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Crystal Structure of $ZnCl_3$ (Methyl-(2-Pyridin-2-yl-Ethyl)-Ammonium)

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Abstract

A new Zn(II) complex with the monodentate ligand methyl-(2-pyridin-2-yl-ethyl)-ammonium, $ZnCl_3C_8H_{13}N_2$, has been prepared and characterized by single crystal X-ray diffraction. The Zn(II) ion is tetracoordinated by one nitrogen atom of organic ligand and three chlorine ligands. In the atomic arrangement, the $ZnNCl_3$ tetrahedra form corrugated chains extending along the *b*-axis. The organic entities are located between these chains through N-H···Cl, C-H···Cl and C-H···N hydrogen bonds to form layers parallel to (b, c) plan. Among these hydrogen bonds two are bifurcated.

Keywords

X-Ray Diffraction, Coordination Compound, Zinc Complex

1. Introduction

Inorganic-organic hybrid compounds provide a class of materials displaying interesting technological importance [1]. The abilities to combine the properties of organic and inorganic compounds within one single molecular scale leads to interesting crystal structures [2]. In these materials, the crystal packing is ensured by hydrogen bonds and π-π stacking interactions. These non-covalent weak forces play a vital role in molecular recognition, self organization of molecule and highly efficient and specific biological reactions associated with supramolecular chemistry [3]. In this area, transition metal complexes are known to be effective against rheumatoid arthritis and they also show anti-ulcer activity [4] [5]. These complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral [6].

As part of our continued involvement in the investigation of metal complexes of nitrogen containing ligands such as, e.g. Schiff bases [7], we report here the synthesis and characterization of two new Zn(II) complex with the monodentate ligand methyl-(2-pyridin-2-yl-ethyl)-ammonium.

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2. Experimental

2.1. Chemical Preparation

A solution of $ZnCl_2$ (0.123 g, 0.90 mmol) in water was added dropwise to a solution of 2-(2-methylaminoethyl) pyridine (0.040 g, 0.30 mmol) in ethanol (6 mL). After stirring during 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after four days by slow evaporation of the filtrate at room temperature (yield = 58%).

2.2. X-Ray Single Crystal Structural Analysis

A single crystal was used for X-ray measurements on Nonius Kappa CCD diffractometer operating at 296 K with the wavelength Kα (Mo) = 0.7107 Å. The structure was solved by direct methods using the SHELXS 86 program [8] and refined by full matrix least-squares techniques using CRYSTALS [9]. All non-hydrogen atoms were refined anisotropically. The drawing were made with Diamond [10] ans Mercury [11]. The details od data collection, refinment and crystallogapfic data are summerized in **Table 1**.

3. Results and Discussion

Single crystal X-ray diffraction analysis reveals that the structure of the title compound is characterized by an isolated structure, based on the protonated 2-(2-methylaminoethyl)pyridine, methyl-(2-pyridin-2-yl-ethyl)-ammonium, ligand coordinating to a zinc atom that is further terminally bonded by three chlorine atoms as in **Figure 1**. The methylenic group adjacent to the aliphatic nitrogen atom forms a weak intramolecular C-H…Cl hydrogen bond with the Cl1 hydrogen atom. This compound is a so called "zwitterions", where the positive charge is localized at the protonated aliphatic nitrogen atom of the methyl-(2-pyridin-2-yl-ethyl)-ammonium moiety and the negative charge in the vicinity of three chlorine atoms. All the crystallographically independent atoms are in general positions. The Zn atom has a slightly distorted tetrahedronal geometry, coordinationg with the aromtic nitrogen atom of the cationic ligand and three terminal chlorine atoms (**Figure 2**). The Zn-Cl distances range from 2.2338(10) to 2.2828(8) Å and the Zn-N of 2.0690(18) Å (**Table 2**), which are comparable to those reported [12]-[15]. The bond angles of Cl-Zn-Cl and N-Zn-Cl range from 104.60 (3) to 117.74 (3), which are close to those in a regular tetrahedron, agree with that previously described [16]. In the atomic arragment, the $ZnNCl_3$ tetrahedra form corrugated chains extending along the *b*-axis (**Figure 3**). These chains are located at (1/2, 0, 1/4) and (1/2, 0, 3/4) (**Figure 4**). The organic entities are inserted between these chains through N-H…Cl, C-H…Cl and C-H…N hydrogen bonds to form layers parallel to (b, c) plan (**Figure 5**, **Table 3**). These layers are situated at x = n/2 (**Figure 6**). A perspective view of the whole atomic arrangment is given in **Figure 7**. It should be pointed out that between the hydrogen bonds two are bifurcated N2—H2A···(Cl1^{i}, Cl2 ^{i}) and N2—H2B···(Cl2^{ii}, Cl3^{ii}) (for symmetry codes, see **Table 3**).

