Crystal Structure, Spectroscopic and Thermal Investigations of a New 4-Ammonio-2,2,6,6-tetramethylpiperidinium Tetrachlorozincate(II)

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Abstract: The new complex of Zn(II) with 4-ammino-2,2,6,6-tetramethylpiperidine, $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$, has been prepared and characterized by various physicochemical studies. This compound crystallizes in the monoclinic system, with the space group $\text{P2}_1/\text{c}$ and the following cell parameters: $a = 9.8682(7)$, $b = 7.5164(5)$, $c = 21.019(2)$ Å, $\beta = 99.003(7)^\circ$, $V = 1539.8(2)$ Å³ and $Z = 4$. The crystal structure was solved and refined to $R = 0.024$ using 3070 reflections. The atomic arrangement can be described by slightly distorted tetrahedral ZnCl_4^{2-} anions and 4-ammonio-2,2,6,6-tetramethylpiperidinium cations holding together by different interactions. The four chlorine atoms of the ZnCl_4^{2-} tetrahedron are acting as acceptors of hydrogen bonds. The crystal packing is influenced by cation-to-anion N-H...Cl and C-H...Cl hydrogen bonds leading to open framework architecture.

Keywords: Complex; X-ray crystal structure; IR spectroscopy; Impedance spectroscopy.

Introduction

Chemists and physicists of the solid state have shown an increasing interest in the study of the organic-inorganic hybrid materials in recent years owing to their potential fundamental and practical interest such as, fuel cell, liquid crystal-material development, second-order nonlinear optical (NLO) responses, magnetism, luminescence, photography and drug delivery, *etc*¹⁻¹¹. Moreover, in the organic inorganic hybrid metal halides, hydrogen bonds play an important role in stabilizing the

frameworks of the organ ammonium cations and their counter inorganic species. The energetic of N-H...halide-metal hydrogen bonds and their possible role in supramolecular chemistry continue to attract much attention¹². It is therefore important to design and synthesize novel hybrid compounds by reaction between the zinc chloride and an organic ligand containing N-H bonds. In the present investigation, we report the synthesis and the physicochemical characterization of $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$.

Experimental

Crystals of the title compound were prepared according to the following chemical reaction:

By slow evaporation of an aqueous solution of 4-amino-2,2,6,6-tetramethylpiperidine, hydrochloric acid and zinc chloride. The crystals are stable under normal conditions of temperature and humidity. The chemical formula was determined during the X-ray crystal structure analysis.

Investigation techniques

X-ray diffraction

The characterization of these salts was carried out using X-ray diffraction, Infrared spectroscopy, thermal analysis and impedance spectroscopy. A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. The intensity data were collected on an Enraf-Nonius MACH3 automated four-circle diffractometer using the graphite monochromated $\text{MoK}\alpha$ radiation at $\lambda = 0.7107 \text{ \AA}$. The structure was solved by direct methods using the SIR97¹³ program and refined by full matrix least-squares techniques using CRYSTALS¹⁴. The drawings were made with Diamond¹⁵. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located by difference-Fourier synthesis and refined with riding restraints. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1. The main geometrical features of the different entities are given in Tables 2 and 3.

Infrared spectroscopy

The infrared spectrum was recorded in the range $4000\text{--}400 \text{ cm}^{-1}$ with a “Perkin-Elmer FTIR-1000” spectrophotometer using a sample dispersed in spectroscopically pure KBr pellets.

Thermal analysis

Thermal analysis was performed using the “multimodule 92 Setaram” analyzer operating from room temperature up to $500 \text{ }^\circ\text{C}$ at an average heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

Impedance spectroscopy

Impedance spectroscopy was used to measure the electrical conductivity¹⁶⁻¹⁷. The impedance diagrams were recorded in the $5 \text{ Hz--}13 \text{ MHz}$ frequency range using a Hewlett Packard HP 4192A analyser. To ensure electrical contacts, the two parallel surfaces of the sample (having a cylindrical shape) were coated by a layer of silver paint. The platinum wires and the sample were held in contact by a weak mechanical pressure controlled by a screw/spring system and transmitted by an alumina rod.

