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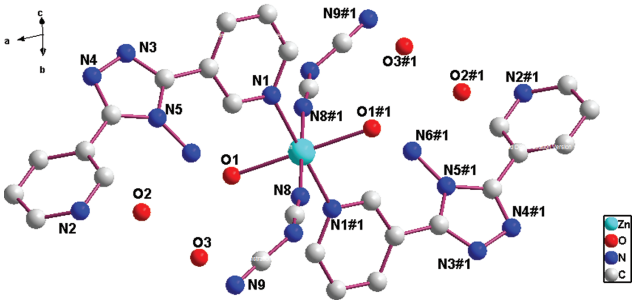
Crystal structure of (*OC*-6-13)-diaqua-bis(3,5-di(pyridin-3-yl)-4*H*-1,2,4-triazol-4-amine-κ^1*N*)-bis(dicyanamido-κ^1*N*)zinc(II) tetrahydrate, $ZnC_{28}H_{32}N_{18}O_6$



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Abstract

$ZnC_{28}H_{32}N_{18}O_6$, monoclinic, $P2_1/c$ (no. 14), $a = 10.472(2)$ Å, $b = 21.668(4)$ Å, $c = 8.1282(15)$ Å, $\beta = 105.763(5)°$, $V = 1775.0(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0459$, $wR_{ref}(F^2) = 0.1133$, $T = 298$ K.

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The crystal structure is shown in the figure. Hydrogen atoms are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A methanolic solution (10 mL) of 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (3-pytz) (1.0 mmol) was added slowly to an aqueous solution (10 mL) of $Zn(NO_3)_2{\cdot}6H_2O$ (0.5 mmol) and $Na[N(CN)_2]$ (1.0 mmol) with stirring. The mixture was stirred at room temperature and the resultant solution was filtered. After the filtrate was allowed to stand for several days, colorless crystals of the title compound were obtained.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.80 × 0.55 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	9.5 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury, ω-scans
θ_{max}, completeness:	25.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16857, 3239, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2016
$N(param)_{refined}$:	259
Programs:	CrystalClear [1], SHELX [2]

Discussion

Supramolecular structures are of great interest due to their structural characteristics, such as manifold coordination modes, intriguing architecture, and porosity, and also due to their physicochemical characteristics and potential applications as functional materials [3, 4]. The successful creation of higher-dimensional supramolecular architectures can be accomplished by employing coordination bonds, hydrogen bonds, aromatic π–π stacking interactions, etc. Recently, dicyanamide (dca) has been used as a building block in both supramolecular chemistry and crystal engineering [5, 6].

In this paper, we select dicyanamide (dca) to react with Zn(II) ions and 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (3-pytz) to obtain a new mononuclear complex. The asymmetric unit of the title structure consists of one half of a Zn^{2+} ion, one 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (3-pytz), three water and one $[N(CN)_2]^-$. Each Zn(II) atom is coordinated by two pyridyl nitrogen atoms from two different 3-pytz ligands, two nitrogen atom from the terminal dicyanamido ligand and two water molecules to furnish a [ZnN4O2] six-coordinate distorted octahedral geometry (*cf.* the figure). The Zn–O bond lengths are 2.167(2) Å, and the Zn–N distances are 2.098(2) and 2.163(2) Å, both of which are in the normal range. The bond angles around the Zn(II) are in the ranges of 89.74(9)–180°.

