Crystalline and Molecular Structure of Hydrated 2,6-Xylidinium Tetrachlorozincate(II)

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Abstract: A new zinc complex compound of formula $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$ has been prepared and characterized by X-ray crystallography, thermal analysis and IR spectroscopy. The complex crystallizes in the monoclinic space group $\text{P}2_1/\text{a}$ with a minimal tetrahedral distortion of the ZnCl_4^{2-} ion, $a = 7.448(1) \text{ \AA}$, $b = 38.486(3) \text{ \AA}$, $c = 8.298(1) \text{ \AA}$, $\beta = 112.52(1)^\circ$, $V = 2197.4(4) \text{ \AA}^3$ and $Z = 4$. The crystal structure was solved and refined to $R = 0.047$ with 3270 independent reflections. It can be described by inorganic layers of $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$ parallel to (010) plane, between which the 2,6-xylidinium cations are located. The grouping is maintained by different types of interactions (electrostatic, H-bonds, Van der Waals and π - π stacking). A characterization of this compound by thermal analysis and IR spectroscopy are also reported.

Keywords: Zinc(II) complex, X-ray crystal structure, H-Bond, Thermal behaviour, IR spectroscopy.

Introduction

Hybrid materials with organic and inorganic components are an attractive field of research due to their ability to combine the properties of organic and inorganic compounds within one single molecular scale, so as to exhibit some interesting crystal structure and some special properties in several areas, such as nonlinear optical (NLO), magnetism, luminescence, *etc*¹⁻⁸. It is therefore vital to design and synthesize novel salts with inorganic anions and organic cations to explore their various properties. A recent advance in this system is to design the coordination frameworks of metal halides by the incorporation of various organic structure-directing agents and generating new supramolecular entities⁹⁻¹³. In the present investigation we report the synthesis and crystal structure of a new organic-inorganic hybrid zinc complex, $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$ (Figure 1). Its characterization by thermal analysis and IR spectroscopy are also reported.

Experimental

Synthesis

Crystals of Zn(II) complex with 2,6-xylydine, $(C_8H_{12}N)_2ZnCl_4 \cdot 2H_2O$, were prepared by slow evaporation of an aqueous solution of 2,6-xylydine, HCl and $ZnCl_2$ (2:2:1) molar. Crystals are stable for a long-time in normal conditions of temperature and humidity. The chemical formula was determined when resolving the crystal structure by X-ray diffraction spectroscopy.

Investigation techniques

X-ray diffraction

A single crystal of the complex was mounted on a MACH 3 Enraf Nonius diffractometer operating at 296 K with a monochromated Mo radiation source ($\lambda=0.7107 \text{ \AA}$). The structure was solved by direct methods using the SIR92¹⁴ program and refined by full matrix least-squares techniques based on F using teXsan¹⁵. The hydrogen atoms were not refined, and all non-hydrogen atoms were refined anisotropically. Further details of structural analyses are summarized in Table 1.

Table 1. Crystal and experimental data.

Empirical formula	$C_{16}H_{28}Cl_4N_2O_2Zn$
Formula weight	487.60
T (K)	293
Wavelength ($\text{\AA}$)	0.71069
Crystal system	Monoclinic
Space group	$P2_1/a$
a ($\text{\AA}$)	7.448(1)
b ($\text{\AA}$)	38.486(3)
c ($\text{\AA}$)	8.298(1)
β ($^\circ$)	112.52(1)
V ($\text{\AA}^3$)	2197.4(4)
Z	4
D_{calc} (g cm^{-3})	1.474
$\mu(\text{MoK}\alpha)$ (mm^{-1})	1.616
$F(000)$	1008
Reflections collected/unique, R_{int}	8487/5392, (0.021)
Observed data ($I > 3\sigma(I)$)	3270
No. of variables	226
Goodness-of-fit	1.58
R	0.047
R_w	0.058

The final atomic coordinates of the non-hydrogen atoms and their equivalent isotropic displacement parameters, Beq , are given in Table 2. The drawings were made with Diamond¹⁶. Crystallographic data (CIF) for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data centre as supplementary materials No 682367. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK

Table 2. Final atomic coordinates and B_{eq} ($\text{\AA}^2$) of the non-hydrogen atoms of $[2,6-(\text{CH}_3)_2-\text{C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$.

