

Short communication

In Situ Synthesis, Crystal Structure and Fluorescence of $\text{Zn}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_2(\text{H}_2\text{O})_2 \cdot 2\text{Cl}$

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Abstract

$\text{Zn}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_2(\text{H}_2\text{O})_2 \cdot 2\text{Cl}$ (**1**) has been synthesized in situ via hydrothermal reaction and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group $P2_1/c$ with $a = 6.342(2)$, $b = 10.164(3)$, $c = 13.717(4)$ Å, $\beta = 113.62(1)^\circ$, $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_6\text{Zn}$, $M_r = 418.54$, $V = 810.1(4)$ Å³, $Z = 2$, $D_c = 1.716$ g/cm³, $S = 1.063$, $\mu(\text{MoK}\alpha) = 1.875$ mm⁻¹, $F(000) = 424$, $R = 0.0276$ and $wR = 0.0780$. The crystal structure analysis of **1** reveals that the title compound features a structure consisting of isolated units, based on discrete chloride ions and octahedral zinc cations six-coordinated by four oxygen and two nitrogen atoms. The chloride ions and $[\text{Zn}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_2(\text{H}_2\text{O})_2]^{2+}$ moieties are interconnected by hydrogen bonding interactions to yield a 3-D supramolecular framework. Luminescent investigation reveals an emission in blue region, which may be originating from $\pi \rightarrow \pi^*$ charge-transfer interaction of the pyridine-2-carboxylic acid.

Keywords: Hydrothermal, 2-cyanopyridine, pyridine-2-carboxylic acid, photoluminescence

1. Introduction

During the past decades, in situ reactions under hydrothermal environments have attracted growing interest, because in situ synthesis leads to the generation of novel compounds with structural diversities or promising properties for variously potential applications.^{1–3} Up to now, a lot of new compounds synthesized in situ have been documented and many of them are transition metal compounds.^{4–6} Transition metal compounds containing group 12 metals are very attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the d^{10} configuration of the group 12 metal ions, photoelectric properties, and fluorescent properties, etc. Our recent efforts are focused largely on the synthesis of novel group 12-based compounds. Herein, we report the in situ synthesis, crystal structure and fluorescence of $\text{Zn}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_2(\text{H}_2\text{O})_2 \cdot 2\text{Cl}$ (**1**).

2. Experimental

2.1. Synthesis of

$\text{Zn}(\text{C}_5\text{H}_4\text{NCO}_2\text{H})_2(\text{H}_2\text{O})_2 \cdot 2\text{Cl}$ (**1**)

All reactants of A.R. grade were obtained commercially and used without further purification. ZnCl_2

(1 mmol, 136 mg), 2-cyanopyridine (2 mmol, 208 mg) and distilled water (10 mL) were loaded into a Teflon-lined stainless steel autoclave (23 mL) and kept at 453 K for 7 days. After being slowly cooled to room temperature at a rate of 6 K/h, colorless crystals suitable for X-ray analysis were obtained. Yield: 71% (based on zinc).

2.2. X-ray Structure Determination

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) by using a φ and ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction.⁷ The structure was solved by the direct method using the Siemens SHELXTL™ Version 5 package of crystallographic software.⁸ The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The hydrogen atom positions were generated theoretically and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but was not refined. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Table 1: Summary of Crystallographic Data and Structure Analysis for **1**.

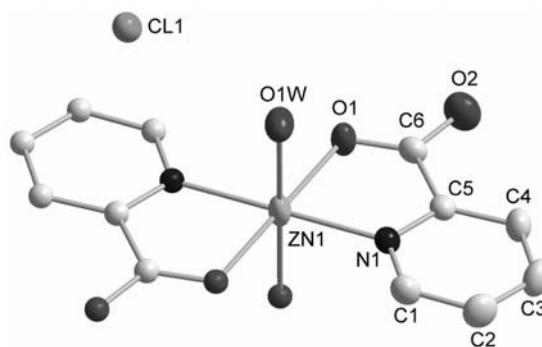
Formula	C ₁₂ H ₁₄ Cl ₂ N ₂ O ₆ Zn
<i>F</i> _w	418.54
Color	colorless block
Crystal size/mm ³	0.13 0.07 0.05
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.342(2)
<i>b</i> (Å)	10.164(3)
<i>c</i> (Å)	13.717(4)
β (°)	113.62(1)
<i>V</i> (Å ³)	810.1(4)
<i>Z</i>	2
θ _{min} (°)	2.58
2θ _{max} (°)	25.0350.06
Reflections collected	4715
Independent, observed reflections (<i>R</i> _{int})	1405, 1324 (0.0179)
Absorption correction	multi-scan
<i>T</i> _{max}	0.912
<i>T</i> _{min}	0.854
<i>d</i> _{calcd.} (g/cm ³)	1.716
μ (mm ⁻¹)	1.875
<i>T</i> (K)	293(2)
<i>F</i> (000)	424
<i>R</i> 1, <i>wR</i> 2	0.0276, 0.0780
<i>S</i>	1.063
Largest and Mean Δ/ <i>σ</i>	0.002, 0
Δρ (max, min) (e/Å ³)	0.615, -0.572

