Hydrothemal synthesis and crystal structure of a new compound $[Cd(edpa)(2,2'\text{-bpy})(H_2O)]_n$, $C_{19}H_{17}CdN_3O_5$

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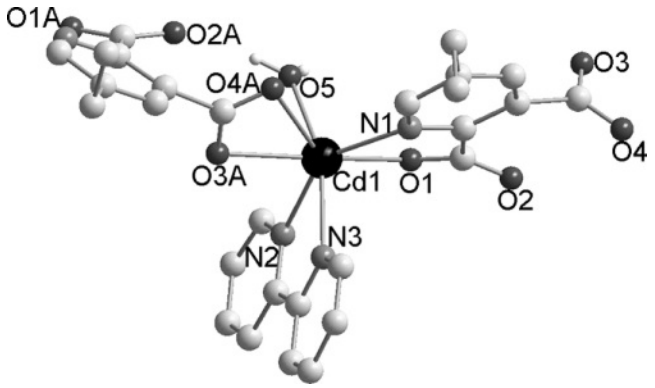

Abstract

$C_{19}H_{17}CdN_3O_5$, monoclinic, *C*2/*c* (no. 15), $a = 27.369(3)$ Å, $b = 9.126(1)$ Å, $c = 15.326(2)$ Å, $\beta = 104.285(1)°$, $V = 3709.6$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0288$, $wR_{ref}(F^2) = 0.0626$, $T = 296$ K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.11×0.21×0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.14 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8964, 3412
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2715
$N(param)_{refined}$:	254
Programs:	SHELX [7]

Source of material

The mixtures of 5-ethyl-pyridine-2,3-dicarboxylic acid (0.2 mmol, 39.1 mg), 2,2'-bpy (0.1 mmol, 15.6mg), $Cd(Ac)_2{\cdot}2H_2O$ (0.1mmol, 26.7 mg), NaOH (0.1mmol), and H_2O (8.0 ml) were sealed in a 23 ml Teflon-lined autoclave, heated to 393K for 4 days, and then slowly cooled down to room temperature for crystallization. Colourless block-shaped crystals of the title compound were obtained.