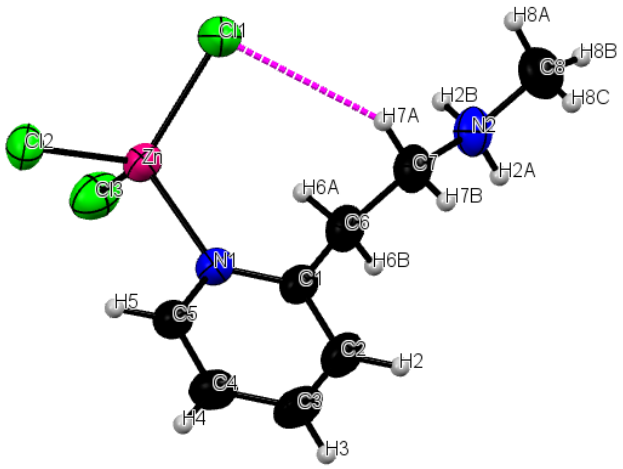

Figure 1. Asymmetric unit of $ZnCl_3C_8H_{13}N_2$ with the atom numbering scheme and thermal ellipsoids at 50% probability. The dotted lines indicate hydrogen bond.

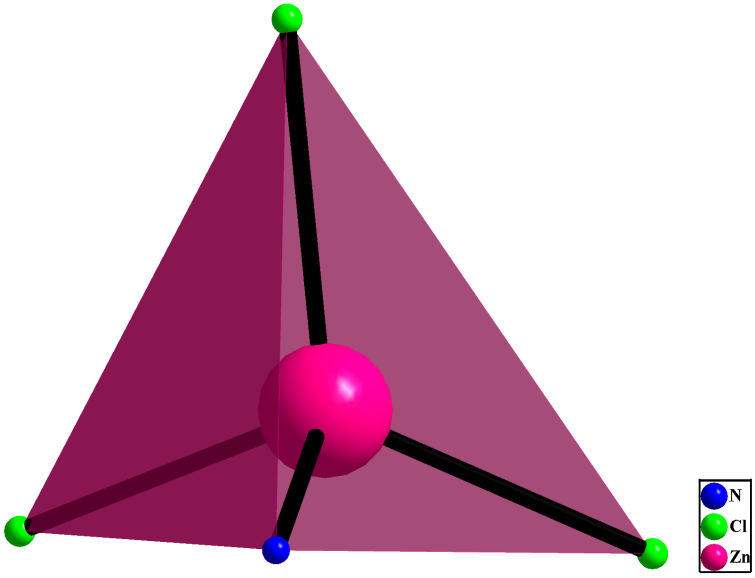

Figure 2. Geometry around the Zn(II) cation in $ZnCl_3C_8H_{13}N_2$.

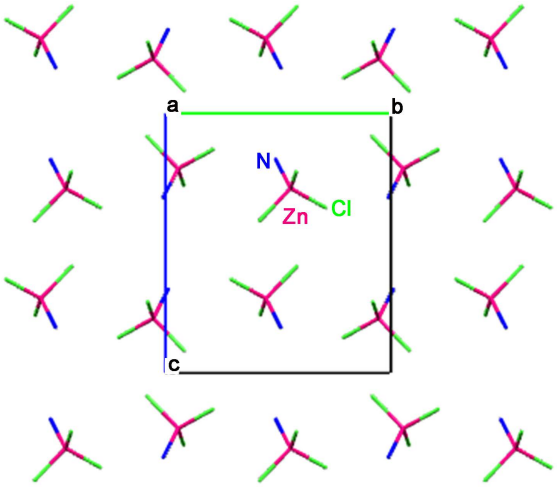

Figure 3. Inorganic corrugated chains of $ZnCl_3N$ tertrahedra in the title compound. Organic radicals are omitted for figure clarity.

