

含非交换氘的四唑-锌配合物

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First Crystallographically Characterized Zinc Tetrazole Complex with Partial Non-exchange Deuterium

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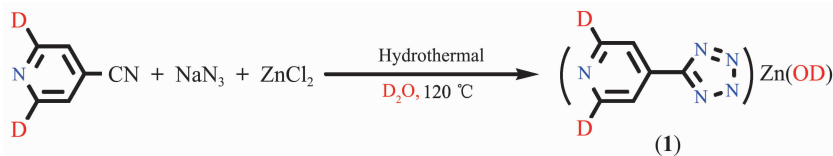
Abstract: The solvothermal reaction (D_2O) of 2,6-dideuterium-4-cyanopyridine with $ZnCl_2$ in the presence of NaN_3 offers a novel complex $Zn(OD)(C_6H_2D_2N_4)$ (**1**) in which Zn has a distorted tetrahedron composed of two N atoms from one tetrazoyl group and pyridyl group and two O atoms from two deuteratohydroxy OD groups. Crystal data for **1**: $Pbcn$, $a=1.456\ 8(5)$ nm, $b=0.659\ 2(2)$ nm, $c=1.645\ 3(5)$ nm, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$, $V=1.580\ 0(9)$ nm³, $Z=8$, $M=231.54$, $D_c=2.236$ Mg·m⁻³, $\mu=3.070$ mm⁻¹, $R_1=0.043\ 4$, $wR_2=0.120\ 6$, $S=1.029$. CCDC: 660629.

Key words: deuterium; zinc(II) complex; solvothermal reaction; crystal structure

The non-exchanged-deuterium organic compounds have been found widespread applications in the labeled compounds especially with radiation-property elements, such as ^{13}C and $^3H^{[1]}$. Organic compounds with tetrazole group have been widely used in medicinal manufacturing fields, especially Valsartan, commercial product used as treatment for hypertension. As we are aware, the partially deuterated organic tetrazole has never been found before, especially its metal complex^[2~10]. Herein we report the crystallographically characterized Zn-tetrazole complex with partial deuterated non-

exchanged deuterium. The reaction of 2,6-dideuterium-4-cyanopyridine with $ZnCl_2$ in the presence of NaN_3 under solvothermal reaction condition (D_2O as solvent) gives a novel complex $Zn(OD)(C_6H_2D_2N_4)$ (**1**), which forms the 2D laminar framework. (Scheme 1).

IR spectrum of **1** definitely shows the presence of OD stretching vibration peak at $2\ 400\ cm^{-1}$ while $1\ 400$ and $1\ 300\ cm^{-1}$ is a typical peak of tetrazole group. In addition, the electronic spray mass spectra for the extraction solution of **1** confirm the presence of 2,6-dideuterium-4-pyridyltetrazole ($m/z=149.18$, -p) from



Scheme 1

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its precursor ligand 2,6-dideuterium-4-cyanopyridine ($m/z = 107.21$, +p) (Fig.1). The IR spectrum of **1** is consistent with the structure determination, which shows one OD group, one unique ligand and one unique zinc center. In the crystal $\text{Zn}(\text{OD})(\text{C}_6\text{H}_2\text{D}_2\text{N}_4)$ exhibits a two-dimension laminar structure consisting of continuing square nets in which zinc is at a tetrahedral center, each zinc is coordinated by two O atoms from two different OD groups (O1-Zn1 0.193 3 nm), one pyridyl N atom from one 2,6-dideuterium-4-pyridyl-tetrazole (N1-Zn1 0.207 9 nm), and one tetrazoyl N from different

2,6-dideuterium-4-pyridyltetrazole (N5B-Zn1 0.202 1 nm) (Fig.2a). On the other hand, each O atom of OD group links two different zinc, four zinc centers (Zn1-Zn1B-Zn1D-Zn1A) form a rhombohedra net as shown in Fig.2b.

Crystal data for **1**: $Pbcn$, $a=1.456\ 8(5)$ nm, $b=0.659\ 2(2)$ nm, $c=1.645\ 3(5)$ nm, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=90^\circ$, $V=1.580\ 0(9)$ nm³, $Z=8$, $M=231.54$, $D_c=2.236$ Mg·m⁻³, $\mu=3.070$ mm⁻¹, $R_1=0.043\ 4$, $wR_2=0.120\ 6$, $S=1.029$.