Atoms	x(σ)	y(σ)	z(σ)	B_{eq}
Zn(1)	0.17423(6)	0.127982(10)	0.07366(5)	2.753(9)
Cl(1)	0.2910(2)	0.16848(3)	-0.05600(13)	4.20(2)
Cl(2)	0.1546(2)	0.07808(2)	-0.07917(13)	3.78(2)
Cl(3)	0.3811(2)	0.12374(3)	0.35975(12)	3.91(2)
Cl(4)	-0.1185(2)	0.14056(3)	0.0808(2)	4.63(3)
O(1)	0.5072(5)	0.36774(9)	0.5345(4)	5.63(8)
O(2)	0.5303(5)	0.09524(9)	0.8188(4)	6.39(10)
N(1)	0.7197(5)	0.06959(8)	0.6202(4)	3.26(7)
N(2)	0.7039(5)	0.17973(8)	0.3284(4)	3.57(7)
C(1)	0.7347(5)	0.03355(9)	0.5698(4)	2.73(7)
C(2)	0.7354(5)	0.02733(10)	0.4045(5)	3.13(8)
C(3)	0.7548(6)	-0.00735(11)	0.3639(5)	3.70(9)
C(4)	0.7743(6)	-0.03369(10)	0.4815(6)	3.85(9)
C(5)	0.7732(6)	-0.02615(10)	0.6431(5)	3.55(9)
C(6)	0.7535(5)	0.00752(9)	0.6919(4)	2.85(8)
C(7)	0.7141(7)	0.05568(12)	0.2759(5)	4.64(11)
C(8)	0.7494(6)	0.01519(10)	0.8691(5)	3.50(9)
C(9)	0.7100(5)	0.21607(9)	0.3894(5)	2.75(7)
C(10)	0.7020(5)	0.24251(10)	0.2731(5)	3.08(8)
C(11)	0.7094(6)	0.27648(10)	0.3350(6)	3.95(10)
C(12)	0.7214(6)	0.28286(11)	0.5021(6)	4.50(11)
C(13)	0.7268(6)	0.25569(12)	0.6103(5)	4.19(10)
C(14)	0.7224(5)	0.22149(10)	0.5586(5)	3.23(8)
C(15)	0.6891(6)	0.23591(11)	0.0905(5)	3.91(9)
C(16)	0.7296(7)	0.19200(13)	0.6798(5)	4.84(11)

Estimated standard deviations are given in parentheses.

IR Spectroscopy

IR spectrum was recorded in the range $4000\text{--}400\text{ cm}^{-1}$ with a "Perkin-Elmer Spectrum 1000" spectrophotometer using a sample dispersed in spectroscopically pure KBr pellet.

Thermal analysis

Thermal analysis was performed using the "multimodule 92 Setaram analyzer" operating from room temperature up to 723 K at an average heating rate of $5\text{ K}\cdot\text{min}^{-1}$.

Results and Discussion

Structure description

The main geometrical features of different entities are reported in Table 3. Figure 1 shows the ORTEP¹⁷ plot of the asymmetric unit of $[2,6-(\text{CH}_3)_2-\text{C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$, containing two 2,6-xylidinium cations, two water molecules and one tetrachlorozincate anion. A view of the structure projected along the axis is given in Figure 2. This projection shows that the most striking feature of this architecture is the assembly of the $(\text{ZnCl}_4)^{2-}$ anions and the water molecules into two-dimensional network, parallel to ac planes at $y=(2n+1)/8$, with the hydrogen-bonded cations protruding on both sides of the network. Adjacent two-dimensional networks interpenetrate each other and pack through π - π stacking interactions

between the xylidinium cations. There are two different π - π interactions between identical antiparallel cations, with face to face distances of 3.649 and 3.735 Å, less than 3.8, maximum value accepted for π - π interactions¹⁸. As shown in Figure 3, in the crystal structure of the title complex, the inorganic and organic species interact by mean of a network of four O-H...Cl, two N-H...O and four N-H...Cl hydrogen bonds (Table 4), giving rise to a porous layer. It is notable that the distances H...Cl varies between 1.83 and 2.58 Å. These values are smaller than the sum of the radii of Van Der Waals of the chlorine and hydrogen atoms ($r_{\text{Cl}} + r_{\text{H}} \leq 2.81$ Å). Consequently, these values correspond well to strong bonds. All these hydrogen bonds, as well as coulombic attractions, Van der Waals forces and π - π interactions, act as an important and predictable structural organizing tool and increase so the structure stability of the title hybrid material.

