Hua-Rui Wang*

Crystal structure of poly[di aqua-(μ_3 -fumarato)-(μ_3 -maleato)-(μ_4 -1,2,4,5-tetrakis((1*H*-1,2,4-triazol-1-yl)methyl)benzene)tetracadmium(II)] dihydrate, $C_{34}H_{32}N_{12}O_9Cd_4$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.26 × 0.21 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.08 mm ⁻¹
Diffractometer, scan mode:	Rigaku Saturn 724, ω
$\theta_{\max}$, completeness:	27.9°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12,985, 4985, 0.025
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4319
$N(\text{param})_{\text{refined}}$:	316
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

<https://doi.org/10.1515/ncrs-2021-0475>

Received December 15, 2021; accepted February 3, 2022;
published online February 18, 2022

Abstract

$C_{34}H_{32}N_{12}O_9Cd_4$, monoclinic, $P\bar{1}$ (no. 2), $a = 9.894(2)$ Å, $b = 9.942(2)$ Å, $c = 10.896(2)$ Å, $\alpha = 94.35(3)^\circ$, $\beta = 96.80(3)^\circ$, $\gamma = 93.35(3)^\circ$, $V = 1058.7(4)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0406$, $wR_{\text{ref}}(F^2) = 0.0984$, $T = 293(2)$ K.

CCDC no.: 2149837

A part of the title coordination polymer is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Maleic acid (0.012 g, 0.1 mmol), 1,2,4,5-tetrakis(1,2,4-triazol-1-ylmethyl)benzene (0.02 g, 0.05 mmol) and cadmium(II)

acetate (0.023 g, 0.1 mmol) were added to the mixture of acetonitrile (7 mL) and water (1 mL) in a Teflon-lined stainless steel reactor. The mixture was heated at 433 K for three days, and then slowly cooled down to room temperature. Colorless crystals of the title compound were obtained.

Experimental details

The crystallographic data of title complex was collected on a Rigaku Saturn 724 CCD diffractometer at room temperature. Absorption corrections were applied by using multi-scan program [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [4] refinement package. The H atoms bonded to C atoms were fixed, with C–H distance of 0.93 Å; and/or positioned geometrically in the riding-model approximation, with C–H distance of 0.97 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Comment

A series of complexes based on flexible 1,2,4-triazole-containing ligands were reported, as 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bttz), 1,4-bis(1,2,4-triazol-1-yl)butane (btb),

*Corresponding author: Hua-Rui Wang, College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, LuoYang Normal University, Luoyang, Henan 471934, P. R. China, E-mail: wanghrly@126.com. <https://orcid.org/0000-0003-4069-3350>