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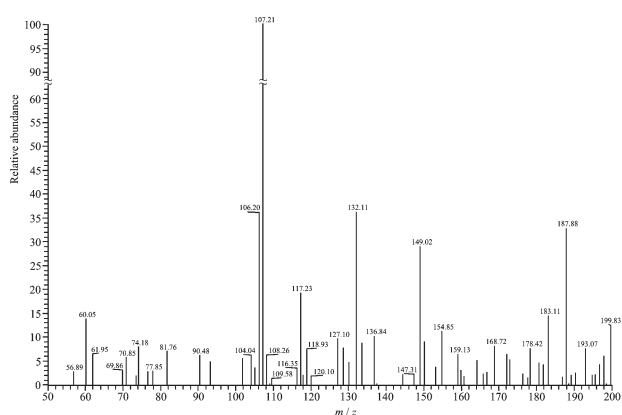
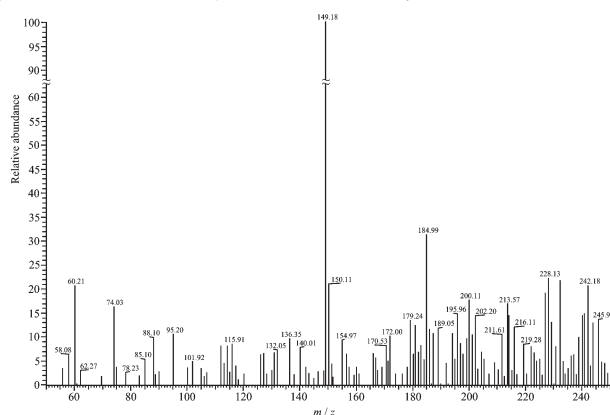


Fig.1 Electronic spray mass spectra for the extraction of ligand 2,6-dideuterium-4-pyridyltetrazole and its precursor 2,6-dideuterium-4-cyanopyridine

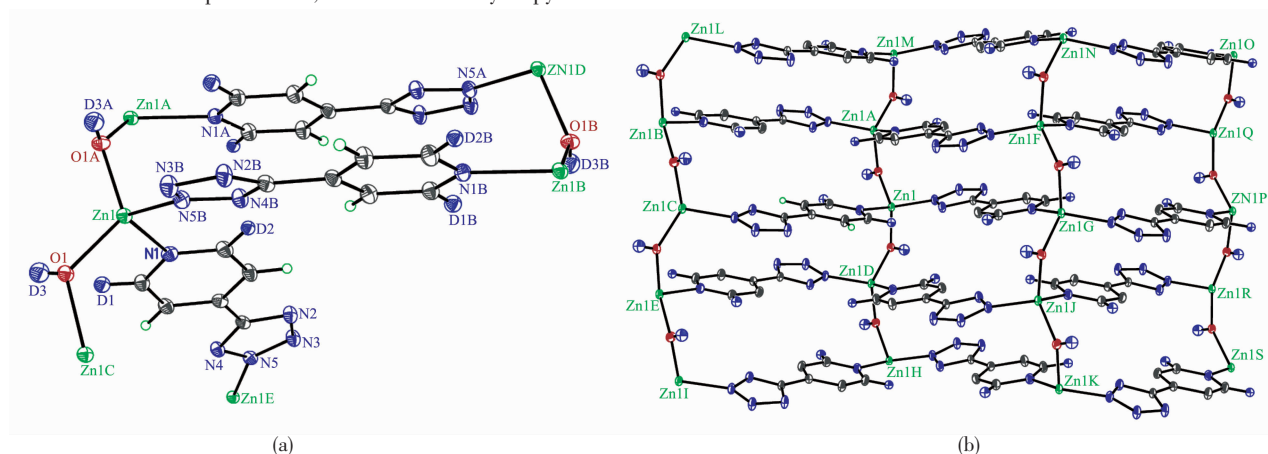


Fig.2 (a) Asymmetric unit of $\text{Zn}(\text{OD})(\text{C}_6\text{H}_2\text{D}_2\text{N}_4)$; (b) 2D square grid structure of $\text{Zn}(\text{OD})(\text{C}_6\text{H}_2\text{D}_2\text{N}_4)$

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