3. Results and Discussion

Hydrothermal reactions have been known as a powerful method in the preparation of solid-state materials and this technique is well-known for its effectiveness in the in situ reactions. When superheated, water behaves very differently from what is observed under ambient conditions. The significantly lowered viscosity, for example, increases the solubility as well as the diffusion rate of the reagents, therefore possibly leading to in situ reactions. A variety of novel compounds synthesized in situ have been

reported so far. However, 2-cyanopyridine-containing in situ reactions are rare. As for the synthesis of the title compound, the starting material is 2-cyanopyridine, but pyridine-2-carboxylic acid is found in the final product, suggesting that in situ reaction has happened to 2-cyanopyridine under hydrothermal conditions.

Single-crystal X-ray diffraction analysis reveals that compound **1** features a 0-D discrete structure, comprising of chloride ions and [Zn(C₅H₄NCO₂H)₂(H₂O)₂]²⁺ moieties. All the crystallographic independent atoms except for Zn(1) atom are in the general positions. The coordination environment around each Zn^{II} ion is N₂O₄, with two nitrogen and two oxygen atoms from two different pyridine-2-carboxylic acid ligands and two oxygen atoms from two coordinated water molecules, and can be described as a distorted octahedron with the bond lengths of Zn(1)-N(1), Zn(1)-O(1) and Zn(1)-O(1W) being of 2.045(2), 2.085(2) and 2.219(2) Å (Figure 1 and Table 2), respectively, which are normal and comparable with the counterparts found in the literature.^{9,10} The existence of steric hindrances in rigid ligand moieties leads to the substantially longer bond distance of Zn(1)-O(1W) (2.219(2) Å). The basal plane is formed by atoms N(1), O(1), N(1)(-x, -y-1, -z), O(1)(-x, -y-1, -z), and the axial sites are occupied by atoms O(1W)

**Fig. 1:** ORTEP drawing of **1** with 50% thermal ellipsoids. Hydrogen atoms were omitted for clarity.**Table 2:** Selected bond lengths (Å) and bond angles (°).

Bond	Dist.	Bond	Dist.
Zn(1)-N(1)	2.045(2)	Zn(1)-O(1)	2.085(2)
Zn(1)-O(1W)	2.219(2)		
Angle	(°)	Angle	(°)
N(1)-Zn(1)-N(1) ¹	180.00(6)	O(1)-Zn(1)-O(1W) ¹	88.73(7)
N(1)-Zn(1)-O(1)	79.60(7)	O(1) ¹ -Zn(1)-O(1W) ¹	91.27(7)
N(1) ¹ -Zn(1)-O(1)	100.40(7)	N(1)-Zn(1)-O(1W)	88.69(7)
N(1)-Zn(1)-O(1) ¹	100.40(7)	N(1) ¹ -Zn(1)-O(1W)	91.31(7)
N(1) ¹ -Zn(1)-O(1) ¹	79.60(7)	O(1)-Zn(1)-O(1W)	91.27(7)
O(1)-Zn(1)-O(1) ¹	180.0	O(1) ¹ -Zn(1)-O(1W)	88.73(7)
N(1)-Zn(1)-O(1W) ¹	91.31(7)	O(1W) ¹ -Zn(1)-O(1W)	180.00(9)
N(1) ¹ -Zn(1)-O(1W) ¹	88.69(7)		

Symmetry codes: ¹ -x, -y-1, -z.

and O(1W)(-x, -y-1, -z). The four basal atoms are perfectly coplanar and the Zn(1) atom is exactly in this plane. Each pyridine-2-carboxylic acid ligand is bound to the Zn^{II} center providing a five membered Zn–N–C–O–chelate ring. The chelated angle value of N(1)–Zn(1)–O(1) being of 79.605° is significantly smaller than the ideal value of 90° and are the primary sources of distortion in the geometry, and this is in good agreement with the values found in several other Zn-pyridine-2-carboxylic acid compounds.^{9,10} Two pyridine-2-carboxylic acids are in *cis* position around Zn(1), and they are perfectly coplanar to each other with a dihedral angle of 0°.

For the title compound, there are several hydrogen bonding interactions between the chloride ions and the [Zn(C₅H₄NCO₂H)₂(H₂O)₂]²⁺ moieties. The chloride ions and [Zn(C₅H₄NCO₂H)₂(H₂O)₂]²⁺ moieties are interconnected by hydrogen bonding interactions to construct a 3-D supramolecular network (Figure 2 and Table 3). The hydrogen bonding interactions and the electrostatic interactions between the [Zn(C₅H₄NCO₂H)₂(H₂O)₂]²⁺ cationic moieties and Cl⁻ anions contribute to the stabilization of the crystal packing of the title compound. Result of the bond valence calculations indicates that the zinc atom is in +2 oxidation state (Zn1: 2.163).^{11,12}

