Crystal Structure of Bis(5-Chloro-2,4-Dimethoxyanilinium) Tetrachlorozincate Trihydrate

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Abstract: The new inorganic-organic hybrid complex of Zn(II) with 5-Chloro-2,4-dimethoxyaniline, (5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$, has been prepared and characterized by X-ray crystallography. The complex crystallizes in the triclinic space group $P\bar{1}$ with a = 7.4614 (2), b = 9.8734 (2), c = 18.5678 (4) Å, α = 102.3578 (14), β = 91.0686 (15), γ = 91.2373 (12)°, V = 1335.49 (5) $Å^3$, Z = 2. Crystal structure has been determined and refined to R = 0.035 and R_w = 0.036 using 5107 independent reflections. In the atomic arrangement of the title compound, $ZnCl_4^{2-}$ inorganic entities, water molecule and $–NH_3^+$ groups have a layered organization around the planes z = 1/4 and z = 3/4. The crystal structure is stabilized by N-H…O, O-H…O, N-H…Cl and O-H…Cl hydrogen bonds.

Keywords: Single-crystal X-ray diffraction, tetrachlorozincate, 5-Chloro-2,4-dimethoxyanilinium.

INTRODUCTION

Organic-inorganic hybrid materials have received extensive attention in recent years owing to their great fundamental and practical interest such as second-order nonlinear optical (NLO) responses, magnetism, luminescence [1], photography and drug delivery [2]. However, the energetic of N-H….Cl-M (M = metal) hydrogen bonds and their possible roles in supramolecular chemistry have only been recently described in details [3]. It is therefore vital to design and synthesize novel organic inorganic hybrid compound to explore their various properties.

MATERIALS AND METHODOLOGY

The title compound (Fig. **1**) was prepared in a Petri dish by slow evaporation of an aqueous solution of 5-Chloro-2,4-dimethoxyaniline, zinc chloride and 1 M hydrochloric acid at room temperature. The crystals remained stable under normal conditions of temperature and humidity. The chemical formula was determined by an X-ray crystal structure analysis.

A single crystal was used for X-ray measurements on a Nonius Kappa CCD diffractometer operating at 293 K with the wavelength Kα(Mo) = 0.7107 Å. The structure was solved by direct methods using the SIR97 [4] program and refined by full matrix least-squares techniques using CRYSTALS [5]. All non-hydrogen atoms were refined anisotropically. The drawings were made with Diamond [6]. The hydrogen atoms were located by difference-Fourier synthesis and refined with riding restraints. The details of data collection, refinement and crystallographic data are summarized in Table **1**.

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RESULTS

The main geometrical features of the title compound, (5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$, are listed in Tables **2** and **3**. The scheme is given in Fig. (**1**).

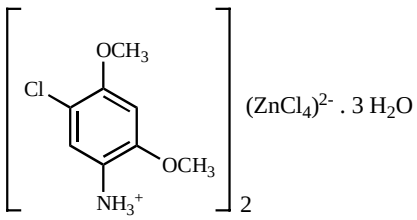

Fig. (1). Chemical scheme of the title compound.

A perspective view of the asymmetric unit of the structure drawing with 50% probability thermal ellipsoids is depicted in Fig. (**2**), while the complete atomic arrangement is shown in Fig. (**3**) and Fig. (**4**).

DISCUSSION

Fig. (**3**) shows that the $ZnCl_4^{2-}$ inorganic entities, water molecules and $–NH_3^+$ groups have a layered organization around the planes z = 1/4 and z = 3/4.

