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Crystal structure of tetraaqua-bis(4-(5-tetrazolato)pyridyl-*N*)zinc(II) dihydrate, $Zn(H_2O)_4(C_6H_4N_5)_2 \cdot 2H_2O$

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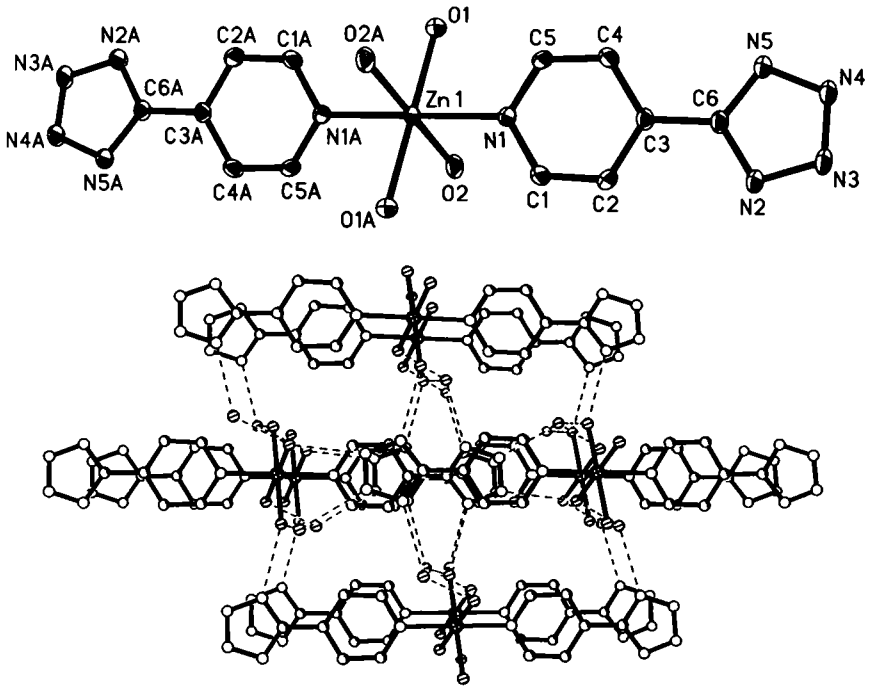

Abstract

$C_{12}H_{20}N_{10}O_6Zn$, triclinic, $P\bar{1}$ (no. 2), a = 7.231(1) Å, b = 7.762(2) Å, c = 8.709(2) Å, α = 88.867(3)°, β = 89.985(3)°, γ = 79.813(3)°, V = 481.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.105, T = 296 K.

Source of material

The title complex was synthesized under hydrothermal conditions. A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.1098 g, 0.5 mmol), 5-(4-pyridyl)-1*H*-tetrazole (0.0736 g, 0.5 mmol; PTZ), 0.05 ml Et_3N and 8 ml deionized water was sealed in a Teflon-lined stainless vessel (25 ml) and heated at 423 K for 86 h under autogenous pressure, then cooled slowly to room temperature. Colorless block crystals were obtained by filtration.

Experimental details

While water H atoms were located in a Fourier difference map and refined with restraints, the other H atoms were placed at calculated positions and refined using a riding model.

Discussion

Tetrazole as functional group plays an increasingly important role in coordination chemistry as ligand [1], in medical chemistry as a metabolically stable surrogate for carboxylic acid group [2] and in various materials science applications, including special explosives [3,4].

In the crystal structure of $Zn(4\text{-PTZ})_2(H_2O)_4 \cdot 2H_2O$, the zinc atom has an approximate octahedral environment (figure top), where two 4 PTZ anions act as monodentate ligands via their pyridine-N atoms in *trans* positions (d(Zn—N) = 2.135(3) Å). The structure also contains six water molecules, four act as monodentate ligands (d(Zn—O1) = 2.122(2) Å, d(Zn—O2) = 2.131(3) Å) and the remaining two as lattice water molecules. Within the equatorial plane, the sum of the bond angles (∠O1–Zn–O2 = 89.6(1)° and ∠O2–Zn–O1^i = 90.4(1)°) around Zn(II) atom is 360°. The apical N–Zn–N bond angle is 180°. The environment of the central atom is similar to that of [Mn{5-(4-pyridyl)-tetrazolato}$_2$(H$_2$O)$_4$] [5], in which the central Mn also has an octahedral environment and lies on the crystallographic inversion center. The supramolecular title complex possesses two types of hydrogen bonds. One type occurs between coordinating water and lattice water molecules with d(O···O) = 2.741 Å – 2.771 Å and ∠O–H···O = 165.1° – 173.5°. The other type is between the non-coordinating N atoms of the tetrazolato ligands and six water O atoms with d(N···O) = 2.779 Å – 2.924 Å and ∠N–H···O = 159.4° – 176.7°. Through these hydrogen bonds, the adjacent mononuclear units are linked into infinite rows parallel to the *b*,*c* plane. A 3D network structure is formed by the face-to-face π-π interactions of the pyridine ring and the tetrazolate ring ligands belonging to adjacent dimeric units with distances of about 3.3 Å – 3.5 Å (figure bottom).

