Crystal structure of aqua-*bis*-(1,10-phenanthroline)-(5-norbornene-2,3-dicarboxylic acid)-cadmium(II)-hydrate, $[Cd(C_9H_8O_4)(C_{12}H_8N_2)(H_2O)]\cdot(H_2O)$, $C_{42}H_{40}Cd_2N_4O_{12}$

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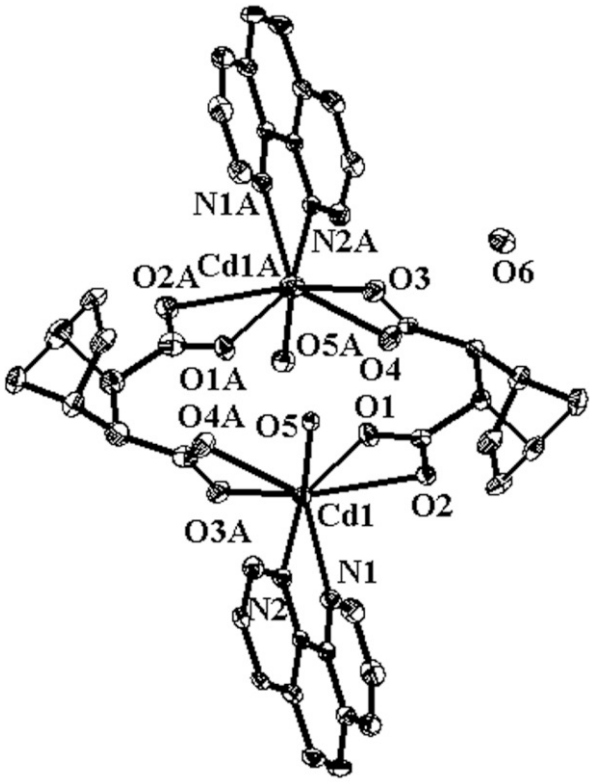

Abstract

$C_{42}H_{40}Cd_2N_4O_{12}$, monoclinic, $P2_1/c$ (no. 14), a = 9.475(1) Å, b = 10.879(1) Å, c = 18.819(2) Å, β = 101.092(1)°, V = 1903.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.0192, $wR_{ref}(F^2)$ = 0.0498, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.16×0.27×0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.91 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13804, 3542
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3233
$N(param)_{refined}$:	271
Programs:	SHELXS-97 [9]

Source of material

A mixture of 5-norbornene-2,3-dicarboxylic acid (0.1 mmol, 18.2 mg), 1,10-phenanthroline (phen) (0.2 mmol, 39.7 mg), $Cd(OAc)_22\cdot H_2O$ (0.1 mmol, 26.6 mg), NaOH (0.1 mmol), and H_2O (6.0 ml) were placed in a 23ml Teflon lined stainless steel reactor. The vessel was heated to 393 K for 4 days, and then slowly cooled to room temperature. Colourless crystals were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield 52 %.