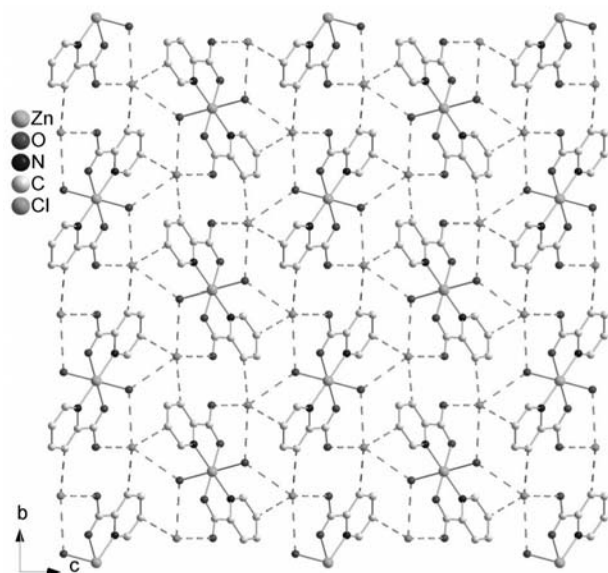


Fig. 2: Packing diagram of **1** with the dashed lines representing hydrogen bonding interactions.

Table 3: Hydrogen bonding interactions

Hydrogen bonding interaction	Distance (Å)
O(1W)–H(1)···Cl(1)	3.197(2)
O(1W)–H(2)···Cl(1)	3.299(2)
O(2)–H(2A)···Cl(1)	3.322(2)
C(2)–H(2B)···Cl(1)	3.709(3)
C(4)–H(4A)···Cl(1)	3.676(3)

The fluorescent emission spectra of the title compound are investigated at room temperature. The emission spectrum of the title compound is given in Fig. 3. The fluorescent spectrum study shows that the title compound displays a blue-light emission band with a maximum wavelength of 442 nm upon photo-excitation at 382 nm. The luminescent spectra of **1** should be assigned as a $\pi \rightarrow \pi^*$ transition of pyridine-2-carboxylic acid. Thus, this compound may be a candidate in blue-light luminescent materials.

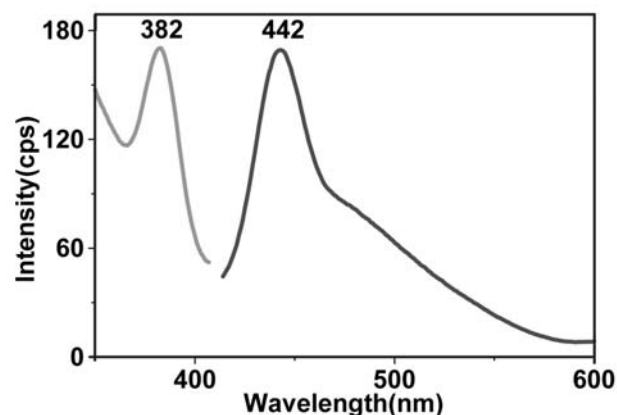


Fig. 3: The emission and excitation spectra of **1** at room temperature. Red line: emission spectrum; green line: excitation spectrum.

4. Conclusions

In summary, a new Zn-based compound Zn(C₅H₄NCO₂H)₂(H₂O)₂ · 2Cl, in which the pyridine-2-carboxylic acid was generated in situ, has been synthesized via hydrothermal reaction. The title compound is characteristic of a 3-D supramolecular framework formed by hydrogen bonding interactions. The title compound exhibits an emission in blue region, which may be originating from $\pi \rightarrow \pi^*$ charge-transfer interaction of the pyridine-2-carboxylic acid. Further investigations on this field are in progress in our laboratory.

5. Acknowledgements

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6. Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 740873. Copies of the data can be obtained

free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

7. References

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Povzetek

Zn(C₅H₄NCO₂H)₂(H₂O)₂ · 2Cl (**1**) smo sintetizirali s hidrotermalno reakcijo. Spojino smo karakterizirali z rentgensko difrakcijo. Kristal je monoklinski, prostorska skupina P2₁/c, s parametri osnovne celice $a = 6.342(2)$, $b = 10.164(3)$, $c = 13.717(4)$ Å, $\alpha = 113.62(1)^\circ$, C₁₂H₁₄Cl₂N₂O₆Zn, $M_r = 418.54$, $V = 810.1(4)$ Å³, $Z = 2$, $D_c = 1.716$ g/cm³, $S = 1.063$, $\mu(\text{MoK}\alpha) = 1.875$ mm⁻¹, $F(000) = 424$, $R = 0.0276$ in $wR = 0.0780$. Strukturna analiza kristala je razkrila, da sestoji iz kloridnih ionov in cinkovih ionov, ki so oktaedrično koordinirani s štirimi kisikovimi in dvema dušikovima atomoma. Kloridni ioni in enote [Zn(C₅H₄NCO₂H)₂(H₂O)₂]²⁺ so povezani z vodikovimi vezmi v supramolekularno 3-D strukturo. Raziskave luminescence so pokazale emisijo v modrem območju, ki je lahko posledica $\pi \rightarrow \pi^*$ interakcije piridin-2-karboksilne kisline.