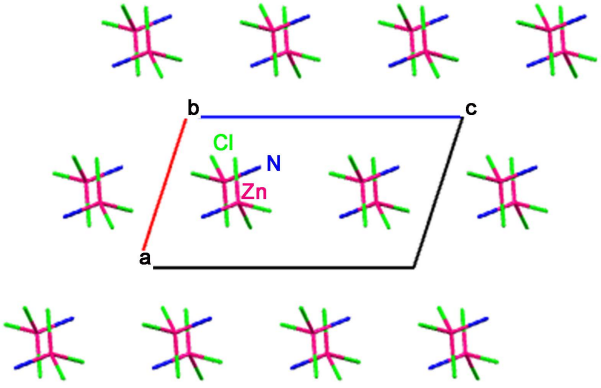

Figure 4. Projection along the *b*-axis of the inorganic chains. Organic radicals are omitted for figure clarity.

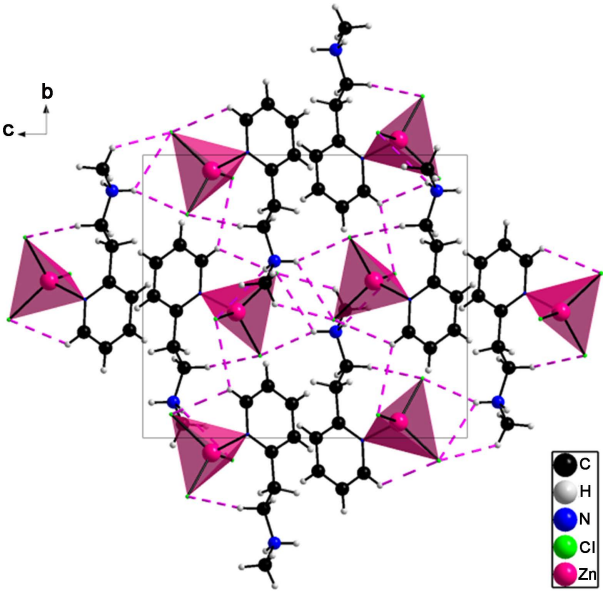

Figure 5. Inorganic-organic layer in $ZnCl_3C_8H_{13}N_2$. The dotted lines indicate hydrogen bonds.

Table 1. Experimental details.

Crystal data	
Chemical formula	$C_8H_{13}Cl_3N_2Zn$
M_r	308.92
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	8.020 (3), 11.529 (4), 13.973 (4)
β (°)	108.015 (2)
V (Å^3)	1228.6 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.62
Crystal size (mm)	0.17 × 0.11 × 0.09
Data collection	
Diffractometer	Nonius Kappa CCD diffractometer
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8636, 2912, 2308
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.657
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.090, 1.06
No. of reflections	2912
No. of parameters	131
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.50

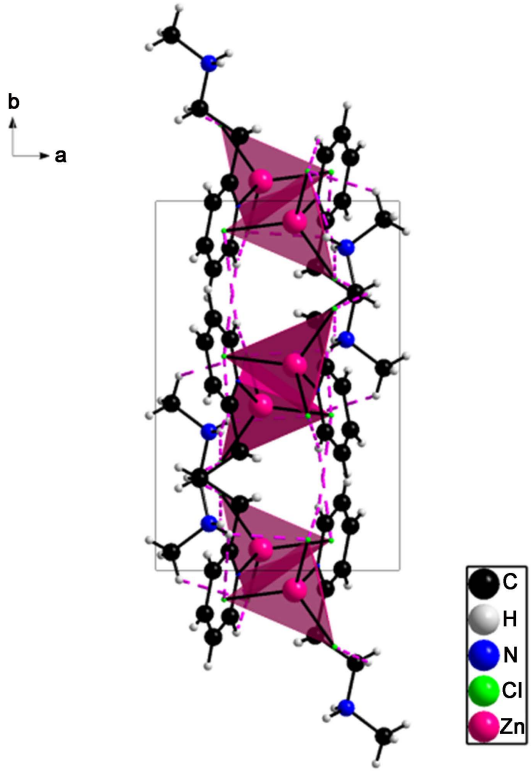

Figure 6. Projection of a layer along the *c*-axis in $ZnCl_3C_8H_{13}N_2$. The dotted lines indicate hydrogen bonds.