Discussion

Self-assembly of organic and inorganic compounds with metal centers is one of the most efficient and widely utilized approaches for the construction of polymers [1-3]. Among them, divalent metal coordination polymers containing tethering dicarboxylate ligands are among the most commonly employed linkers in MOFs chemistry [4-6], because different metal coordination environments and carboxylate group binding and bridging modes can provide a wide scope of underlying coordination polymer structural topologies. Unfortunately, a remarkable multidentate carboxylic ligand, 5-norbornene-2,3-dicarboxylic acid are under developed in MOFs chemistry, though initial inference on the existence of a number of new structures seems reasonable. Simultaneously, the usage of nitrogen-donor ligands is an effective process for the construction of novel MOFs because they can satisfy and even mediate the coordination needs of the metal centers so as to generate more meaningful architectures [7,8]. The asymmetric unit of the complex under investigation contains one Cd^{2+} ion, one 5-norbornene-2,3-dicarboxylic anion, one phen coligand, one ligated water and one crystal water molecule. The Cd ion displays a highly distorted pentagonal bipyramid with four oxygen atoms from two chelating carboxylate group belonging to different 5-norbornene-2,3-dicarboxylic molecules (Cd-O: 2.2651(15) Å -2.6024(16) Å), two nitrogen atoms from one chelate phen ligand (Cd–N: 2.3571(17) Å and 2.3748(17) Å), and one ligated water molecule (Cd–O: 2.4137(15) Å). Each 5-norbornene-2,3-dicarboxylic anion acts as a bidentate ligand connecting adjacent Cd ions to develop Cd carboxylate dimers. Notably, the presence of coordinated and non-coordinated water molecules lead to the formation of extensive H-bonding interactions. Besides intramolecular hydrogen bonds, interlayer O(5)–H(1W)···O(2) interactions further extend the adjacent dimers to produce a 1D double chain along the crystallographic a axis. Strong π-π stacking interactions (the face to face distance is 3.92 Å) existing between both aromatic rings of phen coligands from two adjacent 1D chains, result in a zipper-like 2D layer. The adjacent 2D layers stack in a slightly off-set parallel fashion with the weak effect of van der Waals force to form the 3D supermolecular sructure.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1W)	4*e*	0.4597	0.5373	1.0812	0.054
H(2W)	4*e*	0.3272	0.5800	1.0913	0.054
H(3W)	4*e*	0.0839	0.6361	0.0837	0.064
H(4W)	4*e*	0.1125	0.6829	0.0257	0.064
H(1)	4*e*	0.3499	0.3824	0.7967	0.042
H(2)	4*e*	0.3234	0.5716	0.8604	0.032
H(3)	4*e*	0.1327	0.6655	0.8063	0.031
H(4)	4*e*	–0.0297	0.5518	0.7157	0.043
H(5A)	4*e*	0.1788	0.4391	0.6828	0.053
H(5B)	4*e*	0.2411	0.5640	0.7206	0.053
H(6)	4*e*	–0.0789	0.3489	0.7685	0.049
H(7)	4*e*	0.1465	0.2457	0.8138	0.050
H(10)	4*e*	0.0637	0.1501	0.9407	0.045
H(11)	4*e*	0.0731	–0.0506	0.9007	0.052
H(12)	4*e*	0.2539	–0.1785	0.9563	0.048
H(14)	4*e*	0.4722	–0.2115	1.0569	0.049
H(15)	4*e*	0.6193	–0.1407	1.1572	0.048
H(17)	4*e*	0.6900	0.0308	1.2496	0.045
H(18)	4*e*	0.6565	0.2300	1.2845	0.046
H(19)	4*e*	0.4911	0.3537	1.2117	0.040

