Peng Zhang* and Yan Su

Crystal structure of poly[di- μ_2 -aqua)-diaqua-bis(μ_6 -4,4',4''-(benzene-1,3,5-triyltris(oxy))tribenzoato- κ^6 O¹:O²:O³:O³:O⁵:O⁶)tricadmium(II)] dihydrate, C₅₄H₄₂Cd₃O₂₄

<https://doi.org/10.1515/ncrs-2019-0042>

Received January 14, 2019; accepted March 11, 2019; available online March 21, 2019

Abstract

C₅₄H₄₂Cd₃O₂₄, triclinic, $P\bar{1}$ (no. 2), $a = 7.9122(5)$ Å, $b = 9.0693(6)$ Å, $c = 18.6637(11)$ Å, $\beta = 100.765(6)^\circ$, $V = 1241.99(15)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0266$, $wR_{\text{ref}}(F^2) = 0.0646$, $T = 293(2)$ K.

CCDC no.: 1902408

A part of the title crystal 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.

Source of material

A mixture of 1,3,5-tris(4-carbonylphenoxy)benzene (H₃TCPB, 0.004 mmol, 1.9 mg), Cd(NO₃)₂·4 H₂O (0.008 mmol, 2.5 mg), and 5 mL mixed solution of EtOH/H₂O ($v/v = 1/4$) was added to a glass tube, pumped to a near-vacuum, heated at 140 °C for 50 h, and cooled to 25 °C with a decreasing rate

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.26 × 0.18 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.37 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	29.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10241, 5600, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4844
$N(\text{param})_{\text{refined}}$:	377
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3]

of 2 °C/h. Colorless block crystals of the title complex were obtained with the yield of ca. 48% (based on H₃TCPB).

Experimental details

H atoms bonded to C atoms from organic ligands were positioned geometrically and refined using a riding model, with C–H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

Comment

The design and synthesis of coordination polymers (CPs) have gained great interests for their interesting modular structures and potential applications in the fields of fluorescent probes and magnetism [4–6]. The selection of suitable organic ligands plays an important role in the final structure and property of the as-prepared CPs. According to previous reports,

*Corresponding author: Peng Zhang, School of pharmacy, Shaanxi University of Chinese Medicine, Xianyang, Shaanxi, China, e-mail: peng_zhang666@126.com

Yan Su: School of pharmacy, Shaanxi University of Chinese Medicine, Xianyang, Shaanxi, China

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cd1	0.76554(2)	0.41011(2)	0.00740(2)	0.02280(6)
Cd2	0.500000	0.000000	0.000000	0.02298(7)
O1	0.4397(3)	0.1793(2)	0.08104(10)	0.0350(5)
O2	0.6937(3)	0.3805(2)	0.11671(11)	0.0383(5)
O3	0.0557(2)	0.54997(19)	0.07793(9)	0.0228(4)
O4	0.0896(3)	0.7949(2)	0.12424(11)	0.0386(5)
O5	0.5456(3)	0.3034(2)	−0.09691(11)	0.0424(5)
O6	0.3550(3)	0.0688(3)	−0.09491(11)	0.0479(6)
O7	0.5750(3)	0.2077(2)	0.43028(11)	0.0358(5)
O8	0.1599(3)	0.5070(2)	0.42122(10)	0.0331(4)
O9	0.1132(2)	0.1030(2)	0.56798(10)	0.0319(4)
O10	0.8005(3)	0.1613(2)	0.00188(11)	0.0267(4)
O11	0.7336(4)	0.6489(3)	0.00533(15)	0.0611(7)
H11A	0.741048	0.691435	0.049390	0.092*
H11B	0.629410	0.640636	−0.021503	0.092*
C1	0.0818(3)	0.6574(3)	0.13226(14)	0.0220(5)
C2	0.1048(3)	0.6145(3)	0.20792(13)	0.0207(5)
C3	0.1196(3)	0.4692(3)	0.21939(14)	0.0250(5)
H3	0.113945	0.397411	0.179410	0.030*
C4	0.1428(4)	0.4301(3)	0.28981(15)	0.0272(6)
H4	0.152253	0.332477	0.297170	0.033*
C5	0.1519(3)	0.5380(3)	0.34937(14)	0.0247(5)
C6	0.1372(4)	0.6833(3)	0.33886(14)	0.0271(6)
H6	0.143669	0.755139	0.378927	0.033*
C7	0.1128(3)	0.7206(3)	0.26826(14)	0.0255(5)
H7	0.101650	0.817685	0.260972	0.031*
C8	0.5787(4)	0.2220(3)	0.35630(14)	0.0275(6)
C9	0.4577(4)	0.1074(3)	0.30133(16)	0.0342(6)
H9	0.378553	0.019913	0.313440	0.041*
H10A	0.836(5)	0.165(4)	−0.035(2)	0.051*
H10B	0.868(5)	0.149(4)	0.032(2)	0.051*
C10	0.4548(4)	0.1231(3)	0.22819(16)	0.0306(6)
H10	0.373561	0.045906	0.191024	0.037*
C11	0.5730(3)	0.2542(3)	0.20991(14)	0.0230(5)
C12	0.6962(3)	0.3662(3)	0.26603(14)	0.0273(6)
H12	0.777248	0.453019	0.254293	0.033*
C13	0.7000(4)	0.3503(3)	0.33964(15)	0.0301(6)
H13	0.783536	0.425338	0.377095	0.036*
C14	0.5697(3)	0.2727(3)	0.13063(14)	0.0257(5)
C15	0.1965(3)	0.1278(3)	0.64167(13)	0.0223(5)
C16	0.3378(4)	0.2601(3)	0.67622(15)	0.0296(6)
H16	0.386830	0.336288	0.648994	0.036*
C17	0.4060(4)	0.2790(3)	0.75139(15)	0.0285(6)
H17	0.498684	0.369720	0.774802	0.034*
C18	0.3378(3)	0.1642(3)	0.79238(14)	0.0226(5)
C19	0.1963(3)	0.0313(3)	0.75666(14)	0.0263(6)
H19	0.148978	−0.046176	0.783590	0.032*
C20	0.1251(3)	0.0125(3)	0.68187(14)	0.0260(5)
H20	0.029970	−0.076697	0.658552	0.031*
C21	0.4198(3)	0.1806(3)	0.87246(14)	0.0272(6)
C22	0.2229(4)	0.3891(3)	0.44462(14)	0.0266(5)
C23	0.1373(4)	0.3053(3)	0.49400(14)	0.0272(6)
H23	0.037859	0.324670	0.507784	0.033*
C24	0.2040(4)	0.1932(3)	0.52175(13)	0.0267(6)
C25	0.3507(4)	0.1589(3)	0.50163(14)	0.0293(6)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H25	0.392960	0.081926	0.520755	0.035*
C26	0.4311(4)	0.2442(3)	0.45190(14)	0.0274(6)
C27	0.3712(4)	0.3609(3)	0.42445(14)	0.0278(6)
H27	0.430043	0.419786	0.392757	0.033*
O12	0.0594(3)	0.1073(2)	0.10174(14)	0.0455(5)
H12A	0.165024	0.130014	0.093056	0.068*
H12B	0.030340	0.016771	0.114082	0.068*