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Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.07 × 0.28 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.31 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2459, 1685
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1432
$N(param)_{refined}$:	152
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.1678	0.6149	0.9488	0.054
H(2)	2*i*	0.2459	0.4188	0.7586	0.053
H(4)	2*i*	0.1861	0.8211	0.4591	0.044
H(5)	2*i*	0.0995	1.0033	0.6561	0.041
H(1A)	2*i*	−0.178(7)	1.267(2)	0.808(5)	0.080
H(2A)	2*i*	−0.239(7)	0.775(5)	0.959(4)	0.080
H(3A)	2*i*	0.441(7)	0.158(6)	0.666(4)	0.080
H(1B)	2*i*	−0.282(3)	1.142(7)	0.827(6)	0.080
H(2B)	2*i*	−0.288(6)	0.859(7)	1.101(4)	0.080
H(3B)	2*i*	0.504(7)	−0.001(3)	0.708(5)	0.080

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	1*a*	0	0	0	0.0400(4)	0.0213(4)	0.0183(3)	0.0026(2)	0.0045(2)	−0.0046(2)
N(1)	2*i*	0.1173(4)	0.8289(3)	0.8224(3)	0.039(2)	0.020(1)	0.023(1)	0.002(1)	0.003(1)	−0.004(1)
N(2)	2*i*	0.3387(4)	0.3013(4)	0.4819(3)	0.051(2)	0.025(2)	0.027(2)	0.006(1)	0.000(1)	−0.008(1)
N(3)	2*i*	0.3549(5)	0.2338(4)	0.3409(3)	0.052(2)	0.029(2)	0.031(2)	0.004(2)	0.001(2)	−0.014(1)
N(4)	2*i*	0.2953(4)	0.3567(4)	0.2379(3)	0.049(2)	0.028(2)	0.027(2)	0.005(1)	−0.002(1)	−0.010(1)
N(5)	2*i*	0.2383(4)	0.5086(4)	0.3092(3)	0.050(2)	0.025(2)	0.026(2)	0.002(1)	0.000(1)	−0.006(1)
O(1)	2*i*	−0.1714(4)	1.1618(3)	0.8372(3)	0.043(2)	0.028(1)	0.029(1)	−0.002(1)	−0.003(1)	0.002(1)
O(2)	2*i*	−0.2132(4)	0.8441(3)	1.0264(3)	0.053(2)	0.039(2)	0.027(1)	−0.015(1)	0.011(1)	−0.011(1)
O(3)	2*i*	0.4791(4)	0.1001(3)	0.7470(3)	0.047(2)	0.028(1)	0.027(1)	0.002(1)	0.005(1)	−0.005(1)
C(1)	2*i*	0.1667(7)	0.6566(5)	0.8479(4)	0.083(3)	0.027(2)	0.020(2)	0.006(2)	0.005(2)	−0.001(2)
C(2)	2*i*	0.2159(6)	0.5377(5)	0.7342(4)	0.079(3)	0.019(2)	0.031(2)	0.005(2)	0.004(2)	−0.003(2)
C(3)	2*i*	0.2210(5)	0.5952(4)	0.5825(4)	0.028(2)	0.026(2)	0.024(2)	0.001(1)	0.001(1)	−0.006(1)
C(4)	2*i*	0.1793(5)	0.7746(4)	0.5578(4)	0.055(2)	0.028(2)	0.021(2)	0.007(2)	0.004(2)	0.001(1)
C(5)	2*i*	0.1283(5)	0.8836(4)	0.6772(4)	0.053(2)	0.018(2)	0.028(2)	0.007(2)	0.004(2)	0.001(1)
C(6)	2*i*	0.2655(5)	0.4708(4)	0.4589(4)	0.030(2)	0.026(2)	0.025(2)	0.000(1)	0.002(1)	−0.006(1)

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