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A Three-Dimensional Coordination Polymer Based on 3,5-Pyrazoledicarboxylic Acid (H_3Pdc): $[Cd_2(HPdc)_{1.5}Cl(H_2O)_2]_n$[1]

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Abstract—The title coordination polymer, $[Cd_2(HPdc)_{1.5}Cl(H_2O)_2]_n$ (**I**) (H_3Pdc = 3,5-pyrazoledicarboxylic acid), has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction (CIF file CCDC no. 1037505). Complex **I** crystallizes in orthorhombic space group *Pbcn* with a = 10.2631(11), b = 17.1997(18), c = 14.3044(15) Å, V = 2525.0(5) Å^3, $C_{15}H_{14}Cd_4Cl_2N_6O_{16}$, M = 1054.82, ρ_c = 2.775 g/cm^3, $\mu(MoK_\alpha)$ = 3.627 mm^{-1}, $F(000)$ = 2000, GOOF = 1.067, Z = 4, the final R_1 = 0.0562 and wR_2 = 0.1301 for $I > 2\sigma(I)$. The Cd(1) ions and $HPdc^{2-}$ ligands connect to form a serial of the 2D corrugated 6^3 sheets packing parallel along the z axis. Each 6^3 sheet is connected with the two neighboring sheets by the Cl^- and Cd(2) ions to construct the 3D framework of **I**. The 3D structure can also be rationalized as a 4-connected trinodal $(4.5.7^2.8.9)(4.5^2.6^2.7)(4.5.6.7^3)$ topological network (the long Schläfli symbol is $(4.5.7.7.10_2)(4.12_4.5.6.5.7)(4.5.6.7.7.7)$) by considering the Cd(1), Cd(2) ions and $HPdc^{2-}$ ligands as 4-connected nodes, the Cl^- ions as linkers, respectively.

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INTRODUCTION

According to the definition of IUPAC, a coordination polymer (CP) is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions. However, a metal-organic framework (MOF) is a coordination network with organic ligands containing potential voids [1]. Both of them have attracted much interest because of their intriguing structural topologies and their interesting applications as functional materials in guest sensing and recognition [2–5], catalysis [6–8], magnetism [9, 10], etc. The preparations of CPs and MOFs are self-assembly process of the various components under hydrothermal or solvothermal conditions, which depend strongly on the several factors, such as the coordination nature of ligand structure, the solvent systems, counterions, and so on [11, 12]. Undoubtedly, the ligand is the key factor for manipulating the topologies of CPs and MOFs.

3,5-Pyrazoledicarboxylic acid (H_3Pdc) is a multifunctional ligand possessing many advantages, such as multiple coordination sites involving two pyrazole nitrogen atoms and four carboxylate oxygen atoms, three different abstractable hydrogens, sterically compact planar heteroaromatic dicarboxylates, etc. [13–17]. In this work, based on H_3Pdc, we synthesize a three dimensional coordination polymer $[Cd_2(HPdc)_{1.5}Cl(H_2O)_2]_n$ (I) and describe its structure in detail.

EXPERIMENTAL

All chemicals were reagent grade and used as received. Elemental analyses for C, H and N were performed on a PerkinElmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. The crystal structure was determined by single-crystal X-ray diffraction and using SHELXS-97, SHELXL-97 software for structure solution and refinement correspondingly.

Synthesis of complex I. A mixture of $CdCl_2$ (0.2 mmol, 36.7 mg), H_3Pdc (0.2 mmol, 34.8 mg), CH_3CN (2 mL) and H_2O (5 mL) was sealed in a 15 mL Teflon-lined bomb and heated at 140°C for 3 days. The reaction mixture was slowly cooled to room temperature in a rate of 10°C/30 mins. Colorless block crystals of **I**

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[1] The article is published in the original.

suitable for X-ray diffraction analysis were isolated in 23% yield.

For $C_{15}H_{14}N_6O_{16}Cl_2Cd_4$

anal. calcd., %:	C, 17.08;	H, 1.34;	N, 7.97.
Found, %:	C, 17.34;	H, 1.17;	N, 7.84.

