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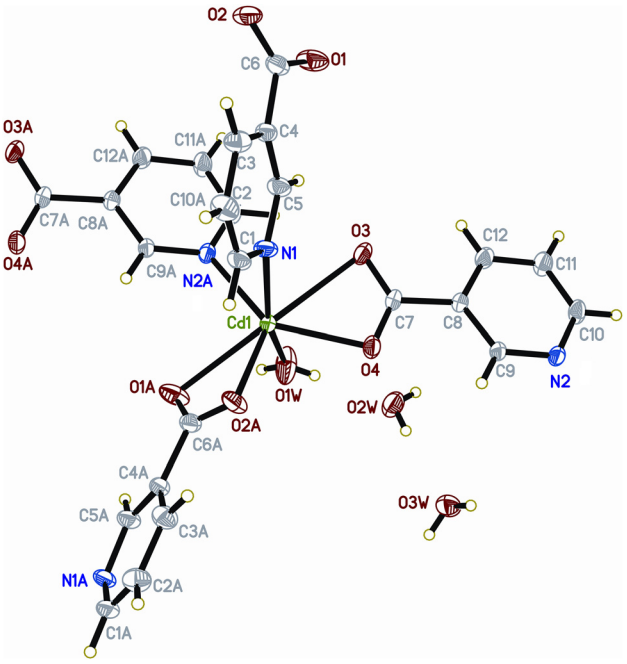
Crystal structure of poly[aqua-(pyridine-3-carboxylato-κ^1*N*)(pyridine-3-carboxylato-κ^2*O*,*O*′) cadmium(II)] dihydrate, $C_{12}H_{14}N_2O_7Cd$



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Abstract

$C_{12}H_{14}N_2O_7Cd$, monoclinic, $P2_1/c$ (no. 14), a = 13.105(7) Å, b = 7.927 (4) Å, c = 15.281 (9) Å, β = 110.220(9)°, V = 1489.6(14) Å^3, Z = 4, $R_{gt}(F)$ = 0.0246, $wR_{ref}(F^2)$ = 0.0530, T = 293 K.

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Table 1: Data collection and handling.

Crystal:	Colorless rod
Size:	0.32 × 0.25 × 0.21 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.50 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7804, 2917, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,494
$N(param)_{refined}$:	217
Programs:	Olex2,[1,2] SHELX[3]

A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

The title compound $[Cd(H_2O)(C_6H_4NO_2)_2]\cdot 2H_2O$ was synthesized by means of a mixed solvothermal method. The mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.16 g), pyridine-3-carboxylic acid ($C_6H_5NO_2$, 0.12 g), ethylene glycol (3.0 mL) and H_2O (1.5 mL) was transferred into 50 mL Teflon-lined stainless steel vessels and heated at 160 °C for 144 h. After cooling it to the room temperature, the colorless rod crystals were isolated, washed with distilled water and dried at the room temperature (yield: 83 % based on $Cd(NO_3)_2\cdot 4H_2O$).

