Crystal structure of (4,4'-bipyridine)-(4-hydroxypyridine-2,6-dicarboxylato)-zinc(II) hydrate, $[Zn_2(C_{10}H_8N_2)(C_7H_3NO_5)_2(H_2O)_2]\cdot 4H_2O$, $C_{24}H_{26}N_4O_{16}Zn_2$

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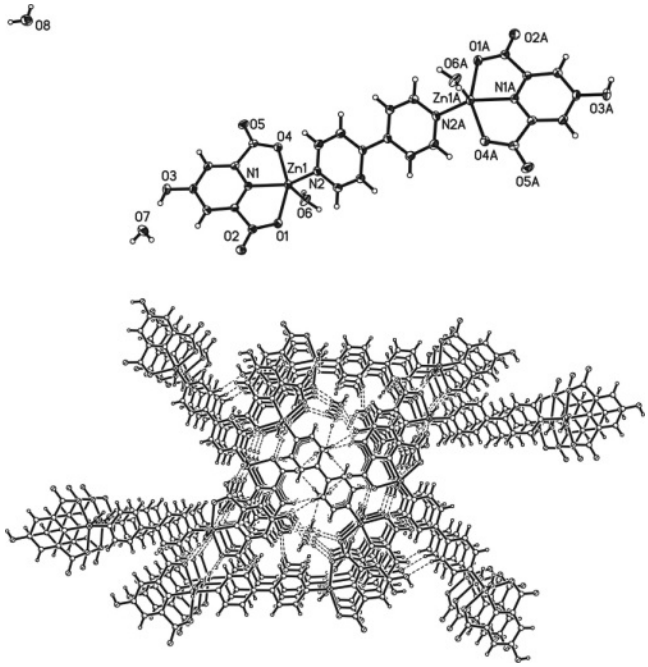

Abstract

$C_{24}H_{26}N_4O_{16}Zn_2$, orthorhombic, *Pbca* (no. 61), a = 19.904(3) Å, b = 7.0438(9) Å, c = 20.240(3) Å, V = 2837.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0279, $wR_{ref}(F^2)$ = 0.0772, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.25×0.25×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.78 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	52.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14434, 2895
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2430
$N(param)_{refined}$:	228
Programs:	SHELX [8]

Source of material

The (4,4'-bipyridine)-(4-hydroxypyridine-2,6-dicarboxylato)-zinc(II) was prepared hydrothermally. A mixture of $ZnSO_4\cdot 7H_2O$ (0.10 mmol), 4,4'-bipyridine(0.10 mmol), 4-hydroxypyridine-2,6-dicarboxylic acid (cam, 0.10 mmol) and water (10 ml) was stirred for 30 min. The mixture was then transferred to a 23 ml Teflon-lined autoclave and kept at 433 K for 72 h under autogenous pressure. Then the mixture was cooled to room temperature slowly. Colourless single crystals of the title compound suitable for X-ray structure analysis were obtained from the reaction mixture.

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Discussion

The self-assembled construction of supramolecular structures is of current interest because controlling the molecular organization in the solid state can lead to materials with novel structures and promising properties [1]. Supramolecular chemistry uses molecular recognition processes that rely heavily on the understanding of the recognition properties of the functional groups involved in these interactions. Recently, increasing investigations have been focused on the constructions of supramolecular structures using heterocyclic carboxylic acids such as pyridine-[2,3], pyrazole-[4], and imidazole-carboxylic acids [5-7] as building blocks. These building blocks contain several oxygen and nitrogen atoms and can coordinate the metal ions in different ways, resulting in the formation of various metal-organic frameworks with specific topologies and useful properties. In this aspect, 4-hydroxypyridine-2,6-dicarboxylic acid (cam), which has six potential donor atoms, is a quite versatile ligand for the construction of metal-organic hybrid compounds. We hydrothermally synthesized the title compound from a cam ligand, 4,4'-bipy and $ZnSO_4\cdot 7H_2O$. It exhibits a binuclear structure (Fig. top), and the asymmetric unit consists of two Zn^{2+} ions, one cam^{2-} ion, half of a 4, 4'-bipy ligand, one coordinated water molecule and two lattice water molecules. It is worth noting that each completely deprotonated cam^{2-} ion coordinates one Zn^{2+} ion in a tridentate chelating coordination mode. Interestingly, the adjacent binuclear molecular recognize each other to generate a 3D supramolecular structure via O–H···O hydrogen bonding interaction (Fig. bottom).