Table 1. Crystal data, experimental parameters used for the intensity data collection, strategy and final results of the structure determination [C₉H₂₂N₂]₂ZnCl₄

Crystal data	
C ₉ H ₂₂ N ₂ · ZnCl ₄	$V = 1539.8 (2) \text{ \AA}^3$
$M_r = 365.48$	$Z = 4$
Monoclinic, $P2_1/c$	$D_x = 1.576 \text{ Mg m}^{-3}$
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation
$a = 9.8682 (7) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 7.5164 (5) \text{ \AA}$	Cell parameters from 7057 reflections
$c = 21.019 (2) \text{ \AA}$	$\theta = 2.6\text{--}29.3^\circ$
$\beta = 99.003 (7)^\circ$	$\mu = 2.27 \text{ mm}^{-1}$
$0.46 \times 0.26 \times 0.24 \text{ mm}$	$T = 293 \text{ K}$
$F_{000} = 752$	Needle, colorless
Data collection	
Goniometer Xcalibur, detector: Eos (Nova) diffractometer	$R_{\text{int}} = 0.026$
ω scans	$\theta_{\text{max}} = 29.5^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.325$, $T_{\text{max}} = 0.58$	$h = -13 \rightarrow 13$
14412 measured reflections	$k = -10 \rightarrow 10$
3700 independent reflections	$l = -22 \rightarrow 27$
3070 reflections with $I > 2.0\sigma(I)$	Monochromator: graphite
Refinement	
Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.024$	Method = Modified Sheldrick
$wR(F^2) = 0.059$	$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.7P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3690 reflections	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
234 parameters	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$
	Extinction correction: Larson ³⁴ (1970), Equation 22
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 81 (7)

Table 2. Main inter-atomic distances (Å) and bond angles (°) in the inorganic groups of [C₉H₂₂N₂]₂ZnCl₄

The ZnCl ₄ tetrahedron				
Zn	Cl1	Cl2	Cl3	Cl4
Cl1	2.2964(5)	3.788(12)	3.636(11)	3.639(1)
Cl2	112.42(2)	2.2613(5)	3.721(1)	3.637(8)
Cl3	106.12(2)	111.06(2)	2.2528(5)	3.778(4)
Cl4	106.12(2)	107.24(2)	113.86(2)	2.2561(5)

The 4-ammonio-2,2,6,6-tetramethylpiperidinium group			
N1 - C1	1.496(2)	N1 - C1 - C2	110.21(14)
C1 - C2	1.522(2)	N1 - C1 - C5	110.88(14)
C1 - C5	1.512(2)	C2 - C1 - C5	110.02(13)
C2 - C3	1.525(2)	C1 - C2 - C3	111.65(14)
C3 - N2	1.527(2)	C2 - C3 - N2	106.81(13)
C3 - C8	1.525(2)	C2 - C3 - C8	111.29(15)
C3 - C9	1.522(2)	N2 - C3 - C8	106.07(13)
N2 - C4	1.537(2)	C2 - C3 - C9	112.88(14)
C4 - C5	1.530(2)	N2 - C3 - C9	110.75(15)
C4 - C6	1.523(2)	C8 - C3 - C9	108.81(16)
C4 - C7	1.521(2)	C3 - N2 - C4	120.19(12)
		N2 - C4 - C5	108.10(13)
		N2 - C4 - C6	105.44(13)
		C5 - C4 - C6	110.96(15)
		N2 - C4 - C7	110.61(14)
		C5 - C4 - C7	112.06(14)
		C6 - C4 - C7	109.46(16)
		C4 - C5 - C1	112.00(13)

Results and Discussion

Structure description

As shown in Figure 1, to ensure charge equilibrium, the organic species is doubly protonated at N1 and N2 nitrogen atoms. Thus, the structure associates to each 4-ammonio-2,2,6,6-tetramethylpiperidinium cation one tetrachlorozincate anion. Figure 2 shows that the atomic arrangement of the title compound can be described by inorganic ZnCl_4^{2-} species isolated by the organic cations. These entities are held together by coulombic attraction and multiple hydrogen bonds to form a three dimensional infinite network. This figure shows columns, formed by two ZnCl_4^{2-} anions and two 4-ammonio-2,2,6,6-tetramethylpiperidinium cations, running along the b-axis at $x = \frac{1}{2}$ and $z = n/2$.