multicarboxylate ligands are widely used to build CPs with multi-dimensional architectures and interesting properties because of their rich coordination modes [7]. In this study, we choose the flexible multicarboxylate ligand 1,3,5-tris(4-carboxylphenyloxy)benzene (H₃TCPB) to build targeted CPs because the flexible ligands have been shown to be capable of improve the performances of CPs in terms of adsorption and separation, sensing, and shape memory [8].

A single crystal X-ray diffraction study reveals that the title complex shows a three-dimensional framework structure. The asymmetric unit contains one and a half of crystallographically independent Cd²⁺ ions, one TCPB^{3−} ligand, one μ₂-coordinated water molecule, one coordinated water molecule, and one lattice water molecule. The distorted octahedral coordination environment of Cd1 is shaped by four carboxylato oxygen atoms, one μ₂-coordinated water molecule and one H₂O ligand; Cd2 is six-coordinated with four carboxylato oxygen atoms and two μ₂-H₂O ligands, which also result in a distorted octahedral coordination environment.

The H₃TCPB ligand is completely deprotonated and adopts (κ⁰-κ²)-(κ¹-κ¹)-(κ¹-κ¹)-μ₆ coordination mode to form a 3D framework. The structure of the title complex is similar to the Mn(II)-based coordination polymer reported by Liu and Hu [9, 10].

References

- Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.35.15. Agilent Technologies UK Ltd, Oxford, UK (2011).
- 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.* **42** (2009) 339–341.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Du, Z.-Y.; Xu, T.-T.; Huang, B.; Su, Y.-J.; Xue, W.; He, C.-T.; Zhang, W.-X.; Chen, X.-M.: Switchable guest molecular dynamics in a perovskite-like coordination polymer toward sensitive thermoresponsive dielectric materials. *Angew. Chem. Int. Ed.* **54** (2015) 914–918.
- Shanmugaraju, S.; Dabadie, C.; Byrne, K.; Savyasachi, A. J.; Umadevi, D.; Schmitt, W.; Kitchen, J. A.; Gunnlaugsson, T.:

- A supramolecular troger's base derived coordination zinc polymer for fluorescent sensing of phenolic-nitroaromatic explosives in water. *Chem. Sci.* **8** (2017) 1535–1546.
6. Gong, T.; Lou, X.; Fang, J.-J.; Gao, E.-Q.; Hu, B.: A novel coordination polymer based on Co(II) hexanuclear clusters with azide and carboxylate bridges: structure, magnetism and its application as a Li-ion battery anode. *Dalton Trans.* **45** (2016) 19109–19116.
 7. Wang, H.; Wang, K.; Sun, D.; Ni, Z.-H.; Jiang, J.: Synthesis, crystal structures, and luminescent properties of Cd(II) coordination polymers assembled from asymmetric semi-rigid V-shaped multicarboxylate ligands. *CrystEngComm* **13** (2011) 279–286.
 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.* **43** (2014) 5867–5895.
 9. Zhang, J.; Huo, L.; Wang, X.; Fang, K.; Fan, L.; Hu, T.: Structural diversity, magnetic properties, and luminescent sensing of the flexible tripodal ligand of 1,3,5-tris(4-carbonylphenyloxy)benzene based Mn(II)/Cd(II) coordination polymers. *Cryst. Growth Des.* **17** (2017) 5887–5897.
 10. Chen, M.; Hu, M.; Zhao, H.; Tian, J.-Y.; Liu, C.-S.: Solvent-controlled construction of two 3D manganese(II) coordination polymers based on flexible tripodal multicarboxylate linker and rod-shaped SBUs. *Z. Anorg. Allg. Chem.* **642** (2016) 778–784.