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Hydrothermal synthesis and crystal structure of *catena*-poly[bis(4-((pyridin-4-ylmethyl)amino)benzoato- $\kappa^3 N:O,O'$)zinc(II) – 1,2-di(pyridin-4-yl)ethene – water (1/1/1), $C_{38}H_{34}N_6O_5Zn$

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Abstract

$C_{38}H_{34}N_6O_5Zn$, triclinic, $P\bar{1}$, $a = 9.1991(4)$ Å, $b = 9.7349(4)$ Å, $c = 19.5840(8)$ Å, $\alpha = 102.770(4)^\circ$, $\beta = 90.522(3)^\circ$, $\gamma = 100.879(4)^\circ$, $V = 1677.31(13)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0405$, $wR_{ref}(F^2) = 0.0928$, $T = 293(2)$ K.

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The asymmetric unit (displacement ellipsoid representation) of the title crystal structure is shown in the figure. 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

All chemicals for synthesis were of reagent grade and used as received without further purification. The mixtures of 4-[(pyridin-4-ylmethyl)amino]benzoic acid (H_2L , 11.4 mg, 0.05 mmol), 1,2-bis(4-pyridyl)ethene (bpe, 9.1 mg, 0.05 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (43.9 mg, 0.2 mmol), and H_2O

Table 1: Data collection and handling.

Crystal:	Block, clear light colourless
Size:	$0.32 \times 0.28 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.79 mm^{-1}
Diffractometer, scan mode:	SuperNova, φ and ω -scans
$\theta_{\max}$, completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12357, 6193, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5277
$N(\text{param})_{\text{refined}}$:	463
Programs:	CrysAlis ^{PRO} [1], SHELX [2], OLEX2 [3]

(6 mL) was placed in a 23 mL Teflon-lined autoclave at 393 K for 4 days, then cooled to room temperature. Colourless block crystals were obtained in ca. 56% yield. Elemental analysis calcd. (%) for $C_{38}H_{34}N_6O_5Zn$: C, 63.41; H, 4.85; N, 11.23. Found: C, 63.38; H, 4.76; N, 11.67.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon and nitrogen atoms and 1.5 times U_{eq} for the hydrogen atoms at water.

Discussion

Coordination polymers (CPs) have attracted extensive attention due to their beautiful structures and potential applications in a wide variety of fields [4–9]. It is well known that the selection of suitable ligands is the most critical

