Synthesis and Crystal Structure of 1-Ethylpiperazine-1,4-dium Tetrachlorozincate

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A new inorganic-organic hybrid compound, $[\text{C}_6\text{H}_{16}\text{N}_2]\text{ZnCl}_4$, has been synthesized and characterized by X-ray single-crystal structure analysis. The crystals of the title compound are orthorhombic, $Pcab$, with the following cell parameters: $a = 9.642(5)$, $b = 11.514(4)$, $c = 23.792(4)\text{Å}$, $V = 2641.5(14)\text{Å}^3$ and $z = 8$. The crystal structure was solved and refined to $R_1 = 0.027$ with 2319 independent reflections. The atomic arrangement can be described as being built up by infinite chains of ZnCl_4^{2-} and $(\text{C}_6\text{H}_{16}\text{N}_2)^{2+}$ groups. The crystal packing is influenced by cation-to-anion $\text{N-H}\cdots\text{Cl}$ strong hydrogen bonds. Only two chlorine atoms of ZnCl_4^{2-} anion are act as acceptors of hydrogen bonds.

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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, photography and drug delivery.¹ However, the energetics of $\text{N-H}\cdots\text{Cl-M}$ ($M = \text{metal}$) hydrogen bonds and their possible role in supramolecular chemistry have been recently described in detail.² It is therefore vital to design and synthesize novel organic inorganic hybrid compounds to explore their various properties. The present work is devoted to determine the detailed structure of $[\text{C}_6\text{H}_{16}\text{N}_2]\text{ZnCl}_4$ (Fig. 1). This compound was prepared according to the chemical reaction

by slow evaporation of an aqueous solution of 1-ethylpiperazine, zinc chloride and 1 M hydrochloric acid.³ The crystals remained stable under normal conditions of temperature and humidity. The chemical formula was determined by an X-ray crystal structure analysis.

The crystal structure of the title compound was determined using a single crystal. The experimental conditions of data collection, strategy followed for the structure determination and the final results are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-square based on F for all data with CRYSTALS software.

All non-hydrogen atoms of $[\text{C}_6\text{H}_{16}\text{N}_2]\text{ZnCl}_4$ were refined anisotropically. The hydrogen atoms were found in a difference

Fig. 1 Chemical diagram of the title compound.

Fourier synthesis and refined with riding constraints. The main geometrical features of the different entities are indicated in Table 2. An ORTEP view of the molecular structure is shown in Fig. 2.

A view of the structure projected along the b axis is given in Fig. 3. This projection shows that the main feature of the atomic arrangement in this compound is the existence of infinite chains composed of ZnCl_4^{2-} and $(\text{C}_6\text{H}_{16}\text{N}_2)^{2+}$ groups, spreading in $Z = 0$ and $Z = (2n+1)/2$ or $y = 0$ and $y = (2n+1)/2$ planes. In such chains, the ZnCl_4^{2-} anions and the 1-ethylpiperazine-1,4-dium

Table 1 Crystal and experimental data

Chemical Formula:	$\text{C}_6\text{H}_{16}\text{N}_2\text{Cl}_4\text{Zn}$
Formula weight:	323.4
Crystal system:	orthorhombic
Space group:	$Pcab$
Z :	8
a :	$9.642(5)\text{Å}$
b :	$11.514(5)\text{Å}$
c :	$23.792(5)\text{Å}$
V :	$2641.3(2)\text{Å}^3$
D_x :	1.626 g cm^{-3}
Linear absorption factor:	2.632 cm^{-1}
$F(000)$:	1312
Crystal dimensions:	$0.20 \times 0.25 \times 0.35\text{ mm}$
θ range for data collection:	2.46 to 24.96°
No. of reflections measured:	2319 ($R_{\text{int}} = 0.04$)
No. of reflections used:	1992 with $I > 3\sigma(I)$
No. of parameters:	119
R :	0.0276
R_w :	0.0302
Goodness-of-fit:	1.122
$(\Delta\sigma)_{\text{max}}$:	0.001
$(\Delta\rho)_{\text{max}}$:	0.47 eÅ^{-3}
$(\Delta\rho)_{\text{min}}$:	-0.68 eÅ^{-3}
Measurement:	Enraf-Nonius MACH3
$\lambda(\text{Mo } K\alpha)$:	0.71069 Å
Program system:	SHELXL 97
Structure determination:	direct method (SIR 92)
Refinement:	full-matrix on F^2
CCDC:	670142