Figure 1. Asymmetric unit of $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$ with atom labels and 40% probability displacement ellipsoids for non- H atoms

Figure 2. Projection of the structure of $[\text{C}_9\text{H}_{22}\text{N}_2][\text{ZnCl}_4]$ along the b axis. ZnCl_4 is given in polyhedral representation. Hydrogen bonds are denoted by dotted lines

The $\text{Zn}(\text{II})$ ion is in a tetrahedral coordination environment composed of four Cl^- anions. Each ZnCl_4^{2-} group is connected to its four adjacent neighbour's organic cations by $\text{N-H}\dots\text{Cl}$ and $\text{C-H}\dots\text{Cl}$ interactions involving four chlorine atoms (Table 3). The $(\text{N})\text{-H}\dots\text{Cl}$ distances, varying between 2.37 and 2.56 Å, are smaller than the sum of Van der Waals radii of the chlorine and hydrogen atoms [$r(\text{Cl}) + r(\text{H}) = 2.81$ Å]. Consequently, these values correspond well to strong hydrogen bonds. However, the $\text{C-H}\dots\text{Cl}$ hydrogen bonds play a subordinative role in stabilizing the structure^{18, 19}. Moreover, the remarkable feature in the complex salt is the $\text{N-H}\dots\text{Cl}$ hydrogen bonding which form $\text{R}_2^2(26)$ of hydrogen-bonded ring type²⁰ as shown in Figure 3.

Figure 3. Hydrogen bonding which form representation of $\text{R}_2^2(26)$ $\text{N-H}\dots\text{Cl}$ hydrogen-bonded ring type in $[\text{C}_9\text{H}_{22}\text{N}_2][\text{ZnCl}_4]$

Previous studies of tetrachlorozincates have shown that the Zn-Cl bond lengths and Cl-Zn-Cl bond angles in the ZnCl_4^{2-} anion are not equal to one another but depend on the environment around the anion²¹. For example, the presence of hydrogen bonds or repulsions influences appreciably these geometrical parameters. Indeed, the fact that the Zn-Cl1 bond length is the longest meets the expectation derived from hydrogen bonding effects, because the atom Cl1 accepts three hydrogen bonds, while the remaining Cl2, Cl3 and Cl4 chlorine atoms are doubly acceptors (Table 3). However, the mean values of the Zn-Cl bond lengths and Cl-Zn-Cl bond angles are 2.266(5) Å and 109.47(2)°, respectively, are in agreement with those found in 2,6-Xylidinium tetrachlorozincate dihydrate [2.267 Å and 109.5°]²². In the title hybrid material, the Cl-Zn-Cl angles range from 106.12(2) to 113.86(2)°. These values indicate that the geometry around the zinc atom is approximately tetrahedral, according to the Bis(quinolinium) tetrachlorozincate(II) where the corresponding limit angles are 106.33(3) and 112.34(4)°²³. However, in the 4-(2-ammonioethyl) morpholin-4-ium tetrachlorozincate these angle values vary from 98.90(4) to 114.74(4)° indicating that the coordination geometry of Zn atom could be regarded as a distorted tetrahedron²⁴.