Discussion

Metal-organic coordination complexes, especially those which are constructed by the effective combination of coordinative bonds, hydrogen bonding, and π-π stacking interactions, have been extensively studied due to their intriguing structures and multifunctional properties [1-3]. Pyridinedicarboxylates are extremely popular as efficient linkers in the construction of coordination polymers [4-5]. *N*-donor auxiliary 2,2'-bipyridine (2,2'-bipyridine = 2,2'-bpy) has obviously great effect on the structures of the complexes, which can easily offer potential supramolecular recognition sites for π-π aromatic stacking interactions [6]. With these considerations in mind, we report herein the hydrothermal synthesis and structural characterization of the one dimensional polymer $[Cd(edpa)(2,2'\text{-bpy})(H_2O)]_n$ (H_2edpa = 5-ethyl-pyridine-2,3-dicarboxylic acid). Single-crystal X-ray analysis shows that the structure of **1** contains one Cd(II) ion, two 5-ethyl-2,3-pyridinedicarboxylate anions,one coordinated water molecule and one 2,2'-bpy molecule as shown in Fig.1. Each Cd(II) center is seven-coordinated by three nitrogen atoms and four oxygen atoms from one 2,2'-bpy ligand, one water molecule and two different $edpa^{2-}$ ligands in a slightly distorted pentagonal bipyramidal coordination geometry. All of the Cd–N bond lengths are in the range of 2.353(3) - 2.392(2) Å and the Cd–O bond distances range from 2.318(2) to 2.609(3) Å.The coordination mode adopted by the $edpa^{2-}$ ligand can be classified as μ-(κ_4N,O2:O3,O3') [5], that is, one oxygen atom of the α-carboxyl group and the pyridyl nitrogen atom (N1) chelate one Cd atom and two oxygen atoms of the β-carboxyl group jointly link another Cd(II) ion to form a 1D carboxylate chain running along the *c*-axis with a Cd–Cd distance of 8.0570(9) Å. There exist intramo lecular hydrogen bonds between coordinated water molecules and α-carboxylate oxygen atoms of $edpa^{2-}$ dianion (d(O5···O2A): 2.814(3) Å, and O–H–N is 168.3°) within the 1D chain, while intermolecular hydrogen bonds between coordinated water molecules from one chain and the α-carboxylate O atoms from the other chain (O5···O1B with the bond distance of 2.774(3) Å and bond angle of 162.6°) connect the adjacent chains to form the double-chain structure along the *c*-axis. The double-chain is also involved in π-π stacking interaction between pyridine rings of lateral 2,2'-bpy ligands from adjacent 1D chains and the centroid-centroid distance is 3.9861(4) Å. In addition, the lateral 2,2'-bpy molecules from adjacent double-chains have additional weak π-π stacking interactions with the centroid-centroid distance of 3.9851(4) Å leading to a two-dimensional structure in the *bc*-plane. Here in **1** the hydrogen bonds and π-π interactions play an important role in forming and stabilizing the resulting structure.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2W)	8*f*	0.4504	–0.0877	1.1450	0.058
H(1W)	8*f*	0.4822	–0.0823	1.0832	0.058
H(4)	8*f*	0.2710	–0.1328	0.6914	0.058
H(6)	8*f*	0.2861	0.0249	0.9379	0.054
H(7A)	8*f*	0.2073	–0.2045	0.7686	0.097
H(7B)	8*f*	0.2170	–0.1704	0.8722	0.097
H(8A)	8*f*	0.1900	0.0643	0.8395	0.171
H(8B)	8*f*	0.1477	–0.0467	0.7939	0.171
H(8C)	8*f*	0.1803	0.0303	0.7363	0.171
H(10)	8*f*	0.5245	0.1778	1.1259	0.073
H(11)	8*f*	0.5836	0.3474	1.1964	0.079

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12)	8*f*	0.5614	0.5911	1.1876	0.083
H(13)	8*f*	0.4808	0.6587	1.1131	0.076
H(16)	8*f*	0.4053	0.7095	1.0521	0.068
H(17)	8*f*	0.3212	0.7533	0.9868	0.076
H(18)	8*f*	0.2688	0.5601	0.9291	0.073
H(19)	8*f*	0.3024	0.3291	0.9376	0.065