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Table 2 Main interatomic distances (Å) and bond angles (°) in (C₆H₁₆N₂)ZnCl₄ atomic arrangement. Estimated standard deviations are given in parentheses

The ZnCl ₄ tetrahedron				
Zn	Cl(1)	Cl(2)	Cl(3)	Cl(4)
Cl(1)	2.314(1)	3.672(1)	3.637(1)	3.678(1)
Cl(2)	106.10(4)	2.280(0)	3.739(1)	3.664(1)
Cl(3)	106.17(4)	111.85(4)	2.233(1)	3.835(1)
Cl(4)	107.12(4)	107.69(4)	117.25(4)	2.257(1)
(C ₆ H ₁₆ N ₂) ²⁺ cation				
N1–C1	1.492(3)	C1–N1–C4	111.1(2)	
N1–C4	1.496(4)	C1–N1–C5	109.4(2)	
N1–C5	1.521(3)	C4–N1–C5	112.3(2)	
N2–C2	1.486(4)	C2–N2–C3	111.0(2)	
N2–C3	1.491(4)	N1–C1–C2	111.3(2)	
C1–C2	1.512(4)	N1–C4–C3	111.9(2)	
C4–C3	1.519(4)	N2–C2–C1	110.2(2)	
C5–C6	1.498(5)	N2–C3–C4	109.7(2)	
		C6–C5–N1	112.0(3)	
Hydrogen bonds				
N–H...Cl	N–H	H...Cl	N...Cl	N–H...Cl
N1–H1 ... Cl1	0.9100	2.3700	3.218(2)	155.00
N2–H6 ... Cl1	0.8100	2.5600	3.254(3)	144.00
N2–H7 ... Cl2	0.9100	2.3400	3.208(3)	159.00

cation are held together by coulombic attraction and hydrogen bonds, which stabilize the crystal packing. The Zn^{II} ion is in a tetrahedral coordination environment composed of four Cl anions. Each ZnCl₄²⁻ group is connected to its adjacent neighbour's organic cations by three N–H...Cl hydrogen bonds involving only two chloride atoms. The Cl1 chloride atom hydrogen bonds with H1 and H6 hydrogen atoms, while the Cl2 participates only to the N2–H7...Cl2 hydrogen bond. The H...Cl–Zn angles, (average angle = 88.40°) are typically acute, which can be related to a simple bonding model in which the chloride p-type lone pair is more basic than the sp-type lone pair.⁴ The (N)–H...Cl distances, varying between 2.34 and 2.56 Å, are smaller than the sum of the Van der Waals radii of the chlorine and hydrogen atoms [*r*(Cl) + *r*(H) = 2.81 Å]. Consequently, these values correspond well to strong hydrogen bonds.

Generally, the Zn–Cl bonds lengths and Cl–Zn–Cl bond angles in the [ZnCl₄]²⁻ anion are not equal to one another, but vary with the environment around the Cl atoms. In the title compound, because only the atoms Cl1 and Cl2 are involved in N–H...Cl hydrogen bonds, the Zn–Cl1 and Zn–Cl2 are obviously longer than Zn–Cl3 and Zn–Cl4. The Zn–Cl1 bond length 2.314(1)Å is the longest one because the Cl1 chloride atom participates with two N–H...Cl links. The value of the Zn–Cl bond lengths vary between 2.234(1) and 2.315(1)Å. The Cl–Zn–Cl angles range from 106.10(4) to 117.25(4)°. Owing to the obvious differences in the Zn–Cl bond lengths and the Cl–Zn–Cl angles, the coordination geometry of the Zn atom can be regarded as being a distorted tetrahedron.⁵

An examination of the organic moiety geometrical features shows that the 1-ethylpiperazine-1,4-dium cation ring adopts a typical chair conformation, and its geometric parameters [*d*_{av}(C–N) = 1.491(4) and *d*_{av}(C–C) = 1.515(4)Å] are in full agreement with those found in piperazinium tetrachlorozincate monohydrate.⁶

Fig. 2 Perspective view of the asymmetric unit of [C₆H₁₆N₂]ZnCl₄ with the atom numbering scheme and thermal ellipsoids at 40% of probability.

Fig. 3 Arrangement of [C₆H₁₆N₂]ZnCl₄ in projection along the *b*-axis. ZnCl₄ is given in the polyhedral representation. Hydrogen bonds are denoted by dotted lines.

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