Crystal structure of 3,5-dichloro-2-hydroxy-benzoic acid, $C_6H_2Cl_2(OH)COOH$

Z.-W. Gao*, C.-Y. Zhang, L.-X. Gao, G.-F. Wang, D.-H. Wu and Z.-T. Liu

Shaanxi Normal University, School of Chemistry and Materials Science, Xian, Shaanxi, 710062 P. R. China

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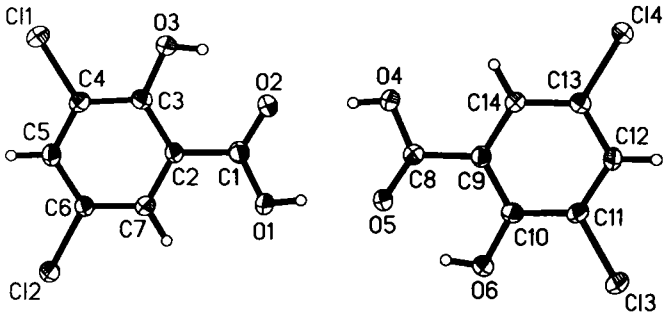

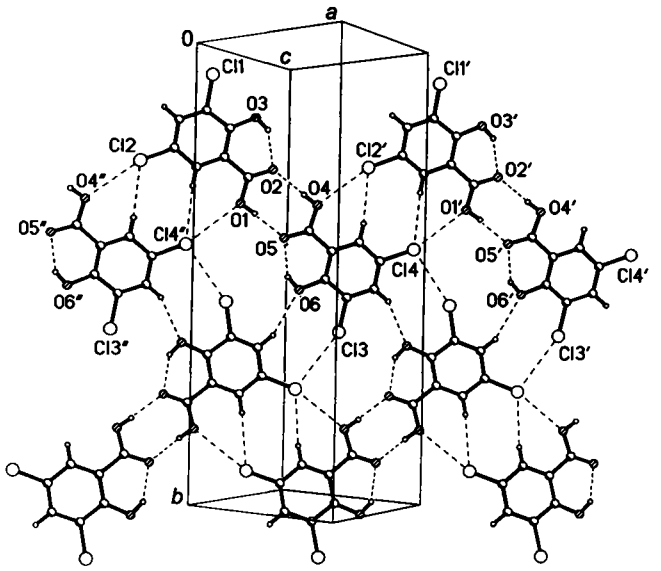

Abstract

$C_7H_4Cl_2O_3$, monoclinic, $P12_1/c1$ (no. 14), $a = 8.734(4)$ Å, $b = 21.63(1)$ Å, $c = 8.437(4)$ Å, $\beta = 100.927(8)°$, $V = 1565.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.117$, $T = 298$ K.

Source of material

The salicylic acid was slowly dissolved in glacial acetic acid. A current of chlorine was then passed through the solution for 8 h. The solid thus obtained was collected, washed and crystallized from glacial acetic acid [1], then recrystallized with dichloromethane-hexane. Colorless crystals of 3,5-dichlorosalicylic aid suitable for single-crystal X-ray diffraction were obtained at RT.

Experimental details

The structure contains a local pseudo-inversion center which is obviously connected with the pseudo-orthorhombic C cell with $a = 10.933$ Å, $b = 13.244$ Å, $c = 21.631$ Å, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 88°$.

* Correspondence author (e-mail: zwgao@snnu.edu.cn)

Discussion

The crystal structure of 3,5-dichlorosalicylic acid has two crystallographically independent molecules in the asymmetric unit, and their conformations are similar. Extensive hydrogen bonds exist in the crystal structure. Two intramolecular hydrogen bonds O3–H3···O2 (2.663(3) Å, 172°) and O6–H6···O5 (2.624(3) Å, 145°) comparable with [2,3] contribute to the formation of two six-membered rings of the molecule structures. Two stronger intermolecular O–H···O hydrogen bonds (O1–H1···O5($1-x,-y,-z$), 2.663(3) Å, 172° and O4–H4···O2($-1+x,½-y,-½+z$), 2.708(4) Å, 172 °) link the two molecules of the asymmetric unit to form a dimer. The C–H···X interactions (C7–H7···Cl4($x,½-y,½+z$), 3.730(3) Å, 175°; C14–H14···Cl2($1+x,½-y,½+z$), 3.702(3) Å, 162°; comparable to [2]) together with the subsystem of van der Waals interactions (Cl2···O4, 3.216(3) Å, 157(11)° and Cl4···O1, 3.224(3) Å, 162(10)°) link adjacent dimers to form one-dimensional zigzag ribbons. Further, a closer inspection of the molecular packing revealed that the crystal structure is stabilized by C–H···O hydrogen bonds (C5–H5···O6($x,½-y,-½+z$), 3.408(4) Å, 157°; C12–H12··· O3($1-x,-y,1-z$), 3.357(4) Å, 155°; and by X···X interactions comparable to [3,4], Cl1···Cl4 (3.477 Å, 105.2°) and Cl2···Cl3 (3.508 Å, 149.9°). An infinite two-dimensional network structure is formed by the above interactions. Adjacent layers are tied by aromatic π-π stacking stabilizing the three dimensional supramolecular structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.41 × 0.46 × 0.53 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.85 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8053, 2756
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2071
$N(param)_{refined}$:	217
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	−0.1865	0.6363	0.6402	0.078
H(3)	4e	−0.2477	0.8208	0.6060	0.078
H(4)	4e	0.5903	0.6796	0.4418	0.074
H(6)	4e	0.6920	0.4975	0.4461	0.073
H(5)	4e	0.2285	0.8669	1.0213	0.049
H(7)	4e	0.0966	0.6940	0.8917	0.046
H(12)	4e	0.2491	0.4477	−0.0060	0.047
H(14)	4e	0.3360	0.6201	0.1613	0.045