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

Atom	Site	x	y	z	U_{iso}
H(3)	8*c*	0.2698	0.6158	0.4899	0.072
H(3A)	8*c*	0.1609	0.6371	0.4526	0.040
H(5)	8*c*	0.3249	0.7451	0.3411	0.038
H(8)	8*c*	0.1547	0.6002	0.1083	0.051
H(9)	8*c*	0.1117	0.4739	0.0137	0.050
H(11)	8*c*	–0.0715	0.6337	0.0726	0.045
H(12)	8*c*	–0.0237	0.7546	0.1663	0.046
H(6A)	8*c*	0.048(1)	1.142(3)	0.212(1)	0.056
H(6B)	8*c*	0.114(1)	1.175(3)	0.215(1)	0.056
H(7A)	8*c*	0.230(1)	0.543(4)	0.596(1)	0.066
H(7B)	8*c*	0.189(1)	0.463(4)	0.553(1)	0.066
H(8A)	8*c*	0.942(1)	0.579(4)	0.440(1)	0.072
H(8B)	8*c*	0.927(1)	0.488(4)	0.502(1)	0.072

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)	8*c*	0.11107(1)	0.82270(4)	0.22390(1)	0.0257(2)	0.0441(2)	0.0258(2)	–0.00151(9)	–0.00492(8)	–0.0011(1)
N(1)	8*c*	0.16949(7)	0.7584(2)	0.30005(8)	0.0213(7)	0.0319(8)	0.0272(8)	–0.0011(7)	–0.0020(6)	–0.0030(7)
N(2)	8*c*	0.06998(8)	0.6908(2)	0.14655(8)	0.0307(9)	0.0409(9)	0.0240(8)	–0.0016(7)	–0.0044(6)	0.0003(7)
O(1)	8*c*	0.03898(7)	0.7240(2)	0.30050(7)	0.0237(7)	0.058(1)	0.0317(8)	–0.0061(6)	–0.0034(6)	0.0043(7)
O(2)	8*c*	0.03727(7)	0.6276(2)	0.40581(7)	0.0329(8)	0.064(1)	0.0379(8)	–0.0050(7)	0.0058(6)	0.0109(8)
O(3)	8*c*	0.29186(8)	0.6500(3)	0.45782(8)	0.0341(8)	0.076(1)	0.0346(8)	0.0053(8)	–0.0115(6)	0.0038(8)
O(4)	8*c*	0.21135(7)	0.8693(2)	0.18541(7)	0.0286(7)	0.0563(9)	0.0294(7)	0.0017(6)	0.0014(6)	0.0058(7)
O(5)	8*c*	0.31957(7)	0.8553(2)	0.21451(8)	0.0256(8)	0.0512(9)	0.0537(9)	0.0020(6)	0.0097(6)	0.0101(8)
C(1)	8*c*	0.0662(1)	0.6842(3)	0.3556(1)	0.026(1)	0.037(1)	0.031(1)	–0.0015(8)	0.0010(8)	–0.0028(9)
C(2)	8*c*	0.14239(9)	0.7062(3)	0.35779(9)	0.0239(9)	0.033(1)	0.0264(9)	0.0004(7)	0.0013(7)	–0.0034(8)
C(3)	8*c*	0.1808(1)	0.6703(3)	0.4127(1)	0.031(1)	0.042(1)	0.026(1)	0.0011(8)	–0.0004(8)	0.0003(9)
C(4)	8*c*	0.2508(1)	0.6849(3)	0.4071(1)	0.029(1)	0.037(1)	0.032(1)	0.0045(8)	–0.0088(8)	–0.0033(9)
C(5)	8*c*	0.27854(9)	0.7363(3)	0.3462(1)	0.0223(9)	0.034(1)	0.039(1)	0.0015(8)	–0.0027(8)	–0.0039(9)
C(6)	8*c*	0.23652(9)	0.7733(3)	0.29430(9)	0.0223(9)	0.0261(9)	0.032(1)	0.0007(7)	0.0014(7)	–0.0028(8)
C(7)	8*c*	0.2588(1)	0.8358(3)	0.22555(9)	0.027(1)	0.029(1)	0.033(1)	0.0010(8)	0.0047(8)	–0.0017(8)
C(8)	8*c*	0.1086(1)	0.6072(4)	0.1010(1)	0.028(1)	0.058(1)	0.042(1)	0.0066(9)	–0.0070(9)	–0.012(1)
C(9)	8*c*	0.0830(1)	0.5313(3)	0.0439(1)	0.030(1)	0.058(1)	0.038(1)	0.006(1)	–0.0027(9)	–0.015(1)
C(10)	8*c*	0.01451(9)	0.5397(3)	0.03102(9)	0.0284(9)	0.033(1)	0.0250(9)	–0.0002(8)	–0.0026(7)	0.0010(8)
C(11)	8*c*	–0.0252(1)	0.6253(3)	0.0786(1)	0.0236(9)	0.057(1)	0.033(1)	–0.0005(9)	–0.0025(8)	–0.007(1)
C(12)	8*c*	0.0039(1)	0.6980(3)	0.1349(1)	0.030(1)	0.056(1)	0.029(1)	0.0016(9)	0.0013(8)	–0.005(1)
O(6)	8*c*	0.08448(8)	1.0933(2)	0.22215(9)	0.0215(7)	0.0430(9)	0.074(1)	0.0005(7)	–0.0049(7)	0.0046(8)
O(7)	8*c*	0.22762(9)	0.5039(3)	0.55739(8)	0.054(1)	0.080(1)	0.0310(8)	0.003(1)	–0.0015(8)	–0.0057(9)
O(8)	8*c*	0.91239(9)	0.5494(3)	0.4690(1)	0.047(1)	0.077(1)	0.056(1)	–0.008(1)	0.0084(8)	0.006(1)

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