Table 2. Selected geometric parameters (Å, °).

Zn—N1	2.0690 (18)	N2—C7	1.483 (3)
Zn—Cl3	2.2338 (10)	C1—C2	1.394 (3)
Zn—Cl1	2.2649 (8)	C1—C6	1.503 (3)
Zn—Cl2	2.2828 (8)	C2—C3	1.378 (4)
N1—C1	1.348 (3)	C3—C4	1.359 (4)
N1—C5	1.349 (3)	C4—C5	1.381 (3)
N2—C8	1.477 (3)	C6—C7	1.524 (3)
N1—Zn—Cl3	109.05 (5)	N1—C1—C2	120.8 (2)
N1—Zn—Cl1	109.52 (5)	N1—C1—C6	119.07 (19)
Cl3—Zn—Cl1	117.74 (3)	C2—C1—C6	120.1 (2)
N1—Zn—Cl2	106.57 (6)	C3—C2—C1	119.4 (2)
Cl3—Zn—Cl2	108.75 (3)	C4—C3—C2	119.8 (2)
Cl1—Zn—Cl2	104.60 (3)	C3—C4—C5	118.7 (2)
C1—N1—C5	118.59 (18)	N1—C5—C4	122.6 (2)
C1—N1—Zn	125.59 (14)	C1—C6—C7	111.80 (18)
C5—N1—Zn	115.81 (14)	N2—C7—C6	111.08 (17)
C8—N2—C7	114.07 (18)		

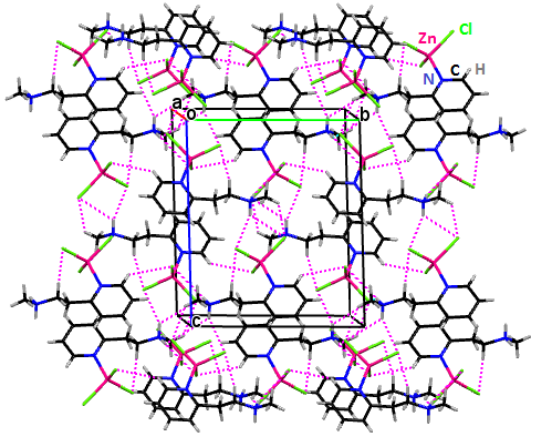

Figure 7. A perspective view of the structure of $ZnCl_3C_8H_{13}N_2$. The dotted lines indicate hydrogen bonds.

Table 3. Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···Cl1^{i}	0.90	2.51	3.302 (2)	147
N2—H2*A*···Cl2^{i}	0.90	2.85	3.441 (2)	124
N2—H2*B*···Cl2^{ii}	0.90	2.51	3.266 (2)	142
N2—H2*B*···Cl3^{ii}	0.90	2.94	3.603 (2)	132
C5—H5···Cl2	0.93	2.85	3.479 (3)	126
C7—H7*A*···Cl1	0.97	2.83	3.582 (3)	135
C8—H8*B*···Cl2^{i}	0.96	2.89	3.560 (3)	128
C5—H5···Cl3^{iii}	0.93	2.96	3.617 (3)	129
C8—H8*A*···N1^{iv}	0.96	2.90	3.570 (3)	128
C8—H8*C*···Cl2^{iv}	0.96	2.85	3.727 (3)	152

Symmetry codes: (i) x, −y+1/2, z + 1/2; (ii) −x + 1, y + 1/2, −z + 1/2; (iii) –x + 1, y − 1/2, −z + 1/2; (iv) −x, y + 1/2, −z + 1/2.

4. Conclusion

A novel complex $ZnCl_3$ (methyl-(2-pyridin-2-yl-ethyl)-ammonium) has been synthesized at room temperature and characterized by single crystal X-ray diffraction. In the crystal structure of the title compound, the Zn(II) ion is tetracoordinated to one nitrogen atom of the monodentate cationic ligand and to three chlorine ligands. All the components of this material are interconnected via N-H···Cl, C-H···Cl and C-H···N hydrogen bonds to form layers parallel to the (b, c) plan.

5. Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 1035723. 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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