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

Atom	x	y	z	U _{iso} ^a /U _{eq}
Cd1	0.38499 (3)	0.60679 (3)	0.26674 (3)	0.04006 (10)
Cd2	0.57500 (3)	0.82836 (3)	−0.01463 (3)	0.04661 (11)
O1	0.4111 (3)	0.7063 (4)	0.0711 (3)	0.0540 (8)
O2	0.2142 (4)	0.6124 (5)	0.0908 (3)	0.0824 (14)
O3	0.4093 (3)	0.4703 (3)	−0.2634 (3)	0.0474 (7)
O4	0.5338 (3)	0.6431 (3)	−0.1625 (3)	0.0538 (8)
O5	0.3158 (4)	0.8051 (4)	0.3513 (3)	0.0603 (9)
O6	0.4559 (4)	0.7031 (4)	0.4779 (3)	0.0587 (9)
O7	0.3467 (5)	1.1137 (4)	0.7466 (4)	0.0935 (16)
O8	0.4597 (4)	0.9954 (3)	0.8763 (3)	0.0518 (8)
O12	0.7248 (4)	0.6799 (4)	0.0854 (4)	0.0772 (12)
H12A	0.7420	0.7300	0.1529	0.116*
H12B	0.6860	0.6208	0.1298	0.116*
N1	−0.2320 (3)	−0.0992 (3)	0.9098 (3)	0.0400 (8)
N2	−0.0813 (3)	0.0178 (3)	0.8250 (3)	0.0328 (7)
N3	−0.0151 (4)	−0.0875 (4)	0.8704 (3)	0.0431 (8)
N4	0.2324 (4)	0.4668 (4)	0.3446 (3)	0.0410 (8)
N5	0.0310 (4)	0.3847 (4)	0.3897 (4)	0.0471 (9)
N6	0.1342 (3)	0.3540 (3)	0.4759 (3)	0.0370 (7)
C1	0.4092 (5)	1.0149 (5)	0.7678 (4)	0.0476 (10)
C4	0.3644 (6)	0.9042 (5)	0.5557 (4)	0.0584 (13)
H4	0.3010	0.9678	0.5384	0.070*
C5	0.4334 (5)	0.9124 (5)	0.6660 (4)	0.0480 (10)
H5	0.5004	0.8522	0.6821	0.058*
C6	0.2374 (4)	0.6923 (5)	−0.1023 (4)	0.0471 (10)
H6	0.1568	0.7361	−0.1127	0.056*
C7	0.1074 (5)	0.2752 (4)	0.5791 (4)	0.0461 (10)
H7A	0.0433	0.3205	0.6259	0.055*
H7B	0.1917	0.2719	0.6339	0.055*
C8	−0.1089 (4)	−0.1541 (4)	0.9205 (4)	0.0419 (9)
H8	−0.0930	−0.2324	0.9600	0.050*
C10	−0.0157 (4)	0.1127 (4)	0.7521 (3)	0.0370 (8)
H10A	0.0758	0.1389	0.7924	0.044*
H10B	−0.0662	0.1934	0.7494	0.044*
C11	0.0576 (4)	0.0764 (4)	0.4190 (3)	0.0353 (8)
H11	0.0974	0.1286	0.3638	0.042*
C12	0.0959 (4)	0.4513 (4)	0.3138 (4)	0.0416 (9)
H12	0.0517	0.4855	0.2438	0.050*
C23	0.0503 (4)	0.1323 (4)	0.5380 (3)	0.0331 (8)
C24	−0.0077 (4)	0.0545 (4)	0.6208 (3)	0.0312 (7)
C25	0.2921 (4)	0.6688 (4)	0.0268 (4)	0.0399 (9)
C26	−0.2103 (4)	0.0081 (4)	0.8486 (3)	0.0347 (8)
H26	−0.2755	0.0681	0.8254	0.042*
C27	0.4213 (4)	0.5867 (4)	−0.2082 (3)	0.0391 (9)
C29	0.2924 (5)	0.6568 (5)	−0.2033 (4)	0.0463 (10)
H29	0.2467	0.6774	−0.2784	0.056*
C30	0.3822 (5)	0.7974 (5)	0.4556 (4)	0.0455 (10)
C31	0.2518 (4)	0.4028 (4)	0.4478 (4)	0.0416 (9)
H31	0.3361	0.3940	0.4931	0.050*
O9 ^a	0.0447 (13)	0.4372 (13)	−0.0431 (14)	0.148 (5)
H9A ^a	−0.0326	0.3931	−0.0537	0.222*
H9B ^a	0.0959	0.3873	−0.0812	0.222*

^aOccupancy: 0.5.

1,3,5-tris(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) [5–12]. To further understand the coordination principle for these coordination complexes, we selected the flexible tetrapodal 1,2,4,5-tetra(1,2,4-triazol-1-ylmethyl)-benzene (*ttyb*) as a functional ligand and used the “mix-ligand” synthetic strategy to explore the assembly with “mixed” *ttyb* and aromatic polycarboxylate ligands [13–15]. In this context, we reacted 1,2,4,5-tetra(1,2,4-triazol-1-ylmethyl)-benzene (*ttyb*) with Cd²⁺ ions, then we added maleic acid (H₂mal) as a precursor of an auxiliary ligand.

The asymmetric unit of compound **1** consists of two crystallographically independent Cd(II) atoms, one half of a *ttyb* ligand, one maleate ligand (*mal*), one fumarate (*fum*) ligand and two water molecules. The Cd1 is six-coordinated by three carboxylate oxygen atoms from two *fum* ligands, two carboxylate oxygen atoms from one *mal* ligand and one nitrogen atom from one *ttyb* ligand. This results in a distorted octahedral coordination of Cd1. The Cd2 is also six-coordinated by two carboxylate oxygen atoms from one *fum* ligand, two carboxylate oxygen atoms from two *mal* ligands, one nitrogen atom from *ttyb* ligand and one oxygen atom from coordinated water molecule. The Cd–O bond lengths are in the range of 2.220(3)–2.451(3) Å. The Cd–N lengths are 2.275(3) Å and 2.268(3) Å. Moreover, in malate dianion, carboxylate groups with two kinds of coordination modes have been found; one is bridging and the other chelating-bridging. In fumarate dianion, carboxylate groups with two chelating-bridging coordination modes have been found. The *fum* ligand coordinates to the three Cd center in chelating mode. Each malate dianion ligand coordinates to three Cd1 and Cd2 atoms to generate a 2D layer. *ttyb* acts as a μ_4 -bridge linking four Cd(II) ions, and connect the 2D layer to extend to a 3D network. H₂male was used as initial reactant, but the *mal* and *fum* ligands were found in the resultant crystal structure. For the *male* ligand, the conformation transformation happened *in situ* hydrothermal reaction process [16, 17].

