Yuhong Long, Xiaoyu Hu and Jingwen Ran*

Crystal structure of poly[(μ_4 -benzene-1,2,4,5-tetracarboxylato)-bis(μ_2 -adipohydrazide) dicadmium], $C_{11}H_{15}N_4O_6Cd$

<https://doi.org/10.1515/ncrs-2021-0309>

Received July 29, 2021; accepted August 29, 2021;

published online September 8, 2021

Abstract

$C_{11}H_{15}CdN_4O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 11.1387(15)$ Å, $b = 10.3933(14)$ Å, $c = 12.2891(17)$ Å, $\beta = 105.319(2)^\circ$, $Z = 4$, $V = 1372.1(3)$ Å³, $R_{\text{gt}}(F) = 0.0286$, $wR_{\text{ref}}(F^2) = 0.0477$, $T = 296(2)$ K.

CCDC no.: 2106207

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The reagents were purchased from commercial sources and used without further purification.

A mixture of benzene-1,2,4,5-tetracarboxylic acid (0.25 mmol, 63.5 mg), NaOH (1.0 mmol, 40 mg) and deionized water (5 mL) was placed in a high-pressure resistant glass bottle (10 mL), the bottle was sealed and heated at 353 K for 30 min. After that, cadmium acetate dihydrate (0.5 mmol, 133 mg) and adipohydrazide (0.5 mmol, 87 mg) were added, and the bottle was sealed and heated at 393 K for 24 h and cooled to room temperature. Colorless prism crystals were obtained by filtration, washed with deionized water and dried in air. Yield 46% based on Cd(II).

Experimental details

H atoms were added using riding models. Their U_{iso} values were set to $1.2U_{\text{eq}}$ of the parent atoms.

Comment

Researchers have focused on coordination polymers due to their versatile architecture and potential applications for

*Corresponding author: Jingwen Ran, Hubei Key Laboratory for Processing and Application of Catalytic Materials, College of Chemistry and Chemical Engineering, Huanggang Normal University, Huanggang 438000, China, E-mail: ranjingwen@hgnu.edu.cn. <https://orcid.org/0000-0001-8701-6192>

Yuhong Long and Xiaoyu Hu, Hubei Key Laboratory for Processing and Application of Catalytic Materials, College of Chemistry and Chemical Engineering, Huanggang Normal University, Huanggang 438000, China

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.32 × 0.31 × 0.28 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.63 mm ⁻¹
Diffractometer, scan mode:	Bruker Apex-III, φ and ω
$\theta_{\max}$, completeness:	27.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7847, 2966, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2324
$N(\text{param})_{\text{refined}}$:	200
Programs:	Bruker [1], SHELX [2, 3], DIAMOND [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cd1	0.60643 (2)	0.19229 (2)	0.16712 (2)	0.01766 (8)
O1	0.82720 (17)	0.1852 (2)	0.16547 (16)	0.0218 (5)
O2	0.69441 (17)	0.0556 (2)	0.04887 (16)	0.0222 (5)
O3	0.82900 (19)	-0.2851 (2)	0.04777 (18)	0.0282 (5)
O4	0.85391 (19)	-0.15641 (19)	0.19838 (17)	0.0254 (5)
O5	0.43704 (19)	0.0986 (2)	0.22782 (19)	0.0316 (6)
O6	0.12613 (19)	0.1328 (2)	0.54508 (17)	0.0288 (5)
N1	0.5739 (2)	-0.0581 (3)	0.3011 (2)	0.0290 (7)
H1	0.586555	-0.133593	0.330668	0.035*
N2	0.6746 (2)	0.0170 (2)	0.2884 (2)	0.0251 (6)
H2A	0.725321	-0.031738	0.260864	0.030*
H2B	0.717310	0.045954	0.355689	0.030*
N3	-0.0373 (2)	0.2228 (3)	0.4215 (2)	0.0279 (7)
H3A	-0.081536	0.229573	0.352884	0.033*
N4	-0.0665 (2)	0.2965 (3)	0.5080 (2)	0.0269 (6)
H4A	-0.130412	0.260780	0.527426	0.032*
H4B	-0.088622	0.375532	0.482705	0.032*
C1	0.8026 (3)	0.0981 (3)	0.0910 (2)	0.0172 (7)
C2	0.9070 (2)	0.0450 (3)	0.0478 (2)	0.0137 (6)
C3	0.9776 (3)	0.1300 (3)	0.0027 (2)	0.0161 (6)
H3	0.962917	0.217875	0.005232	0.019*
C4	0.9307 (2)	-0.0869 (3)	0.0459 (2)	0.0137 (6)
C5	0.8648 (2)	-0.1853 (3)	0.1000 (2)	0.0185 (6)
C6	0.4586 (3)	-0.0109 (3)	0.2668 (3)	0.0251 (7)
C7	0.3576 (3)	-0.1045 (3)	0.2747 (3)	0.0388 (9)
H7A	0.383275	-0.147862	0.347062	0.047*
H7B	0.350671	-0.169223	0.216551	0.047*
C8	0.2300 (3)	-0.0464 (3)	0.2629 (3)	0.0322 (9)
H8A	0.209268	0.007089	0.195782	0.039*
H8B	0.169497	-0.115533	0.251406	0.039*
C9	0.2176 (3)	0.0338 (3)	0.3620 (3)	0.0288 (8)
H9A	0.264359	0.112985	0.364786	0.035*
H9B	0.252117	-0.013060	0.431484	0.035*
C10	0.0814 (3)	0.0653 (3)	0.3518 (3)	0.0274 (8)
H10A	0.048202	0.112498	0.282297	0.033*
H10B	0.035221	-0.014663	0.346518	0.033*
C11	0.0599 (3)	0.1426 (3)	0.4480 (3)	0.0205 (7)