X-ray structure determination. A colorless single crystal of **I** with dimensions of 0.22 × 0.24 × 0.26 mm was mounted on a Bruker Smart Apex CCD area detector diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using the ω–θ scan mode in the range $2.31° \le \theta \le 28.34°$ at 291(2) K. Raw frame data were integrated with the SAINT program [18]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [19]. An empirical absorption correction was applied with the program SADABS [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding mode with C–H = 0.93 Å for sp^2 hybridizated carbon atom, N–H = 0.86 Å for sp^2 hybridizated nitrogen atom, O–H = 0.96 Å for carboxylate oxygen atom, respectively, and $U_{iso}(H) = 1.2U_{eq}$(C, N or O). The H atoms of the water molecules were located in calculated positions and refined as riding mode with O–H = 0.96 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. The final $R_1 = 0.0562$ and $wR_2 = 0.1301$ for 2187 observed reflections with $I > 2\sigma(I)$ ($w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.66P]$, where $P = (F_o^2 + 2F_c^2)/3$). $(\Delta\rho)_{max} = 1.123$ e/Å^3, $(\Delta\rho)_{min} = -1.191$ e/Å^3 and $(\Delta/\sigma)_{max} = 0.001$. Crystallographic details for **I** have been summarized in Table 1. Selected bond lengths and angles for **I** are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1037505; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) or can be obtained from the authors.

Table 1. Crystallographic data and structure refinement for complex **I***

Parameter	Value
Fw	1054.82
Crystal system	Orthorhombic
Space group	*Pbcn*
a , Å	10.2631(11)
b, Å	17.1997(18)
c, Å	14.3044(15)
V, Å^3	2525.0(5)
Z	4
ρ_{calcd}, g cm^{-3}	2.775
μ, mm^{-1}	3.627
F(000)	2000
Reflections collected	14187
Unique reflections	3055
R_{int}	0.0265
GOOF (F^2)	1.067
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0562, 0.1301
R_1, wR_2 (all data)*	0.0662, 0.1319
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.123/–1.191

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

RESULTS AND DISCUSSION

The asymmetric unit of **I** contains two crystallographically independent Cd^{2+} ions, one Cl^- ion, one and a half $HPdc^{2-}$ ligands, two coordinated H_2O molecules (Fig. 1). The Cd(1) ion has the distorted octahedral coordination environment. The coordination sphere of the Cd(1) ion is completed by one oxygen atom (O(1)) and one nitrogen atom (N(1)) from a $HPdc^{2-}$ ligand, two oxygen atoms(O(3)^{i} and O(5)^{ii}) from two other $HPdc^{2-}$ ligands, one Cl^- ion and one oxygen atom (O(1*w*)) from one H_2O molecule. The Cd(2) ion has the distorted pentagonal bipyramid coordination environment. The coordination sphere of the Cd(2) ion is completed by one oxygen atom (O(5)) and one nitrogen atom (N(3)) from a $HPdc^{2-}$ ligand, two oxygen atoms (O(1)^{iii} and O(2)^{iii}) from other $HPdc^{2-}$ ligand, oxygen atom (O(4)^{iv}) from the third $HPdc^{2-}$ ligand, one Cl^- ion and one oxygen atom (O(2*w*)) from one H_2O molecule. The Cd–O bond lengths range from 2.192(5) to 2.485(5) Å, the Cd–N bond lengths range from 2.262(6) to 2.273(6) Å and the Cd–Cl bond lengths range from 2.484(2) to 2.570(2) Å (Table 2), which are comparable to those

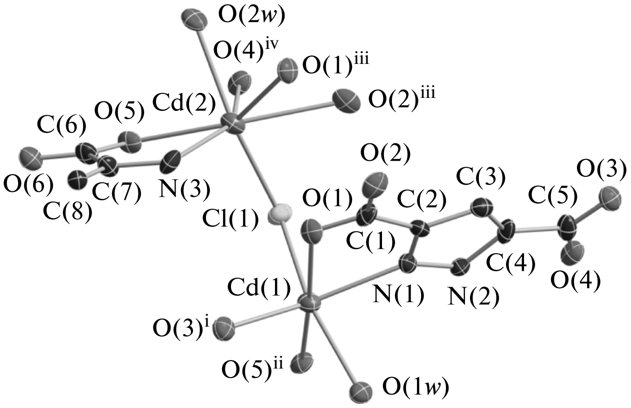


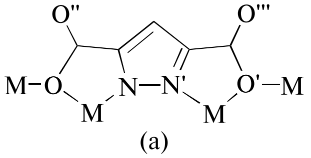
Fig. 1. View of the asymmetric unit of **I** with the thermal ellipsoids drawn at the 50% probability level. All H atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I***