Table 3. Selected bond lengths (Å) and angles (°) in [2,6-(CH₃)₂-C₆H₃NH₃]₂ZnCl₄·2H₂O.

The ZnCl₄ tetrahedron

Zn–Cl1	2.250(1)	Cl4–Zn1–Cl1	114.74(6)
Zn–Cl2	2.2751(13)	Cl4–Zn1–Cl3	105.17(6)
Zn–Cl3	2.2881(13)	Cl1–Zn1–Cl3	108.40(6)
Zn–Cl4	2.256(1)	Cl4–Zn1–Cl2	109.84(6)
Cl3–Zn1–Cl2	113.09(6)	Cl1–Zn1–Cl2	105.80(5)

The 2,6-xylidinium groups

2,6-(CH₃)₂-C₆H₃N(1)H₃

N1–C1	1.465(6)	C1–C2	1.394(6)	C1–C6	1.393(6)
C2–C3	1.398(7)	C3–C4	1.375(7)	C2–C7	1.492(7)
C4–C5	1.375(7)	C6–C8	1.512(6)	C5–C6	1.382(6)
C2–C1–C6	123.7(4)	C2–C1–N1	118.2(4)	C1–C2–C3	116.1(4)
C4–C3–C2	121.7(4)	C1–C2–C7	122.6(4)	C3–C2–C7	121.2(4)
C3–C4–C5	119.8(4)	C6–C5–C4	121.7(5)	C6–C1–N1	118.0(4)
C1–C6–C5	116.9(4)	C1–C6–C8	122.2(4)	C5–C6–C8	120.8(4)

2,6-(CH₃)₂-C₆H₃N(2)H₃

N2–C9	1.482(6)	C9–C10	1.388(6)	C9–C14	
C10–C11	1.398(7)	C11–C12	1.377(7)	C10–C15	1.503(6)
C12–C13	1.369(8)	C14–C16	1.504(7)	C13–C14	1.380(7)
C9–C10–C11	116.4(4)	C10–C9–N2	117.8(4)	C9–C14–C16	122.3(4)
C10–C11–C12	121.0(5)	C11–C12–C13	119.9(5)	C12–C13–C14	122.2(5)
C13–C14–C16	121.4(5)	C13–C14–C9	116.3(5)	C14–C9–N2	118.0(4)
C10–C9–C14	124.2(4)	C9–C10–C15	123.1(4)	C11–C10–C15	120.5(4)

As expected, in the ZnCl₄²⁻ anion, the Zn atom has a tetrahedral coordination surrounded by four Cl atoms. In the [ZnCl₄] tetrahedra, the mean values of Zn–Cl lengths and Cl–Zn–Cl angles are 2.267 Å and 109.5°, respectively, which are in agreement with those found in anilinium tetrachlorozincate^{19–21}. The slightly deviation from the perfect tetrahedron around Z(II) can be explained by the involving of the chlorine ions in the hydrogen bonding. However, the Zn–Cl bond lengths do not differ appreciably from the shortest and longest bond lengths of 2.245(1) and 2.289(1) Å associated to Zn–Cl1 and Zn–Cl3, respectively. In addition, the Cl–Zn–Cl bond angles are also comparable, varying between 105.15(5) and 114.71(6)°. All these data indicate a slight deviation from perfect tetrahedral environment

around the zinc cation, according to literature results²² and in comparison to the tetrachlorocuprate salt²³. Indeed, in this compound, the Cu-Cl bond lengths and Cl-Cu-Cl bond angles vary from 2.216(7) to 2.283(6) Å and from 94.75(2) to 138.95(3)°, respectively, indicating a large deviation from perfect tetrahedral environment around Cu(II). An examination of the organic moiety geometrical features shows that, the carbon atoms building the two phenyl rings of the title compound have a good coplanarity and they form a conjugated planes with average deviation of 0.025 and 0.037 Å, and they form between them a dihedral angle of 7.32°. The two crystallography independent 2,6-xilidinium cations involved in this crystal packing, exhibit C-C and C-N distances and C-C-C and C-C-N angles in the range usually found for this molecule²⁴⁻²⁵.