Table 3. Hydrogen-bond geometry (Å, °) in $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$

D-H...A	D-H(Å)	H...A(Å)	D-A(Å)	D-H...A(°)
N2-H7...Cl1	0.88	2.37	3.239(1)	169
N2-H8...Cl1	0.88	2.56	3.428(2)	166
C8-H19...Cl1	0.94	2.85	3.645(8)	143
N1-H3...Cl2	0.88	2.48	3.306(8)	159
C2-H6...Cl2	0.97	2.74	3.574(5)	144
N1-H2...Cl3	0.87	2.40	3.257(2)	166
C1-H4...Cl3	0.96	2.72	3.600(1)	153
N1-H1...Cl4	0.88	2.43	3.256(5)	155
C5-H10...Cl4	0.96	2.80	3.749(4)	170

Infrared spectroscopy

The IR spectrum of crystalline $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$ is shown in Figure 4. To assign the IR bands to vibrational modes, we have examined the modes and frequencies observed in similar compounds²⁵⁻²⁷. In the high-frequency region, broad bands between 3600 and 2600 cm^{-1} are attributed to the stretching vibrations: $\nu(\text{N-H})$ and $\nu(\text{C-H})$ ²⁸. The vibrations between 1650 and 1200 cm^{-1} are assigned to bending and stretching modes $\delta(\text{N-H})$, $\nu(\text{C-C})$ and $\nu(\text{C-N})$ ^{29,30}. The bands vibrations between 1000 and 750 cm^{-1} are attributed to out of plane bending modes $\gamma(\text{C-H})$, $\gamma(\text{C-C})$ and $\gamma(\text{C-N})$ ³¹.

Figure 4. IR absorption spectrum of $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$

Thermal behaviour

The simultaneous TGA-DTA curves of crystalline $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$ are given in Figure. 5. The DTA curve shows that this compound undertakes a series of endothermic peaks in a wide temperature range (240-500 °C). The most important one appears at about 257.34 °C. It corresponds to a melting point, which is in good agreement with the result obtained by the capillarity tube method. The important weight loss observed in this temperature region is attributed to the degradation of the organic entity confirmed by the black deposit of carbon obtained at the end of the experiment.

Figure 5. DTA and TGA curves of $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$ at rising temperature

Impedance spectroscopy

Typical impedance spectra were carried out in the temperature range 383-423 K for electrolyte (Figure 6). The total conductivity of the samples has been obtained from the extrapolated intercept of the semicircle with the real axis at low frequency. This intercept combines volume and grain boundary components of the total resistance. Figure 7 shows the temperature dependence of the electrical conductivity σ of the title compound. The increase of the conductivity as a function of temperature proves that this material has a non-metal behaviour.

Figure 6. Typical impedance diagrams obtained under air using symmetric cells for $[\text{C}_9\text{H}_{22}\text{N}_2]\text{ZnCl}_4$

Figure 7. Temperature dependence of the conductivity of $[C_9H_{22}N_2]ZnCl_4$

If the carrier concentration remains constant throughout the temperature range measured, the Arrhenius diagram should be a linear plot ($\log(\sigma T)$ vs. $10^3/T$), following the relation:

$$\sigma = \frac{A_0}{T} \exp\left(-\frac{E_a}{kT}\right)$$

Where E_a is the activation energy, k and T are the Boltzmann constant and the absolute temperature, respectively. The A_0 constant includes the carrier concentration as well as other material dependent parameters^{32, 33}. The Arrhenius plot shows that the activation energy is practically constant in the chosen temperature range which can be explained by only one mechanism of conduction. The obtained value for the activation energy (0.15 eV) is relatively weak and is in favour of protonic conductivity mechanism.

Conclusion

The new complex $[C_9H_{22}N_2]ZnCl_4$ was prepared as single crystals at room temperature and characterized by various physicochemical studies. The crystal structure contains isolated slightly distorted tetrahedral $ZnCl_4^{2-}$ anions held to the 4-ammonio-2,2,6,6-tetramethylpiperidinium cations by multiple hydrogen bonds which lead to an open framework architecture. When heated, the title compound undergoes a decomposition of the organic entity in a large temperature range. The activation energy issued from the impedance spectra suggests a protonic conductivity mechanism for this materials.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No CCDC 736280. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1226-336033; e-mail: deposit@ccdc.cam or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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