luminescent properties, magnetic interactions, catalytic ability, and so on [5, 6]. As a versatile ligand benzene-1,2,4,5-tetracarboxylate has been widely used to construct transition metal or rare earth metal complexes using its multiple coordination function modes.

The asymmetric unit of the complex consists of one Cd ion, one adipohydrazide ligand and one half of a fully deprotonated benzene-1,2,4,5-tetracarboxylate (btc⁴⁻). The btc⁴⁻ ligand is located on a center of inversion (see the Figure). The central Cd ion is coordinated by a chelating carboxylate group (O1 and O2) and a monodentate carboxylate group (O4) from two btc⁴⁻ ligands. In addition, two adipohydrazide ligands provide two oxygen atoms (O5 and O6) and two nitrogen atoms (N2 and N4) to coordinate with the central cadmium ion, forming a distorted single capped octahedron. Each Cd ion is connected by two btc⁴⁻ ligands to form a two-dimensional network with a rhombic-shaped grid [7]. The adipohydrazide ligands are interspersed in the two-dimensional structure, ensuring the Cd ion to form a seven-coordinated conformation, enhancing the stability of the coordination polymer. The Cd–O bond distances fall in the range of 2.239(2)–2.4646(19) Å and the Cd–N bond distances are 2.349(2) and 2.356(2) Å. All the bond lengths around the Cd1 center are within the normal range [8, 9]. The N–N bond distances are 1.410(3) and 1.415(3) Å, which are in good agreement with the reported information [10, 11].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by Hubei Provincial Central Committee Guiding Local Science and Technology Development Project (No. 2019ZYYD074).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2, SAINT and SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2009.
2. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.
5. Zhou Y., Yoon J. Recent progress in fluorescent and colorimetric chemosensors for detection of amino acids. *Chem. Soc. Rev.* 2012, *41*, 52–67.

6. Dhakshinamoorthy A., Garcia H. Catalysis by metal nanoparticles embedded on metal-organic frameworks. *Chem. Soc. Rev.* 2012, 41, 5262–5284.
7. Shi R., Zhu X., Lin S. Y., Su Y. Y., Zhang S. Y. Crystal structure of poly [aqua-(μ_4 -benzene-1,2,4,5-tetracarboxylato-bis[μ_2 -1(1H-imidazol-1-yl)benzyl]-1H-1,2,4-triazol-dinickel(II)], $NiC_{17}H_{14}N_5$. *Z. Kristallogr. N. Cryst. Struct.* 2020, 235, 817–819.
8. Cai H., Xu C., Zhou Y. P., Tong X. Q., Guo Y. Molecular tectonics of mixed-ligand metal-organic frameworks: positional isomeric effect, and structural diversification. *J. Mol. Struct.* 2016, 1108, 263–268.
9. Lin J. D., Cheng J. W., Du S. W. Five d_{10} 3D metal-organic frameworks constructed from aromatic polycarboxylate acids and flexible imidazole-based ligands. *Cryst. Growth Des.* 2008, 8, 3345–3353.
10. Lo K. M., Lee S. M., Tiekink E. R. T. Crystal structure of heanedihydrazide, $C_6H_{14}N_4O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2020, 235, 1257–1258.
11. Zabierowski P., Oszejca M., Hodorowicz M., Matoga D. Ladder-chain zinc coordination polymers based on adipic acid dihydrazide precursor: synthesis and structural transformations. *Polyhedron* 2017, 121, 25–36.