Fig. (**4**) represents a projection of such a layer located in the plane z = 3/4. It shows that the $ZnCl_4^{2-}$ groups are connected by strong hydrogen bonds through $–NH_3^+$ as to form infinite chains in the a-direction. These chains themselves are interconnected by means of Ow–H···Cl hydrogen bonds originating from the water molecules to form infinite layers occupied by $ZnCl_4^{2-}$, H_2O and NH_3^+ entities. Alternatively speaking, the water molecules of the structure, located in voids created by $–NH_3^+$ groups, link together the chains to give rise to infinite layers centered approximately by planes located at z = (2n + 1)/4. In fact, as it is most frequently ob-

Table 1. **Crystal and Experimental Data**

Crystal data	
$2(C_8H_{11}ClNO_2).Cl_4Zn.3(H_2O)$	V = 1335.49 (5) Å^3
M_r = 638.50	Z = 2
Triclinic, *P*-1	D_x = 1.588 Mg m^{-3}
a = 7.4614 (2) Å	Mo $K\alpha$ radiation
b = 9.8734 (2) Å	Cell parameters from 13498 reflections
c = 18.5678 (4) Å	θ = 0.7–27.9°
α = 102.3578 (14)°	μ = 1.56 mm^{-1}
β = 91.0686 (15)°	T = 293 K
γ = 91.2373 (12)°	Block, colorless
Data collection	
Area diffractomer	R_{int} = 0.023
φ & ω scans	θ_{max} = 27.9°
Absorption correction: analytical	h = -9 → 9
T_{min} = 0.51, T_{max} = 0.62	k = -12 → 12
10617 measured reflections	l = -23 → 24
6314 independent reflections	0 standard reflections
5107 reflections with $I > 2.0\sigma(I)$	every. reflections
Refinement	
Refinement on *F*	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)]$ = 0.035	Calculated weights Method, part 1, Chebychev polynomial [weight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ... + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.945 0.533 0.613
	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.036	$\Delta\rho_{max}$ = 0.52 e Å^{-1}
S = 1.09	$\Delta\rho_{min}$ = -0.53 e Å^{-1}
4813 reflections	
290 parameters	

served, the water molecules of these layers act as hydrogen bridges (*via* the $-NH_3^+$ group) between the cationic and anionic arrangements.

The 5-chloro-2,4-dimethoxyalinilinium cations are linked to successive layers through hydrogen bonds to establish a three-dimensional network, involving the hydrogen atoms of the NH_3 groups with H(N)…Cl distances varying from 2.37 to 2.72 Å and N…Cl distances between 3.210(2) and 3.255(2) Å (Table **3**).

Regarding the organic cations arrangement, the 5-chloro-2,4-dimethoxyanilinium is localized in the interlayer spacing, and thus neutralizes the negative charge of the anionic part. In this structure there are two independent organic entities, the first is bounded to two different $ZnCl_4^{2-}$ groups, while the second to only one. The organic molecule exhibits a regular spatial configuration with usual distances C-C, C-N, C-O and angles C-C-C, C-C-N, C-O-C. The mean value of the (C-C) length of phenyl ring is 1.386 Å, which is between single bond and double bond and agreeable with those in literature [7]. All the carbon atoms of the phenyl ring are coplanar with an average deviation of 0.002 Å. Furthermore, the distances of C(16)-O(4), C(15)-O(3) and N(2)-C(9)[1.434(3) Å, 1.430(3) Å, 1.457(3) Å], clearly indicate three single bonds. However, the C(12)-O(4) and C(10)-O(3) distances [1.353(3) and 1.357(3)] are shorter which is probably

Table 2. Geometric Parameters (Å, °) *for* (5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$

