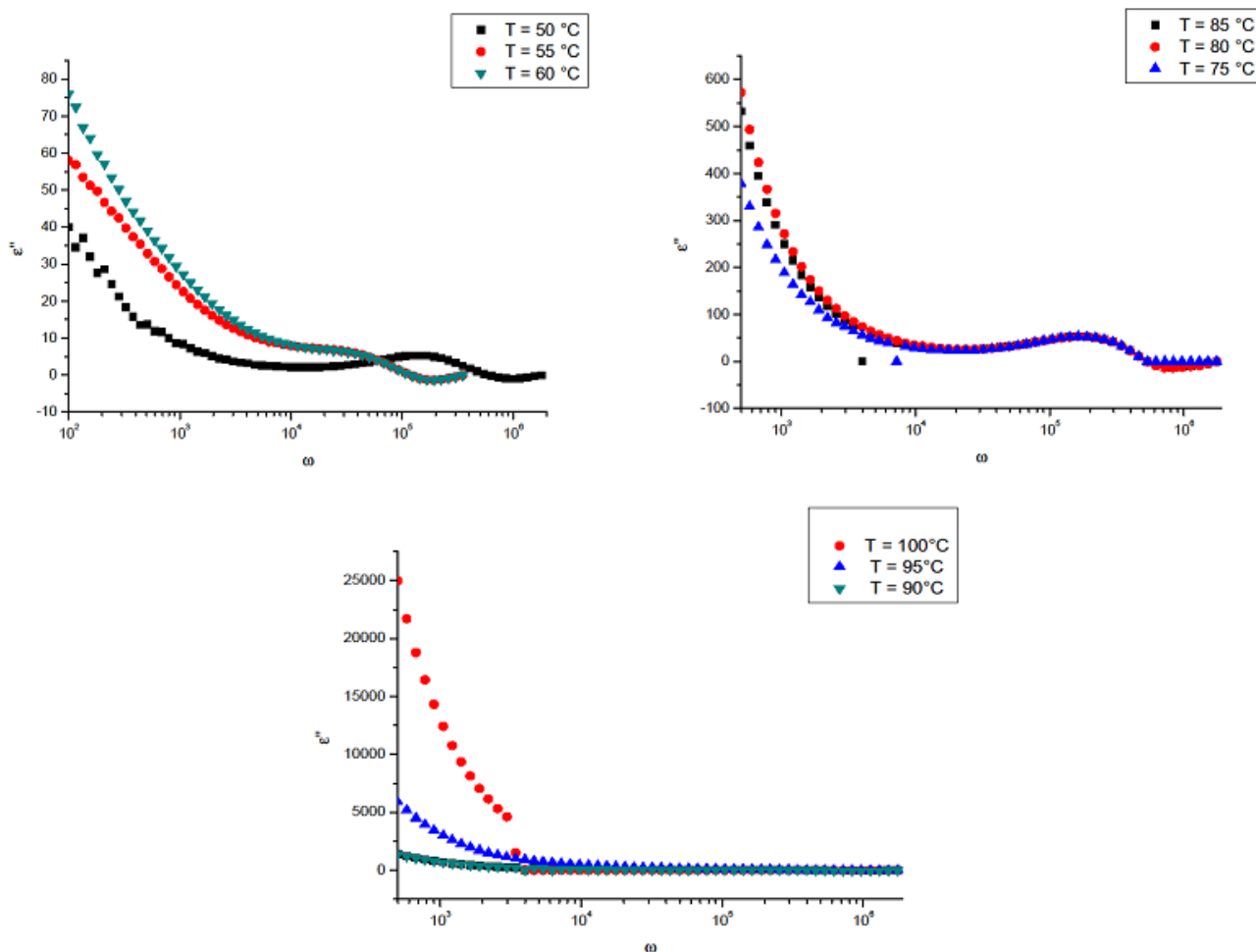


Figure. 8 Temperature evolution of ϵ'' dispersion.

4. Conclusions

The asymmetric unit of the crystal structure of the title compound contains two 3,5-diamino-4*H*-1,2,4-triazol-1-ium cations, two chloride anions and one water molecule. The organic cations containing the N(4), N(5), N(7), N(9) and N(10) nitrogen atoms are interconnected *via* N(7) - H(71)···N(4) hydrogen bonds to form organic chains. The organic cations containing the N(11), N(13), N(14), N(16) and N(17) nitrogen atoms are associated by N(11) - H(111)···N(13) hydrogen bonds leading to the formation of dimers characterized by strong π - π stacking interactions between neighboring triazolium rings. These dimers, the Cl^- anions and the water molecules are located between the organic chains through a set of hydrogen bonds. The ^{13}C CP-MAS NMR spectrum agrees with the structural data. The vibrational properties were investigated by infrared spectroscopy. Dielectric measurements show a deviation from the Debye-type behavior at low frequencies which can be attributed to the DC conductivity.



Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 1012474. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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