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}
Cd(1)	8*f*	0.405812(8)	0.13634(2)	1.02487(2)	0.0345(1)	0.0335(1)	0.0236(1)	–0.0005(1)	0.00697(9)	–0.0011(1)
N(1)	8*f*	0.34652(9)	0.0527(3)	0.8923(2)	0.032(2)	0.044(2)	0.024(2)	–0.003(1)	0.009(1)	–0.001(1)
N(2)	8*f*	0.4684(1)	0.3125(3)	1.0816(2)	0.042(2)	0.037(2)	0.043(2)	–0.002(1)	0.008(1)	0.003(1)
N(3)	8*f*	0.3718(1)	0.3777(3)	0.9989(2)	0.051(2)	0.040(2)	0.033(2)	0.004(1)	0.003(1)	–0.002(1)
O(1)	8*f*	0.44587(8)	0.1042(2)	0.9084(1)	0.033(1)	0.060(2)	0.027(1)	–0.004(1)	0.007(1)	–0.007(1)
O(2)	8*f*	0.43159(9)	0.1207(3)	0.7599(2)	0.057(2)	0.081(2)	0.034(2)	–0.026(1)	0.023(1)	–0.011(1)
O(3)	8*f*	0.3918(1)	–0.1602(3)	0.6696(2)	0.089(2)	0.061(2)	0.066(2)	0.007(2)	0.047(2)	–0.008(2)
O(4)	8*f*	0.3381(1)	–0.0045(4)	0.5903(2)	0.074(2)	0.148(3)	0.025(2)	0.001(2)	0.010(1)	0.010(2)
O(5)	8*f*	0.45429(8)	–0.0590(2)	1.0944(1)	0.037(1)	0.044(1)	0.038(1)	0.004(1)	0.016(1)	0.005(1)
C(1)	8*f*	0.4187(1)	0.0906(3)	0.8289(2)	0.039(2)	0.038(2)	0.030(2)	–0.004(2)	0.015(2)	–0.006(2)
C(2)	8*f*	0.3655(1)	0.0337(3)	0.8205(2)	0.030(2)	0.033(2)	0.023(2)	0.002(1)	0.006(1)	0.002(1)
C(3)	8*f*	0.3376(1)	–0.0354(3)	0.7425(2)	0.037(2)	0.044(2)	0.020(2)	0.001(2)	0.006(1)	0.001(1)
C(4)	8*f*	0.2898(1)	–0.0846(4)	0.7421(2)	0.039(2)	0.082(3)	0.022(2)	–0.010(2)	0.004(2)	–0.005(2)
C(5)	8*f*	0.2693(1)	–0.0646(5)	0.8139(2)	0.034(2)	0.092(3)	0.033(2)	–0.012(2)	0.008(2)	–0.003(2)
C(6)	8*f*	0.2993(1)	0.0075(4)	0.8885(2)	0.033(2)	0.074(3)	0.031(2)	0.001(2)	0.012(2)	0.002(2)
C(7)	8*f*	0.2165(2)	–0.1283(5)	0.8139(3)	0.056(3)	0.138(5)	0.055(3)	0.004(3)	0.024(2)	–0.003(3)
C(8)	8*f*	0.1807(2)	–0.0103(7)	0.7943(3)	0.081(4)	0.184(6)	0.082(4)	0.027(4)	0.029(3)	0.037(4)
C(9)	8*f*	0.3581(1)	–0.0684(4)	0.6614(2)	0.045(2)	0.062(2)	0.029(2)	–0.020(2)	0.013(2)	–0.009(2)
C(10)	8*f*	0.5154(1)	0.2761(4)	1.1242(3)	0.051(2)	0.042(2)	0.083(3)	–0.003(2)	0.007(2)	0.003(2)
C(11)	8*f*	0.5514(2)	0.3770(4)	1.1660(3)	0.048(2)	0.059(3)	0.081(3)	–0.014(2)	–0.002(2)	0.005(2)
C(12)	8*f*	0.5380(2)	0.5201(4)	1.1611(3)	0.069(3)	0.049(3)	0.080(3)	–0.024(2)	0.001(3)	–0.005(2)
C(13)	8*f*	0.4900(2)	0.5604(4)	1.1170(3)	0.065(3)	0.038(2)	0.080(3)	–0.010(2)	0.007(2)	–0.002(2)
C(14)	8*f*	0.4554(1)	0.4543(3)	1.0786(2)	0.054(2)	0.035(2)	0.034(2)	–0.004(2)	0.016(2)	0.003(2)
C(15)	8*f*	0.4024(1)	0.4896(4)	1.0334(2)	0.052(2)	0.036(2)	0.033(2)	0.004(2)	0.017(2)	0.004(2)
C(16)	8*f*	0.3839(2)	0.6323(4)	1.0288(3)	0.064(3)	0.036(2)	0.071(3)	–0.001(2)	0.016(2)	0.002(2)
C(17)	8*f*	0.3338(2)	0.6584(4)	0.9898(3)	0.076(3)	0.045(2)	0.068(3)	0.024(2)	0.018(2)	0.010(2)
C(18)	8*f*	0.3028(2)	0.5449(4)	0.9556(3)	0.062(3)	0.059(3)	0.055(3)	0.021(2)	–0.001(2)	0.001(2)
C(19)	8*f*	0.3234(1)	0.4069(4)	0.9613(2)	0.053(2)	0.051(2)	0.050(2)	0.011(2)	–0.004(2)	–0.004(2)

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