Zn1—Cl1	2.2945 (6)	Cl1—Zn1—Cl2	104.73 (2)
Zn1—Cl2	2.2902 (6)	Cl1—Zn1—Cl3	112.05 (2)
Zn1—Cl3	2.2449 (5)	Cl2—Zn1—Cl3	110.65 (2)
Zn1—Cl4	2.2716 (7)	Cl1—Zn1—Cl4	108.87 (3)
Cl5—C5	1.744 (2)	Cl2—Zn1—Cl4	111.35 (3)
C5—C4	1.392 (3)	Cl3—Zn1—Cl4	109.14 (2)
C5—C6	1.379 (3)	Cl5—C5—C4	119.45 (15)
C4—O2	1.366 (2)	Cl5—C5—C6	119.28 (15)
C4—C3	1.394 (3)	C4—C5—C6	121.27 (18)
O2—C8	1.440 (2)	C5—C4—O2	116.62 (17)
C3—C2	1.384 (3)	C5—C4—C3	119.74 (18)
C2—O1	1.353 (2)	O2—C4—C3	123.64 (17)
C2—C1	1.399 (3)	C4—O2—C8	118.53 (15)
O1—C7	1.427 (3)	C4—C3—C2	119.31 (17)
C1—C6	1.371 (3)	C3—C2—O1	125.66 (17)
C1—N1	1.461 (3)	C3—C2—C1	119.61 (18)
Cl6—C13	1.733 (2)	O1—C2—C1	114.73 (17)
C13—C12	1.397 (3)	C2—O1—C7	119.06 (16)
C13—C14	1.377 (3)	C2—C1—C6	121.48 (18)
C12—O4	1.353 (3)	C2—C1—N1	117.20 (18)
C12—C11	1.395 (3)	C6—C1—N1	121.32 (18)
O4—C16	1.434 (3)	C5—C6—C1	118.59 (18)
C11—C10	1.384 (3)	Cl6—C13—C12	119.27 (17)
C10—O3	1.357 (3)	Cl6—C13—C14	119.80 (16)
C10—C9	1.396 (3)	C12—C13—C14	120.93 (19)
O3—C15	1.430 (3)	C13—C12—O4	116.61 (18)
C9—C14	1.374 (3)	C13—C12—C11	119.36 (19)
C9—N2	1.457 (3)	O4—C12—C11	124.03 (18)
		C12—O4—C16	117.85 (17)
		C12—C11—C10	119.66 (18)
		C11—C10—O3	125.33 (18)
		C11—C10—C9	119.83 (19)
		O3—C10—C9	114.84 (18)
		C10—O3—C15	117.80 (18)
		C10—C9—C14	120.82 (19)
		C10—C9—N2	118.45 (19)
		C14—C9—N2	120.72 (18)
		C13—C14—C9	119.39 (19)

due to the mesomeric effect of the methoxy groups (Fig. **5**). This is supported by the fact that the atoms O(4) and O(3) lie almost in the phenyl ring with a deviation of 0.0073(22) and 0.0056(15) Å, respectively.

Table 3. Hydrogen-Bond Parameters (Å, °) *for* (5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$

D—H...A	*D*—H	H...*A*	D...A	*D*—H...*A*
N1—H2...O5^{i}	0.89	2.27	2.892 (3)	127
N1—H3...O6^{ii}	0.90	2.05	2.922 (3)	164
N2—H13...O6^{iii}	0.91	1.93	2.818 (3)	164
N2—H12...O5^{iii}	0.93	1.90	2.803 (3)	163
O5—H23...O2	0.81	2.08	2.855 (3)	162
O5—H24...O7^{i}	0.81	1.94	2.720 (3)	161
O6—H25...O2	0.81	2.24	2.963 (3)	150
O6—H26...O7^{ii}	0.81	2.02	2.788 (3)	158
O7—H28...O4	0.81	2.23	2.854 (3)	134
N1—H1...Cl1	0.90	2.37	3.218 (2)	156
N1—H2...Cl2	0.89	2.72	3.255 (2)	119
O7—H27...Cl4	0.81	2.29	3.099 (2)	167
N2—H14...Cl2	0.90	2.37	3.218 (2)	134
N2—H14...Cl1	0.89	2.57	3.210 (2)	128