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zn1	−0.17712(3)	0.07147(3)	0.73004(2)	0.03449(10)
O1	−0.1922(2)	0.18933(19)	0.82359(9)	0.0441(4)
O2	−0.3381(2)	−0.01192(19)	0.83358(9)	0.0470(5)
O3	−0.0786(2)	0.22544(18)	0.68634(9)	0.0435(5)
O4	−0.0670(3)	0.0564(2)	0.59304(11)	0.0675(7)
N1	0.6398(2)	0.9691(2)	0.66817(10)	0.0337(5)
N2	0.2749(3)	0.6025(3)	0.49033(12)	0.0518(7)
H2	0.309(4)	0.568(3)	0.4533(17)	0.062*
N3	−0.2828(2)	0.3496(2)	1.15167(11)	0.0359(5)
H3	−0.223(3)	0.426(3)	1.1641(14)	0.043*
N4	0.0295(2)	0.0545(2)	1.25593(11)	0.0363(5)
C1	−0.0395(3)	0.1829(3)	0.62339(13)	0.0373(6)
C2	0.0433(3)	0.2950(3)	0.58968(12)	0.0325(5)
C3	0.1003(3)	0.2554(3)	0.52445(13)	0.0380(6)
H3A	0.0870	0.1587	0.5023	0.046*
C4	0.1759(3)	0.3570(3)	0.49214(13)	0.0417(6)
H4	0.2135	0.3277	0.4485	0.050*
C5	0.1976(3)	0.5037(3)	0.52362(13)	0.0380(6)
C6	0.1399(3)	0.5438(3)	0.58939(13)	0.0370(6)
H6	0.1525	0.6404	0.6118	0.044*
C7	0.0643(3)	0.4402(3)	0.62107(13)	0.0344(6)
H7	0.0265	0.4685	0.6647	0.041*
C8	0.2883(3)	0.7548(3)	0.51334(15)	0.0507(8)
H8A	0.1950	0.7742	0.5319	0.061*
H8B	0.3043	0.7971	0.4729	0.061*
C9	0.4111(3)	0.8285(3)	0.56832(13)	0.0361(6)
C10	0.4487(3)	0.9769(3)	0.58681(14)	0.0429(7)
H10	0.3968	1.0319	0.5663	0.051*
C11	0.5633(3)	1.0427(3)	0.63559(14)	0.0411(6)
H11	0.5888	1.1424	0.6465	0.049*
C12	0.6002(3)	0.8262(3)	0.65138(14)	0.0391(6)
H12	0.6504	0.7735	0.6743	0.047*
C13	0.4898(3)	0.7533(3)	0.60222(14)	0.0403(6)
H13	0.4678	0.6534	0.5916	0.048*
C14	−0.2702(3)	0.1110(3)	0.86053(13)	0.0353(6)
C15	−0.2711(2)	0.1742(2)	0.93656(12)	0.0293(5)
C16	−0.3263(3)	0.0883(3)	0.98189(13)	0.0323(5)
H16	−0.3640	−0.0087	0.9636	0.039*
C17	−0.3272(3)	0.1421(2)	1.05301(12)	0.0319(5)
H17	−0.3631	0.0809	1.0820	0.038*
C18	−0.2745(2)	0.2879(2)	1.08183(12)	0.0294(5)
C19	−0.2153(3)	0.3750(3)	1.03648(13)	0.0331(5)
H19	−0.1770	0.4719	1.0547	0.040*
C20	−0.2130(3)	0.3196(3)	0.96603(13)	0.0336(6)
H20	−0.1723	0.3793	0.9372	0.040*
C21	−0.3145(3)	0.2655(3)	1.20396(13)	0.0384(6)
H21A	−0.4033	0.1932	1.1881	0.046*
H21B	−0.3360	0.3282	1.2469	0.046*
C22	−0.1927(3)	0.1911(3)	1.22061(12)	0.0337(6)
C23	−0.2181(3)	0.0951(3)	1.26363(15)	0.0486(7)
H23	−0.3114	0.0733	1.2809	0.058*
C24	−0.1063(3)	0.0321(3)	1.28081(15)	0.0490(7)
H24	−0.1253	−0.0294	1.3113	0.059*
C25	0.0535(3)	0.1459(3)	1.21336(14)	0.0410(6)
H25	0.1462	0.1623	1.1948	0.049*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C26	−0.0523(3)	0.2166(3)	1.19584(14)	0.0411(6)
H26	−0.0294	0.2816	1.1673	0.049*
O5W	0.0306(3)	0.4159(3)	0.80740(13)	0.0738(7)
H5WA	0.0244	0.3710	0.7656	0.111*
H5WB	−0.0293	0.3718	0.8317	0.111*
N5	0.4194(3)	0.5580(3)	0.34869(12)	0.0506(6)
N6	0.8093(3)	0.7576(3)	−0.06939(13)	0.0537(6)
C27	0.3256(3)	0.5369(3)	0.29362(17)	0.0546(8)
H27	0.2269	0.4973	0.2981	0.066*
C28	0.3639(3)	0.5694(3)	0.23089(15)	0.0513(7)
H28	0.2923	0.5518	0.1946	0.062*
C29	0.5083(3)	0.6282(3)	0.22158(14)	0.0439(7)
C30	0.6085(3)	0.6494(3)	0.27810(16)	0.0491(7)
H30	0.7081	0.6872	0.2745	0.059*
C31	0.5602(3)	0.6142(3)	0.33969(15)	0.0499(7)
H31	0.6294	0.6304	0.3770	0.060*
C32	0.5457(4)	0.6596(3)	0.15236(17)	0.0554(8)
H32	0.4694	0.6336	0.1178	0.066*
C33	0.6721(4)	0.7187(3)	0.13538(17)	0.0536(8)
H33	0.7464	0.7528	0.1709	0.064*
C34	0.7115(3)	0.7380(3)	0.06425(14)	0.0419(6)
C35	0.8561(3)	0.7970(3)	0.05428(17)	0.0524(8)
H35	0.9245	0.8319	0.0923	0.063*
C36	0.8985(3)	0.8039(3)	−0.01241(18)	0.0560(8)
H36	0.9968	0.8438	−0.0176	0.067*
C37	0.6687(3)	0.7053(3)	−0.05925(16)	0.0492(7)
H37	0.6019	0.6757	−0.0980	0.059*
C38	0.6161(3)	0.6922(3)	0.00501(15)	0.0442(7)
H38	0.5169	0.6529	0.0087	0.053*