There are hydrogen bonding interactions between the lattice water molecules O2 and uncoordinated nitrogen atoms N3 and N2 from 3-pytz (O(2)-H(3W)···N(3)#2, O(2)-H(4W)···N(2)#3) to form a 1D chain. Furthermore, water molecules O3 interact with uncoordinated nitrogen atoms N9 from dca (O(3)-H(6W)···N(9)#3) to form 2D layers. Moreover,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	0.5000	0.5000	0.02939(15)
O1	0.20169(19)	0.50834(9)	0.4809(3)	0.0366(4)
H1W	0.271(2)	0.4899(12)	0.549(4)	0.044*
H2W	0.227(3)	0.5463(8)	0.473(4)	0.044*
O2	0.4424(2)	0.63024(11)	0.7832(3)	0.0549(6)
H3W	0.483(3)	0.5953(10)	0.777(5)	0.066*
H4W	0.503(3)	0.6591(11)	0.799(5)	0.066*
O3	0.2947(3)	0.62391(11)	0.4487(3)	0.0609(7)
H5W	0.250(3)	0.6585(13)	0.411(4)	0.073*
H6W	0.330(4)	0.6321(17)	0.561(2)	0.073*
N1	0.0736(2)	0.47660(10)	0.7678(3)	0.0291(5)
N2	0.5916(3)	0.76225(12)	1.2898(4)	0.0607(8)
N3	0.4660(2)	0.49527(10)	1.2267(3)	0.0348(5)
N4	0.5597(2)	0.54070(10)	1.2889(3)	0.0367(5)
N5	0.3813(2)	0.58422(9)	1.1276(3)	0.0286(5)
N6	0.2879(2)	0.62675(11)	1.0346(3)	0.0421(6)
H6B	0.2117	0.6141	0.9743	0.051*
H6C	0.3069	0.6654	1.0380	0.051*
N7	0.0116(4)	0.69394(15)	0.6983(6)	0.0834(12)
N8	0.0002(2)	0.59388(11)	0.5632(3)	0.0422(6)
N9	0.1754(5)	0.77466(19)	0.7449(6)	0.1021(15)
C1	0.0218(3)	0.43072(12)	0.8397(3)	0.0329(6)
H1A	−0.0528	0.4103	0.7740	0.039*
C2	0.0742(3)	0.41257(13)	1.0058(4)	0.0361(6)
H2A	0.0355	0.3806	1.0513	0.043*
C3	0.1855(3)	0.44240(13)	1.1052(3)	0.0346(6)
H3A	0.2233	0.4304	1.2178	0.042*
C4	0.2395(2)	0.49052(11)	1.0333(3)	0.0282(5)
C5	0.1799(3)	0.50582(11)	0.8644(3)	0.0280(5)
H5A	0.2157	0.5381	0.8159	0.034*
C6	0.5247(3)	0.70904(14)	1.2728(5)	0.0501(8)
H6A	0.4363	0.7100	1.2744	0.060*
C7	0.5802(3)	0.65265(12)	1.2529(4)	0.0338(6)
C8	0.7129(3)	0.65176(14)	1.2576(5)	0.0490(8)
H8A	0.7548	0.6146	1.2482	0.059*
C9	0.7827(3)	0.70612(16)	1.2763(6)	0.0633(10)
H9A	0.8721	0.7064	1.2795	0.076*
C10	0.7183(4)	0.75956(16)	1.2900(5)	0.0624(10)
H10A	0.7657	0.7963	1.3001	0.075*
C11	0.3605(2)	0.52257(12)	1.1302(3)	0.0285(5)
C12	0.5075(2)	0.59381(12)	1.2281(3)	0.0308(6)
C13	0.0126(3)	0.64163(13)	0.6226(4)	0.0398(7)
C14	0.1030(4)	0.73500(15)	0.7168(5)	0.0527(8)

the coordinated water molecules and uncoordinated nitrogen atoms N4 from 3-pytz (O(1)-H(1W)$\cdots$N(4)#2) link the 2D layers to form a 3D structure (#1 = $-x$, $-y+1$, $-z+1$; #2 = $-x+1$, $-y+1$, $-z+2$; #3 = x, $-y+3/2$, $z-1/2$). The O2 atoms of lattice water molecules and adjacent oxygen atoms O(3) of the lattice water molecules are involved in the formation of O—H$\cdots$O hydrogen bonds. The hydrogen-bonding interactions play an important role in stabilizing the solid-state [7, 8].

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