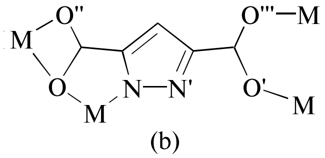
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(1)	2.364(5)	Cd(1)–O(3)^{i}	2.216(5)	Cd(1)–O(5)^{ii}	2.192(5)
Cd(1)–O(1*w*)	2.485(5)	Cd(1)–N(1)	2.273(6)	Cd(1)–Cl(1)	2.570(2)
Cd(2)–O(1)^{iii}	2.417(5)	Cd(2)–O(2)^{iii}	2.466(6)	Cd(2)–O(4)^{iv}	2.382(5)
Cd(2)–O(5)	2.391(5)	Cd(2)–O(2*w*)	2.406(5)	Cd(2)–N(3)	2.262(6)
Cd(2)–Cl(1)	2.484(2)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(5)^{ii}Cd(1)O(3)^{i}	100.89(19)	O(5)^{ii}Cd(1)N(1)	111.8(2)	O(3)^{i}Cd(1)N(1)	143.5(2)
O(5)^{ii}Cd(1)O(1)	175.22(19)	O(3)^{i}Cd(1)O(1)	78.76(18)	N(1)Cd(1)O(1)	69.9(2)
O(5)^{ii}Cd(1)O(1*w*)	83.92(18)	O(3)^{i}Cd(1)O(1*w*)	86.64(19)	N(1)Cd(1)O(1*w*)	81.36(19)
O(1)Cd(1)O(1*w*)	100.80(17)	O(5)^{ii}Cd(1)Cl(1)	86.45(14)	O(3)^{i}Cd(1)Cl(1)	107.90(15)
N(1)Cd(1)Cl(1)	90.31(15)	O(1)Cd(1)Cl(1)	89.12(14)	O(1*w*)Cd(1)Cl(1)	163.88(13)
N(3)Cd(2)O(4)^{iv}	146.9(2)	N(3)Cd(2)O(5)	69.7(2)	O(4)^{iv}Cd(2)O(5)	77.63(18)
N(3)Cd(2)O(2*w*)	97.2(2)	O(4)^{iv}Cd(2)O(2*w*)	72.61(18)	O(5)Cd(2)O(2*w*)	81.75(18)
N(3)Cd(2)O(1)^{iii}	85.9(2)	O(4)^{iv}Cd(2)O(1)^{iii}	118.69(19)	O(5)Cd(2)O(1)^{iii}	141.79(18)
O(2*w*)Cd(2)O(1)^{iii}	72.33(18)	N(3)Cd(2)O(2)^{iii}	129.0(2)	O(4)^{iv}Cd(2)O(2)^{iii}	84.01(18)
O(5)Cd(2)O(2)^{iii}	160.72(17)	O(2*w*)Cd(2)O(2)^{iii}	98.45(18)	O(1)^{iii}Cd(2)O(2)^{iii}	54.05(18)
N(3)Cd(2)Cl(1)	105.46(17)	O(4)^{iv}Cd(2)Cl(1)	81.40(13)	O(5)Cd(2)Cl(1)	94.10(13)
O(2*w*)Cd(2)Cl(1)	153.97(14)	O(1)^{iii}Cd(2)Cl(1)	121.24(13)	O(2)^{iii}Cd(2)Cl(1)	77.20(14)
Cd(2)Cl(1)Cd(1)	114.40(8)				

* Symmetry codes: ^{i} $-x + 1/2, y + 1/2, z$; ^{ii} $x - 1/2, -y + 1/2, -z + 1$; ^{iii} $-x + 1, y, -z + 3/2$; ^{iv} $-x + 1, -y, -z + 1$.

values found in other reported Cd(II) complexes [21, 22]. The Cl^- ion in **I** acts as μ_2-bridging ligand to bridge Cd(1) and Cd(2) ions. The $HPdc^{2-}$ ligands in **I** adopt two coordination modes (a and b) as depicted below:



(a)



(b)