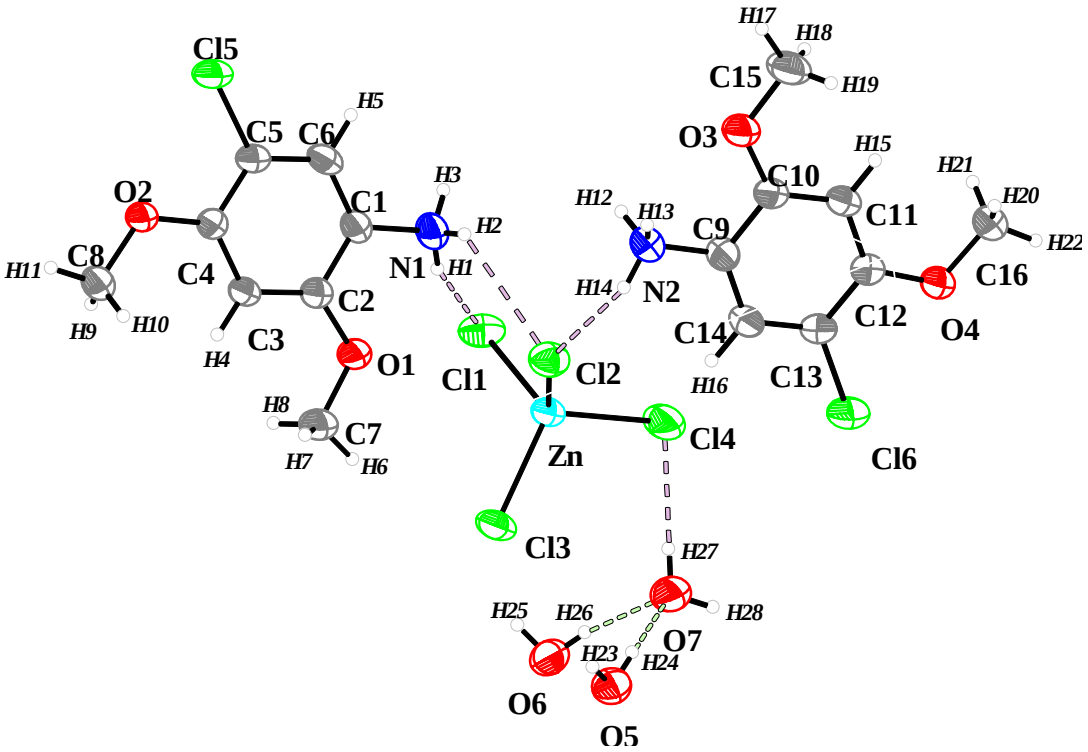

Fig. (2). Perspective view of the asymmetric unit of (5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$ with the atom numbering scheme and thermal ellipsoids at 50 % of probability and arbitrary sphere for the H atoms. The hydrogen bonds are indicated by dashed lines.

The coplanar methoxy groups are characterized by the torsion angles C(13)-C(12)-O(4)-C(16); C(9)-C(10)-O(3)-C(15); C(7)-O(1)-C(2)-C(1) and C(8)-O(2)-C(4)-C(5) being 178.63°, –174.84°, –178.98° and -178.69° respectively. The O(1)-C(2)-C(3) and O(3)-C(10)-C(11) angles (125.67° and 125.33°) are larger than the O(1)-C(2)-C(1) and O(3)-C(10)-C(9) angles (114.73° and 114.84°). This can be attributed to the establishment of weak N-H…O intramolecular hydrogen bond. The formation of this kind of intramolecular hydrogen bond would allow the organic molecule to be highly planar.

CONCLUSION

(5-Cl-2,4-$(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$ was prepared as single crystals at room temperature and characterized by X-ray crystallography. The atomic arrangement of the title

compound can be described by inorganic layers organisation. The interlayer spacing is occupied by the organic molecules. Multiple hydrogen bonds such as N-H…O, O-H…O, N-H…Cl and O-H…Cl assure the structure cohesion.