2 Experimental details

Hydrogen atoms bounded to the C atoms from the pyridine-3-carboxylato anions were positioned geometrically and refined using a riding model, with C–H = 0.93 Å, with U_{iso}(H) = 1.2 times U_{eq}(C). Hydrogen atoms on water molecules (O1W, O2W and O3W) were generated by Fourier difference peaks. The restrictive refinement of dfix was applied to deal with the distance of O1W and H1WB sites in the crystal structure.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.20015 (2)	−0.11585 (2)	0.29145 (2)	0.02936 (8)
C1	−0.0307 (2)	−0.2090 (4)	0.1252 (2)	0.0355 (7)
H1	−0.0588	−0.1989	0.1731	0.043*
C2	−0.0969 (2)	−0.2697 (4)	0.0406 (2)	0.0446 (8)
H2	−0.1690	−0.2972	0.0310	0.054*
C3	−0.0549 (2)	−0.2893 (4)	−0.03006 (19)	0.0415 (7)
H3	−0.0974	−0.3344	−0.0872	0.050*
C4	0.0510 (2)	−0.2412 (3)	−0.01483 (18)	0.0319 (6)
C5	0.1101 (2)	−0.1774 (4)	0.07094 (19)	0.0359 (7)
H5	0.1808	−0.1414	0.0808	0.043*
C6	0.1040 (3)	−0.2669 (4)	−0.0869 (2)	0.0393 (7)
C7	0.2690 (2)	0.1889 (3)	0.23668 (19)	0.0298 (6)
C8	0.30509 (19)	0.3655 (3)	0.22750 (17)	0.0267 (6)
C9	0.2655 (2)	0.5007 (3)	0.26319 (18)	0.0304 (6)
H9	0.2152	0.4792	0.2924	0.036*
C10	0.3702 (2)	0.6881 (4)	0.2180 (2)	0.0394 (7)
H10	0.3935	0.7982	0.2154	0.047*
C11	0.4139 (2)	0.5625 (4)	0.1810 (2)	0.0457 (8)
H11	0.4657	0.5872	0.1538	0.055*
C12	0.3803 (2)	0.3991 (4)	0.1845 (2)	0.0393 (7)
H12	0.4078	0.3120	0.1583	0.047*
N1	0.07228 (18)	−0.1639 (3)	0.14160 (15)	0.0352 (6)
N2	0.29528 (18)	0.6603 (3)	0.25805 (16)	0.0319 (5)
O1	0.19146 (18)	−0.1932 (3)	−0.07813 (15)	0.0578 (6)
O2	0.05941 (18)	−0.3681 (3)	−0.15195 (14)	0.0501 (6)
O3	0.30077 (16)	0.0718 (2)	0.19791 (14)	0.0412 (5)
O4	0.20952 (15)	0.1683 (2)	0.28513 (14)	0.0396 (5)
O1W	0.3677 (2)	−0.0498 (3)	0.4126 (2)	0.0750 (9)
H1WA	0.403 (3)	−0.116 (5)	0.446 (3)	0.090*
H1WB	0.388 (3)	0.045 (3)	0.424 (3)	0.090*
O2W	0.4741 (2)	0.2729 (3)	0.4695 (2)	0.0567 (7)
H2WA	0.515 (3)	0.327 (5)	0.461 (3)	0.068*
H2WB	0.439 (3)	0.329 (5)	0.486 (3)	0.068*
O3W	0.3589 (2)	0.5011 (3)	0.54082 (19)	0.0559 (7)
H3WA	0.305 (3)	0.550 (5)	0.506 (3)	0.067*
H3WB	0.350 (3)	0.471 (5)	0.586 (3)	0.067*