In coordination mode a, the $HPdc^{2-}$ ligand acts in a μ_4-η^2N,O,η^1O,η^2N',O',η^1O' fashion, chelating two Cd(2) ions and bridging two Cd(1) ions, respectively. In coordination mode b, the $HPdc^{2-}$ ligand acts in a μ_4-η^2N,O,η^2O,O'',η^1O',η^1O''' fashion, chelating one Cd(1) and one Cd(2) ions, and bridging one Cd(1) and one Cd(2) ions, respectively. The Cd(1) ions and $HPdc^{2-}$ ligands connect to form the two-dimensional (2D) corrugated 6^3 network (Figs. 2a and 2b). The 6^3 networks pack parallel along the *z* axis and each 6^3 network is connected with the two neighboring networks by the Cl^- and Cd(2) ions to construct the 3D framework of **I** (Fig. 2c). The 3D structure can also be rationalized as a 4- connected trinodal $(4.5.7^2.8.9)(4.5^2.6^2.7)(4.5.6.7^3)$ topological network (the long Schläfli symbol is $(4.5.7.7.10_2)(4.12_4.5.6.5.7)(4.5.6.7.7.7)$) by considering the Cd(1) ions, Cd(2) ions and $HPdc^{2-}$ ligands as 4-connected nodes, the Cl^- ions as linkers, respectively.

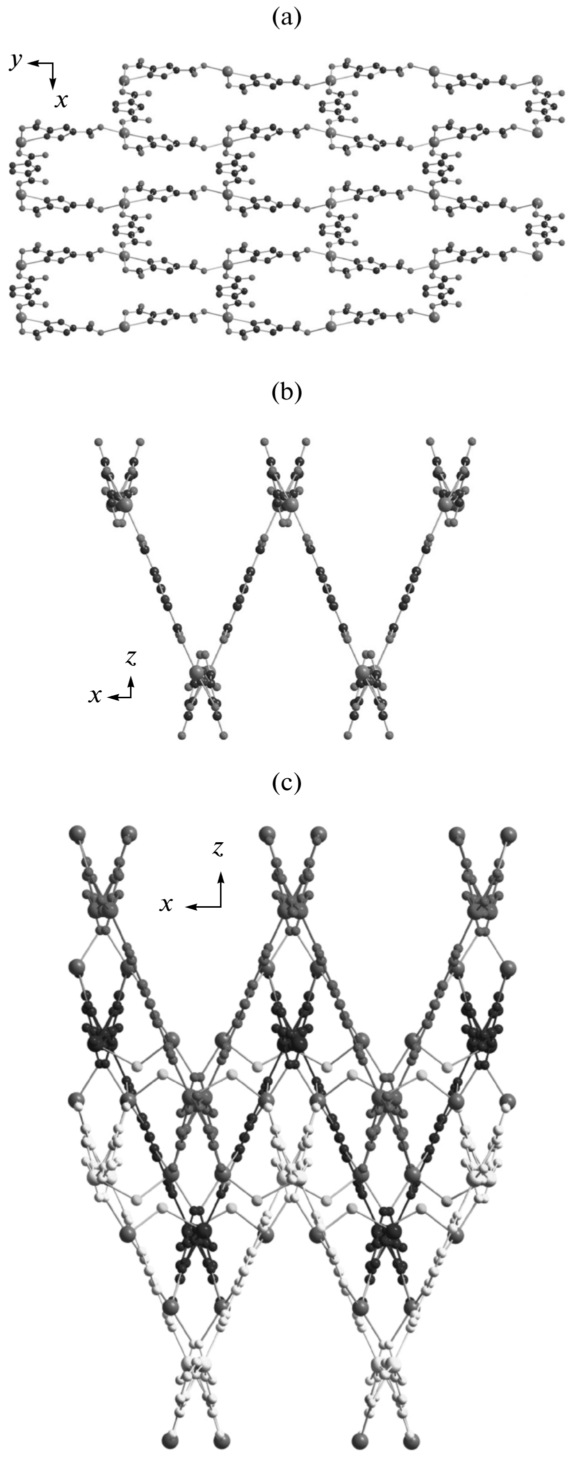


Fig. 2. The 2D corrugated 6^3 sheet consisting of the Cd(1) ions and HPdc^{2-} ligands (a, view along the *z* axis) and (b, view along the *y* axis); 3D framework of **I** (c).

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