Chao-Jun Du*, Yuan-Liang Zhu and Yan Zeng

The crystal structure of 2,5-dichloroterephthalic acid dihydrate, $C_8H_8Cl_2O_6$

<https://doi.org/10.1515/ncrs-2019-0396>

Received June 10, 2019; accepted August 5, 2019; available online August 23, 2019

Abstract

$C_8H_8Cl_2O_6$, monoclinic, $P2_1/c$ (no. 14), $a = 10.6836(9)$ Å, $b = 7.2382(6)$ Å, $c = 6.8585(5)$ Å, $\beta = 92.850(3)^\circ$, $V = 529.71(7)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0315$, $wR_{ref}(F^2) = 0.0811$, $T = 150(2)$ K.

CCDC no.: 1945370

The molecular structure is shown in the figure (Only the asymmetric unit is labelled). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All of starting materials are commercial and used without further purification. The title compound was synthesized in hydrothermal synthesis: solid 2,5-dichloroterephthalic acid (2.35 g, 0.01 mol) was added in 10 mL water in a teflon-lined stainless steel autoclave and heated to 443 K for 3 days, followed by cooling to room temperature automatically and colorless single crystals were obtained, yield: 92.7% (based on 2,5-dichloroterephthalic acid).

***Corresponding author: Chao-Jun Du**, School of Biochemical and Chemical Engineering, Nanyang Institute of Technology, Nanyang, Henan Province 473000, P.R. China, e-mail: hyperchem@126.com
Yuan-Liang Zhu and Yan Zeng: School of Biochemical and Chemical Engineering, Nanyang Institute of Technology, Nanyang, Henan Province 473000, P.R. China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.25 \times 0.15 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.62 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.2° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6562, 949, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 877
$N(\text{param})_{\text{refined}}$:	77
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.76206(18)	0.4252(3)	0.9344(3)	0.0188(4)
C2	0.62744(17)	0.4687(3)	0.9657(3)	0.0145(4)
C3	0.54284(17)	0.3224(3)	0.9737(3)	0.0150(4)
H3	0.57168(17)	0.1997(3)	0.9556(3)	0.0180(5)*
C4	0.41760(17)	0.3522(3)	1.0074(3)	0.0140(4)
Cl1	0.32290(4)	0.15810(6)	1.01995(7)	0.01921(19)
O1	0.84832(13)	0.5239(2)	0.9890(3)	0.0335(4)
O2	0.77662(13)	0.2672(2)	0.8448(2)	0.0304(4)
O1W	1.00806(19)	0.1887(4)	0.8207(5)	0.0893(11)
H1Wa	1.064(3)	0.268(5)	0.865(7)	0.1339(16)*
H1Wb	1.040(4)	0.119(5)	0.732(6)	0.1339(16)*
H2	0.85340(16)	0.2465(19)	0.835(4)	0.0456(6)*

Experimental details

The structure was solved by direct methods with the SHELXS program [2]. All H-atoms from C atoms and N atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{N})$ for all H atoms) using a riding model with C–H = 0.950 Å. The carboxyl and water H-atom positions were fixed as found (O–H = 0.840–0.873 Å, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, respectively).

Comment

Known as one of the derivative of terephthalic acid, 2,5-dichloroterephthalic acid is usually used as rigid organic linkers to build metal-organic frameworks [5–9]. However, the investigation of crystallization of 2,5-dichloroterephthalic acid has not been studied. To the best of our knowledge, only one example of 2,5-dichloroterephthalic acid has been

characterized structurally cocrystallized with piperazine-2,5-dioneone [10]. Therefore, we reported the crystal structure of 2,5-dichloroterephthalic acid dihydrate.

As described in the figure the asymmetric unit contains one half of an acid molecule and one water. Thus water molecules are introduced to stabilize the organic molecules through two kind of hydrogen bonds: H—O—H···O(carboxyl) and COO—H···O (water molecule), by which a three-dimensional supramolecular structure is generated. All the atoms of the organic acid except the four O atoms come from the two carboxyl groups are nearly coplanar. All bond lengths and angles of 2,5-dichloroterephthalic acid dihydrate are comparable to its analogues [10] and the structurally related dibromo compound [11].

Acknowledgements: This study was supported by the Key Scientific Research Projects of Higher Education Institutions in Henan Province (17A430027).

References

1. Bruker. SAINT v8.37A. Bruker AXS Inc, Madison, WI, USA (2015).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. 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. A* **71** (2015) 59–75.
4. 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.
5. Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M.: Geometric requirements and examples of important structures in the assembly of square building blocks. *Proc. Natl. Acad. Sci. USA* **99** (2002) 4900–4904.
6. Xue, M.; Zhang, Z.; Xiang, S.; Jin, Z.; Liang, D.; Zhu, G.-S.; Qiu, S.-L.; Chen, B.: Selective gas adsorption within a five-connected porous metal–organic framework. *J. Mater. Chem.* **20** (2010) 3984–3988.
7. Hao, S. Y.; Hou, S. X.; Hecke, K. V.; Cui, G. H.: Construction of noninterpenetrating and interpenetrating Co(II) networks with halogenated carboxylate modulated by auxiliary *N*-donor co-ligands: structural diversity, electrochemical and photocatalytic properties. *Dalton Trans.* **46** (2017) 1951–1964.
8. Xiao, Q.-Q.; Liu, D.; Wei, Y.-L.; Cui, G.-H.: A new multifunctional two-dimensional cobalt(II) metal–organic framework for electrochemical detection of hydrogen peroxide, luminescent sensing of metal ions, and photocatalysis. *Polyhedron* **158** (2019) 342–351.
9. Kazuhiro Uemura, K.; Yamasaki, Y.; Kita, H.; Ebihara, M.: Two-step adsorption on jungle-gym-type porous coordination polymers: dependence on hydrogen-bonding capability of adsorbates, ligand-substituent effect, and temperature. *Inorg. Chem.* **49** (2010) 10133–10143.
10. Luo, T.-J. M.; Palmore, G. T. R.: Engineering crystalline architecture with supramolecular tapes: studies on secondary donor-acceptor interactions in cocrystals of the cyclic dipeptide of glycine. *Mol. Cryst. Growth Des.* **2** (2002) 337–350.
11. Song, G.-L.; Liu, S.; Liu, H.-J.; Zeng, T.; Zhu, H.-J.: 2,5-Dibromoterephthalic acid dihydrate. *Acta Crystallogr. E* **64** (2008) o1860.