3 Comment

The construction of metal polymers using the organic ligands containing N/O coordinated sites and metal ions have attracted considerable attention due to their varieties of structural features and potential performance.[4–7] Organic Some polydentate ligands can provide multiple coordination sites and exhibit flexible coordination geometry, which not only improved their structural dimensions and enriched the structural chemistry of metal polymers.[8–11] The pyridine-3-carboxylic acid ($C_6H_5NO_2$) can be regarded as an excellent tridentate organic molecule for design and synthesis of metal polymers with new structural architecture. In this text, we reported a new cadmium polymer containing the tridentate ligand pyridine-3-carboxylate by means of a mixed solvothermal method. The polymer exhibited an interesting two-dimensional layered structure constructed by Cd^{2+} cations, pyridine-3-carboxylato anions and coordinated water molecules. The water molecules (O2W and O3W) were located between the layers. The molecular structural unit of the title polymer is shown in figure. Each Cd(II) cation adopts seven-coordinated by four O atoms and two N atoms from surrounding four different pyridine-3-carboxylato ligands and one O atom from the coordinated water molecule, leading to a capped octahedral geometric configuration $\{CdN_2O_5\}$. The bond lengths of Cd–O and Cd–N are in the ranges of 2.260(2)–2.701(2) Å and 2.354(2)–2.325(2) Å, respectively. These bond distances fall in their normal scopes and are well agree with previously reported cadmium coordination polymers.[12–18] It is worth noting that three sites (two O atoms and one N atom) of the ligand are all coordinated with cadmium cations in the title polymer. Through the flexible coordination modes between Cd^{2+} cations and pyridine-3-carboxylato ligands, a fascinating two-dimensional layered structure is formed. The structural features of the title polymer are comparable to those of known cadmium polymers catena-(tetrakis(μ_2-nicotinato–N,O,O′)-bis(μ_2-nicotinato–N,O)-tetraaqua-tri-cadmium(II)) (EKEJIN-221066, $[Cd_3(C_6H_4NO_2)_6{\cdot}4H_2O]$, A),[13] catena-[tetrakis(μ_2-3-pyridylcarboxylato–N,O,O′)-bis(μ_2-3-pyridylcarboxylato)-tetra-aqua-tri-cadmium] (EKEJIN01–288902, $[Cd_{1.5}(C_6H_4NO_2)_3{\cdot}2H_2O]$, B)[17] and catena-(($\mu_2$–Nicotinato–N,O,O′)-diaqua-(nicotinato–O,O′)-cadmium(II)) (EYINUV-248132, $[Cd(C_6H_4NO_2)_2)(H_2O)_2]$, C):[18] (i) for the coordination mode of Cd^{2+} cations, the coordination numbers of Cd(1) sites in the title polymer and the above three polymers are the same (7-coordinated), while their coordination atoms are different: the title polymer, A and B exhibit the $\{CdN_2O_5\}$ coordination modes, and the polymer C displays the $\{CdNO_6\}$ coordination geometry; (ii) In terms of structural dimension, the title polymer, A and B all own the 2D layered structure, while polymer C forms a 1D chain structure; (iii) From the water molecules, the title polymer contains the coordinated water molecules and free water molecules, while the remaining three polymers contain only coordinated water molecules. Within the layered structure, the distance of the adjacent Cd(II)···Cd(II) cations is 7.927(2) Å. In addition, the hydrogen bonds of O–H···O (table) and π–π stacking interactions between parallel pyridine rings belonged to pyridine-3-carboxylato ligands (C1–C5, N1, Centroid-to-Centroid distances: 3.725(1) Å and 3.625(6) Å) can be observed in the packing structure. Under the action of these hydrogen bonds and π–π stacking interactions, a three-dimensional supramolecular structure of the titled compound are generated.