step in making CPs. Most often, a multidentate *O*-donor ligand and a multidentate *N*-donor ligand are used in combination to synthesize a coordination polymer [10–14]. In recent years, the ligands containing both *O* and *N* coordination atoms have been often used to synthesize coordination polymers because of the good coordination ability and wide application of Schiff-base compounds [15, 16]. The ligand we used in this study has a carboxylate group as *O* atom donor and a nitrogen atom as *N* atom donor at the terminal positions and a secondary amine group between the phenyl groups. So they have multiple coordination points and show various coordination modes to form the metal-organic framework or coordination polymers. In this study, we selected the educt 4-[(pyridin-4-ylmethyl)amino]benzoic acid (H₂L), to obtain the zinc coordination polymers and added 1,2-bis(4-pyridyl)ethene (bpe) as a supplement ligand. X-ray crystallographic analysis reveals that the compound features a one-dimensional double-stranded chain structure.

The asymmetry unit contains one Zn(II) ion, two L anions, one free bpe molecule and one guest water, as shown in the figure. (A: $-1 + x, -1 + y, z$; B: $-x, -y, 2 - z$). The Zn(II) center is a distorted tetrahedral [ZnO₂N₂] coordinated by two

carboxylate oxygen atoms from two L anions and two nitrogen atom from two symmetry-related L anions. Among them, the Zn–O bond lengths are 1.9564(18) and 1.9669(17) Å, and Zn–N bond lengths are 2.0235(19) and 2.0480(2) Å, respectively. The Zn(II) centers are bridged by L anions adopting single-bridging coordination mode to form one-dimensional chain along the special [110] direction with a $Zn \cdots Zn$ separation of 12.0660(6) Å, the adjacent chains are linked together through two L anions with a $Zn \cdots Zn$ distance of 11.4869(4) Å to form an one-dimensional double-stranded chain structure. In the complex, there are three kinds of hydrogen bonds. Firstly, it is between the N2 atom of the L anion as a donor and N5 atom from one bpe molecule as acceptor ($N2 \cdots (H2) \cdots N5$: $d = 3.066(3)$ Å). The free bpe molecules as parallel pendent arms are hung on both sides of the double-stranded chain through the H-bond interaction. Secondly, the hydrogen bonding interactions are between guest water O atom act as a twofold donor and the carboxylate O atoms in L anion ($O(5W) \cdots H(5WA) \cdots O(3)$: $d = 2.716(3)$ Å, $O(5W) \cdots H(5WB) \cdots O(1)$: $d = 2.789(3)$ Å). Thirdly, there is one between the N3 atom of L anion and the free water O5W atom ($N3 \cdots (H3) \cdots O5W$: $d = 2.898(3)$ Å). The adjacent double-stranded chains are linked together by the third hydrogen bonding interactions to form a two-dimensional layer. The adjacent layers stack together to form its entire three-dimensional structure via weak van der Waals interactions.

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