Figure 1. ORTEP representation of the molecular configuration of $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$, with atom numbering scheme and thermal ellipsoids at 40% of probability.

Figure 2. Projection of the $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$ structure in the plane (b, c). ZnCl_4 is given in tetrahedral representation. Other atoms are indicated by their symbols. Hydrogen bonds are denoted by dotted lines.

Figure 3. Projection of a layer, viewed down the *b* direction, in the structure of $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$.

Table 4. Hydrogen-bond scheme in $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$.

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A(°)
O(1)-H(1)...Cl3	1.04	2.58	3.619(4)	170.6
O(1)-H(2)...Cl1	1.04	2.52	3.529(4)	163.7
O(2)-H(3) ...Cl4	1.09	2.35	3.203(5)	133.4
O(2)-H(4) ...Cl2	0.87	2.42	3.286(4)	174.7
N(1)-H(5) ...Cl3	1.00	2.46	3.347(4)	146.9
N(1)-H(6) ...Cl2	0.96	2.46	3.261(4)	140.3
N(1)-H(7) ...O2	0.96	1.83	2.732(5)	157.1
N(2)-H(8) ...Cl4	0.95	2.48	3.213(4)	134.4
N(2)-H(9) ...Cl3	0.95	2.43	3.312(4)	153.8
N(2)-H(10) ...O1	0.85	1.97	2.899(6)	165.9

Figure 4. IR spectrum of $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$ in KBr pellet.

IR spectroscopy investigations

The IR spectrum of crystalline $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$ is shown in Figure 4. To assign the IR peaks to vibrational modes, we have used the modes and frequencies observed in similar compounds²⁶⁻²⁷

- The high-frequency region broad bands, between $3600\text{-}2300\text{ cm}^{-1}$, are attributed to the stretching vibrations of organic and hydroxyl groups $\nu(\text{C-H})$, $\nu(\text{N-H})$ and $\nu(\text{O-H})$ of H_2O molecules.
- The vibration bands between 1650 and 1200 cm^{-1} are assigned to bending vibrations of $\delta(\text{NH}_2)$, $\delta(\text{CH}_3)$, $\delta(\text{O-H})$, $\delta(\text{C-C})$, and valence vibrations $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$.
- The bands in the $1000\text{-}700\text{ cm}^{-1}$ range can be attributed to bending modes $\delta(\text{C}_{\text{aryl}}\text{-H})$ and $\delta(\text{C}_{\text{aryl}}\text{-C}_{\text{aryl}})$ and $\delta(\text{C}_{\text{aryl}}\text{-N}_{\text{aryl}})$.

Figure 5. Thermal analysis curves (DTA and TG) under argon of $[2,6-(\text{CH}_3)_2\text{-C}_6\text{H}_3\text{NH}_3]_2\text{ZnCl}_4 \cdot 2\text{H}_2\text{O}$.

Thermal analysis

Curves corresponding to DTA and TGA analysis are reported in Figure 5. The DTA curve shows a succession of endothermic peaks. The first one (89°C) corresponds to an elimination of the two crystallization water molecules, well confirmed by the weight loss observed on TGA curve (% water experimental 7.30, calculated 7.38). After this dehydration, the anhydrous compound melts towards 197°C , confirmed by a separate melting point determination of the title complex. By heating further, the important weight loss observed in the large temperature range, $250\text{-}500^\circ\text{C}$, corresponds to a decomposition of the obtained phase.

Conclusion

Good quality single crystals of 2,6-xylidinium tetrachlorozincate were grown by slow evaporation technique at room temperature. The structure of the title material is stabilized by different types of interactions and particularly an interesting H-bond network. When heated, this complex loses the crystallisation water molecules and continues to decompose in a large temperature range.

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