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References

1. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment—Olex2 Dissected. *Acta Crystallogr.* **2015**, *A71*, 59–75.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Feng, Y.-Q. Crystal Structure of catena-poly[Bis (μ_2-azido-κ^2N: *N'*)-(nitrato-κ^2*O:O'*)-bis (1, 10-phenanthroline-κ^2*N*: *N'*) samarium (III)], $C_{24}H_{16}N_{11}O_3Sm$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 1009–1011.
5. Rosenstengel, K.; Schulz, A.; Villinger, A. Solid State Structure of $Bi(N_3)_3$, $Bi(N_3)_3$. Solvates and the Structural Dynamics in the $[Bi(N_3)_6]^{3-}$ Anion. *Inorg. Chem.* **2013**, *52*, 6110–6126.
6. Zhong, Z.-G.; Li, J.; Feng, Y.-Q. Crystal Structure of Bis (μ_2-azido-κ^2*N: N*)-tetrakis (azido-κ^1*N*)-tetrakis (1, 10-phenanthroline-κ^2*N*, *N'*) Dibismuth (III), $C_{48}H_{32}N_{26}Bi_2$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 983–985.
7. Wang, J.-G.; Huang, C.-C.; Huang, X.-H.; Liu, D.-S. Three-dimensional Lanthanide Thiophenedicarboxylate Framework with an Unprecedented (4,5)-Connected Topology. *Cryst. Growth Des.* **2008**, *8*, 795–798.
8. Wang, H.-P.; Zhang, C.-M.; Huang, G.-P.; Liang, J.-J. The Crystal Structure of (*N*-([1,1′:4′,1″-Terphenyl]-4,4′-diethyl)-2-(bis(pyridin-2-ylmethyl) amino) acetamide-κ^4*N,N, N″,O*)tri(nitrato-κ*O*, *O'*) samarium(III)–Methanol–Acetonitrile (1/1/1), $C_{40}H_{39}SmN_8O_{14}$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 813–815.
9. Feng, Y.-Q.; Zhong, Z.-G.; Wang, H.-W.; Xing, Z.-Z.; Wang, L. Crystal Structure and Luminescence Properties of a New Dinuclear Bismuth(III) Coordination Polymer Containing Three Types of Ligands. *Z. Naturforsch.* **2018**, *73 b*, 155–160.
10. Zhang, W.; Feng, Y.-Q. A Novel Dinuclear Bismuth (III) Coordination Compound: Bis(*u*-pyridine-2, 6-dicarboxylato)-κ^4O_2,*N*,O_6:O_6; κ^4O_2: O_2,*N*,O_6-Bis[(azido-κ*N*)(1, 10-phenanthroline-κ^2*N, N*) bismuth(III)] Tetrahydrate. *Acta Crystallogr.* **2014**, *C70*, 562–565.
11. Feng, Y.-Q.; Chen, S.-Y.; Wang, L.; Xing, Z.-Z. Ionothermal Synthesis, Structure and Luminescent Properties of a New 2–D Bismuth(III) Coordination Polymer with (6, 5)-Connected Topological Sheet. *Chin. J. Struct. Chem.* **2018**, *37*, 1656–1662.
12. Yue, Y.-F.; Gao, E.-Q.; Bai, S.-Q.; He, Z.; Yan, C.-H. High-dimensional Azido-Bridged Cadmium(II) Polymeric Complexes with Bis(bidentate) Diazine Ligands. *CrystEngComm* **2004**, *6*, 549–555.
13. Li, X.; Cao, R.; Bi, W.; Wang, Y.; Wang, Y.; Li, X.; Guo, Z. A New Family of Cadmium (II) Coordination Polymers from Coligands: Effect of the Coexistent Groups (R= H, $-NO_2$, –OH) on Crystal Structures and Properties. *Cryst. Growth Des.* **2005**, *5*, 1651–1656.
14. Luo, J.; Hong, M.; Wang, R.; Cao, R.; Han, L.; Lin, Z. Synthesis Crystal Structure and Fluorescence of Two Novel Mixed—Ligand Cadmium Coordination Polymers with Different Structural Motifs. *Eur. J. Inorg. Chem.* **2003**, *14*, 2705–2710.
15. He, X.; Zhang, J.; Wu, X. Y.; Lu, C. Z. Syntheses, Crystal Structures and Properties of a Series of 3D Cadmium Coordination Polymers with Different Topologies. *Inorg. Chim. Acta* **2010**, *363*, 1727–1734.
16. Chen, H.-J. Polymeric hexa-μ-nicotinato-tricadmium (II) tetrahydrate. *Acta Crystallogr.* **2003**, *C59*, m371–m372.
17. Song, Y. S.; Yan, B.; Chen, Z. X. Hydrothermal Synthesis, Crystal Structure and Luminescence of Four Novel Metal–Organic Frameworks. *J. Solid State Chem.* **2006**, *179*, 4037–4046.
18. Zhang, J.; Li, Z. J.; Wen, Y. H.; Kang, Y.; Qin, Y. Y.; Yao, Y. G. *catena*–Poly [[diaqua (nicotinato-κ^2 *O*, *O'*) cadmium (II)]-μ-Nicotinato-κ^3 *N: O*, *O'*]. *Acta Crystallogr.* **2004**, *C60*, m389–m391.