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)	4*e*	0.23892(2)	0.34894(1)	1.062319(8)	0.02610(9)	0.02446(9)	0.02758(9)	0.00638(6)	0.00436(6)	0.00200(6)
O(1)	4*e*	0.1400(2)	0.4374(2)	0.95535(8)	0.0274(8)	0.0445(9)	0.0338(8)	0.0030(7)	0.0089(7)	0.0115(7)
O(2)	4*e*	0.3697(2)	0.4035(2)	0.95684(8)	0.0314(7)	0.0416(7)	0.0378(7)	0.0045(6)	0.0061(5)	0.0068(6)
O(3)	4*e*	0.0192(2)	0.6908(1)	0.91815(8)	0.0408(7)	0.0334(7)	0.0366(7)	0.0003(6)	0.0089(6)	–0.0067(6)
O(4)	4*e*	–0.1326(2)	0.5648(2)	0.85078(8)	0.0251(8)	0.0430(9)	0.0432(9)	–0.0012(7)	0.0092(7)	–0.0091(7)
O(5)	4*e*	0.3899(2)	0.5239(1)	1.10255(8)	0.0276(8)	0.0362(9)	0.0437(9)	–0.0003(7)	0.0080(7)	0.0019(7)
O(6)	4*e*	0.1496(2)	0.6786(2)	0.07055(9)	0.0342(9)	0.0408(9)	0.051(1)	–0.0032(7)	0.0048(8)	0.0067(8)
N(1)	4*e*	0.2303(2)	0.1430(2)	1.0199(1)	0.0270(9)	0.0281(9)	0.0302(9)	0.0031(7)	0.0048(8)	0.0034(7)
N(2)	4*e*	0.4167(2)	0.2319(2)	1.13783(9)	0.0268(9)	0.0264(9)	0.0297(9)	0.0023(7)	0.0066(7)	0.0034(7)
C(1)	4*e*	0.2541(2)	0.4175(2)	0.7952(1)	0.028(1)	0.043(1)	0.036(1)	0.009(1)	0.0096(9)	–0.007(1)
C(2)	4*e*	0.2419(2)	0.5148(2)	0.8560(1)	0.021(1)	0.029(1)	0.030(1)	–0.0021(8)	0.0071(8)	0.0000(9)
C(3)	4*e*	0.1014(2)	0.5857(2)	0.8218(1)	0.026(1)	0.025(1)	0.027(1)	0.0009(8)	0.0060(8)	0.0029(8)
C(4)	4*e*	0.0455(2)	0.5117(2)	0.7512(1)	0.030(1)	0.049(1)	0.027(1)	0.010(1)	0.0012(9)	–0.003(1)
C(5)	4*e*	0.1894(3)	0.4888(3)	0.7263(1)	0.043(1)	0.062(2)	0.030(1)	0.006(1)	0.013(1)	–0.004(1)
C(6)	4*e*	0.0123(3)	0.3829(2)	0.7724(1)	0.032(1)	0.043(1)	0.046(1)	–0.003(1)	0.006(1)	–0.021(1)
C(7)	4*e*	0.1354(3)	0.3265(2)	0.7976(1)	0.044(1)	0.032(1)	0.050(2)	0.005(1)	0.010(1)	–0.015(1)
C(8)	4*e*	0.2502(2)	0.4486(2)	0.9276(1)	0.024(1)	0.024(1)	0.028(1)	–0.0007(8)	0.0020(9)	–0.0006(8)
C(9)	4*e*	–0.0096(2)	0.6138(2)	0.8679(1)	0.028(1)	0.023(1)	0.028(1)	0.0050(9)	0.0053(9)	0.0034(8)
C(10)	4*e*	0.1362(3)	0.0986(2)	0.9642(1)	0.035(1)	0.042(1)	0.035(1)	–0.002(1)	0.002(1)	0.005(1)
C(11)	4*e*	0.1415(3)	–0.0225(2)	0.9395(1)	0.049(2)	0.045(2)	0.036(1)	–0.015(1)	0.005(1)	–0.002(1)
C(12)	4*e*	0.2479(3)	–0.0986(2)	0.9730(1)	0.052(2)	0.028(1)	0.044(1)	–0.009(1)	0.018(1)	–0.004(1)
C(13)	4*e*	0.3484(2)	–0.0563(2)	1.0327(1)	0.036(1)	0.024(1)	0.038(1)	–0.0017(9)	0.016(1)	0.0031(9)
C(14)	4*e*	0.4604(3)	–0.1317(2)	1.0725(1)	0.048(2)	0.021(1)	0.058(2)	0.006(1)	0.022(1)	0.005(1)
C(15)	4*e*	0.5485(3)	–0.0893(2)	1.1320(1)	0.034(1)	0.032(1)	0.056(2)	0.012(1)	0.014(1)	0.017(1)
C(16)	4*e*	0.5358(2)	0.0339(2)	1.1576(1)	0.024(1)	0.031(1)	0.039(1)	0.0029(9)	0.0093(9)	0.0129(9)
C(17)	4*e*	0.6211(2)	0.0805(2)	1.2215(1)	0.025(1)	0.043(1)	0.043(1)	0.003(1)	0.002(1)	0.018(1)
C(18)	4*e*	0.6022(2)	0.1988(2)	1.2419(1)	0.032(1)	0.048(2)	0.033(1)	–0.008(1)	–0.000(1)	0.007(1)
C(19)	4*e*	0.5006(2)	0.2724(2)	1.1981(1)	0.033(1)	0.035(1)	0.033(1)	–0.004(1)	0.007(1)	–0.0005(9)
C(20)	4*e*	0.4319(2)	0.1134(2)	1.1176(1)	0.023(1)	0.025(1)	0.030(1)	0.0001(8)	0.0111(9)	0.0053(8)
C(21)	4*e*	0.3346(2)	0.0667(2)	1.0545(1)	0.024(1)	0.026(1)	0.030(1)	0.0017(8)	0.0109(9)	0.0036(8)

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