Author contributions: The author has accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by Key Scientific Research Projects of Higher Education of Henan Province (16A150016, DOI: 10.13039/501100013066) and Henan Province Natural Science Foundation (182300410237, DOI: 10.13039/501100006407).

Conflict of interest statement: The author declares no conflicts of interest regarding this article.

References

1. Oxford Diffraction Ltd. CrysAlis^{PRO}: Abingdon, Oxfordshire, England, 2006.
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. SHELXTL – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, A71, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
5. Chang X.-H., Yang X.-G., Zhai Z.-M., Chen J.-Y., Li F.-F. Synthesis, structure and highly enhanced phosphorescence of a cadmium(II) coordination polymer assembled with 1,4-naphthalenedicarboxylic acid and 2-propylimidazole. *Chin. J. Struct. Chem.* 2021, 40, 187–192.
6. Liu X., Du L., Li R., Ma N., You M., Feng X. Different effects in the selective detection of aniline and Fe^{3+} by lanthanide-based coordination polymers containing multiple reactive sites. *CrystEngComm* 2020, 22, 2837–2844.
7. Yang X. G., Zhai Z. M., Lu X. M., Zhao Y., Chang X. H., Ma L. F. Room temperature phosphorescence of Mn(II) and Zn(II) coordination polymers for photoelectron response applications. *Dalton Trans.* 2019, 48, 10785–10789.
8. Lin Z.-J., Lü J., Hong M., Cao R. Metal-organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* 2014, 43, 5867–5895.
9. Qin J.-H., Xu P., Huang Y.-D., Xiao L.-Y., Lu W., Yang X.-G., Ma L., Zang S.-Q. High loading of Mn(II)-metalated porphyrin in MOF for photocatalytic CO_2 reduction in gas-solid condition. *Chem. Commun.* 2021, 57, 8468–8471.
10. Hawes C. S., Hamilton S. E., Hicks J., Knowles G. P., Chaffee A. L., Turner D. R., Batten S. R. Coordination chemistry and structural dynamics of a long and flexible piperazine-derived ligand. *Inorg. Chem.* 2016, 55, 6692–6702.
11. Miao S.-B., Sun X.-J., Wang K.-X., Xu C.-Y., Li Z.-H., Wang Z.-Q. Effect of charge on the structures of Zn(II) coordination polymers with triazole-carboxylate ligands: syntheses, structures, and luminescent properties. *Crystals* 2018, 8, 312.
12. Qin J. H., Zhang H., Sun P., Huang Y. D., Shen Q., Yang X. G., Ma L. F. Ionic liquid induced highly dense assembly of porphyrin in MOF nanosheets for photodynamic therapy. *Dalton Trans.* 2020, 49, 17772–17778.
13. Xu G.-C., Hua Q., Okamura T., Bai Z.-S., Ding Y.-J., Huang Y.-Q., Liu G.-X., Sun W.-Y., Ueyama N. Cadmium(II) coordination polymers with flexible tetradentate ligand 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene: anion effect and reversible anion exchange property. *CrystEngComm* 2009, 11, 261–270.
14. Hua Q., Zhao Y., Xu G.-C., Chen M.-S., Su Z., Cai K., Sun W.-Y. Synthesis, structures, and properties of zinc(II) and cadmium(II) complexes with 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene and multicarboxylate ligands. *Cryst. Growth Des.* 2010, 10, 2553–2562.
15. Hua Q., Su Z., Zhao Y., Okamura T., Xu G. C., Sun W.-Y., Ueyama N. Synthesis, structure and property of manganese(II) complexes with mixed tetradentate imidazole-containing ligand and benzenedicarboxylate. *Inorg. Chim. Acta* 2010, 363, 3550–3557.
16. Zhang S., Huang L., Qu L., Peng H., Zhao Y. Two novel R- and S-malato-bridged coordination polymers by reacting lanthanide chloride and maleic anhydride, 1,10-phenanthroline at hydrothermal condition. *J. Mol. Struct.* 2006, 787, 14–17.
17. Bai H., Ma J., Liu Y., Yang J. Hydrothermal syntheses, crystal structures and topological analyses of four new 3D coordination polymers with mixed ligands. *Inorg. Chim. Acta* 2011, 376, 332–339.