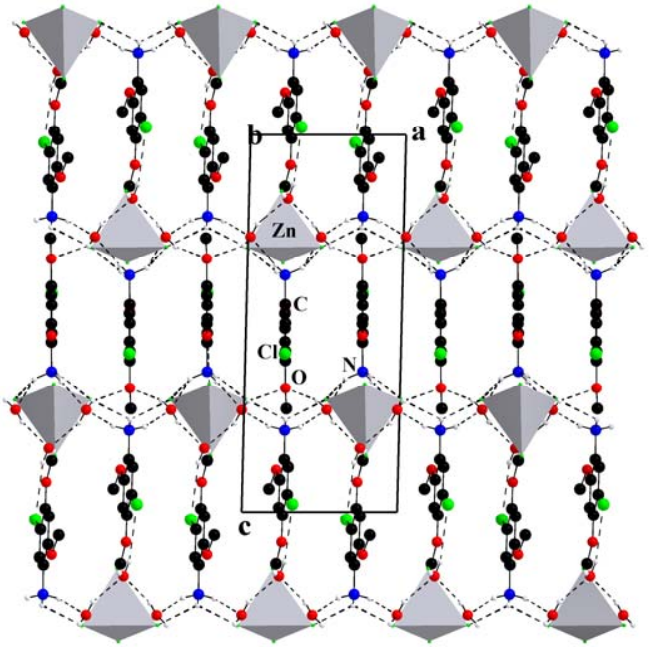

Fig. (3). Projection of the structure of $(5\text{-Cl-2,4-}(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$ along the b axis. A polyhedral representation is used for the $ZnCl_4$ tetrahedron.

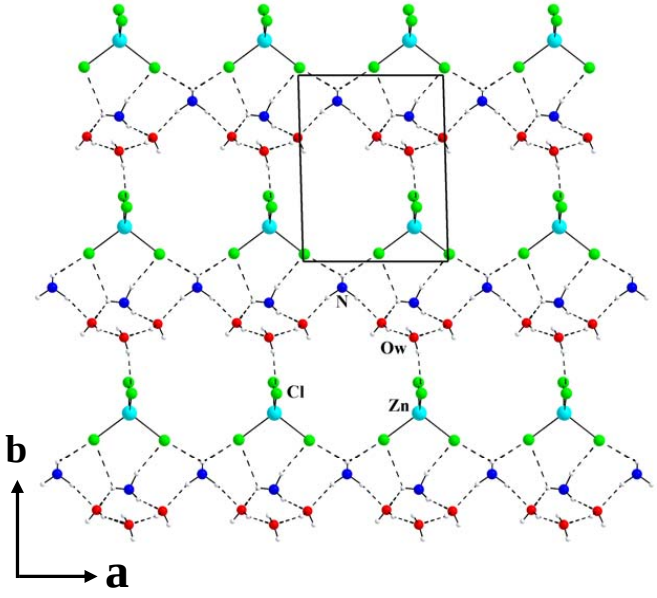

Fig. (4). Layer structure at z = 3/4 for $(5\text{-Cl-2,4-}(OCH_3)_2C_6H_2NH_3)_2ZnCl_4.3H_2O$.

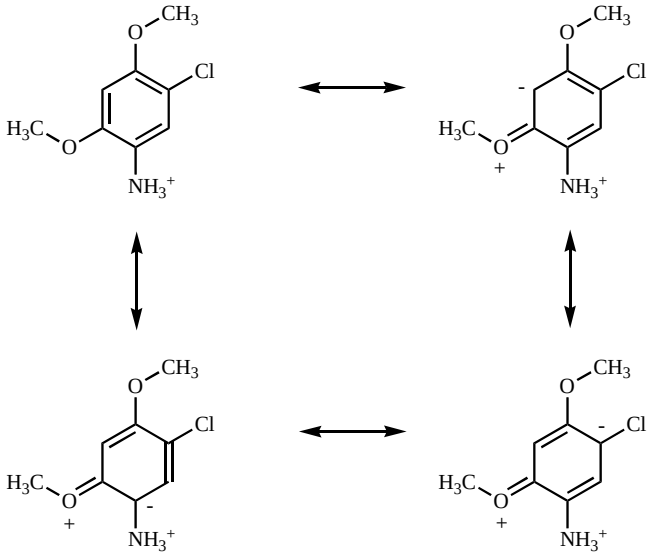

Fig. (5). Resonance in the $(5\text{-Cl 2,4-}(OCH_3)_2C_6H_2NH_3)^+$ cation.

ACKNOWLEDGEMENT

We would like to thank the Ministry of Scientific Research Technology and Competing Development of Tunisia for its financial support.

SUPPLEMENTARY MATERIAL

Supplementary material can be viewed at www.bentham.org/open/tocryj

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Received: May 13, 2008 Revised: December 15, 2008 Accepted: December 15, 2008