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4*e*	0.0039(1)	0.94113(3)	0.8340(1)	0.0570(5)	0.0312(4)	0.0765(6)	0.0016(3)	−0.0033(5)	0.0011(3)
Cl(2)	4*e*	0.3420(1)	0.74780(3)	1.1041(1)	0.0502(5)	0.0380(4)	0.0640(5)	−0.0021(3)	−0.0200(4)	0.0055(3)
Cl(3)	4*e*	0.4836(1)	0.37650(3)	0.18113(9)	0.0613(6)	0.0280(4)	0.0596(5)	0.0036(3)	−0.0031(4)	−0.0003(3)
Cl(4)	4*e*	0.1169(1)	0.56502(3)	−0.0782(1)	0.0602(5)	0.0379(4)	0.0668(6)	0.0032(4)	−0.0269(5)	−0.0009(3)
O(1)	4*e*	−0.1216(3)	0.65757(9)	0.6990(3)	0.052(1)	0.033(1)	0.061(1)	−0.0050(9)	−0.016(1)	−0.0047(9)
O(2)	4*e*	−0.2698(2)	0.73361(9)	0.5738(3)	0.042(1)	0.042(1)	0.057(1)	−0.0016(9)	−0.011(1)	−0.005(1)
O(3)	4*e*	−0.1933(2)	0.84822(9)	0.6545(3)	0.051(1)	0.037(1)	0.059(1)	0.0012(9)	−0.015(1)	0.0045(9)
O(4)	4*e*	0.5347(2)	0.65803(8)	0.3743(2)	0.054(1)	0.032(1)	0.052(1)	0.0025(9)	−0.012(1)	−0.0099(9)
O(5)	4*e*	0.6916(2)	0.58377(8)	0.4956(2)	0.045(1)	0.038(1)	0.045(1)	0.0000(9)	−0.010(1)	−0.0057(9)
O(6)	4*e*	0.6466(2)	0.46990(9)	0.3890(2)	0.051(1)	0.036(1)	0.050(1)	0.0028(9)	−0.015(1)	−0.0007(9)
C(1)	4*e*	−0.1561(3)	0.7157(1)	0.6742(4)	0.036(2)	0.041(2)	0.040(2)	−0.003(1)	0.004(2)	−0.003(1)
C(2)	4*e*	−0.0484(3)	0.7589(1)	0.7729(3)	0.035(2)	0.035(1)	0.034(2)	−0.002(1)	0.002(1)	−0.001(1)
C(3)	4*e*	−0.0728(3)	0.8229(1)	0.7562(3)	0.035(2)	0.037(1)	0.036(2)	0.000(1)	0.003(1)	0.003(1)
C(4)	4*e*	0.0327(3)	0.8621(1)	0.8525(3)	0.042(2)	0.030(1)	0.041(2)	−0.002(1)	0.006(1)	0.001(1)
C(5)	4*e*	0.1590(3)	0.8399(1)	0.9590(3)	0.039(2)	0.038(2)	0.041(2)	−0.007(1)	0.000(1)	−0.003(1)
C(6)	4*e*	0.1817(3)	0.7767(1)	0.9726(3)	0.036(2)	0.034(2)	0.040(2)	−0.004(1)	−0.002(1)	0.003(1)
C(7)	4*e*	0.0799(3)	0.7363(1)	0.8813(3)	0.040(2)	0.030(1)	0.042(2)	0.000(1)	0.002(1)	−0.002(1)
C(8)	4*e*	0.5808(3)	0.6006(1)	0.3915(3)	0.036(2)	0.033(2)	0.040(2)	0.002(1)	0.005(1)	−0.003(1)
C(9)	4*e*	0.4890(3)	0.5570(1)	0.2769(3)	0.038(2)	0.033(1)	0.032(2)	−0.003(1)	0.004(1)	−0.002(1)
C(10)	4*e*	0.5279(3)	0.4942(1)	0.2830(3)	0.038(2)	0.035(2)	0.033(2)	0.002(1)	0.004(1)	0.004(1)
C(11)	4*e*	0.4362(3)	0.4546(1)	0.1748(3)	0.043(2)	0.026(1)	0.040(2)	0.001(1)	0.006(1)	0.002(1)
C(12)	4*e*	0.3095(3)	0.4752(1)	0.0645(3)	0.043(2)	0.031(1)	0.040(2)	−0.007(1)	−0.002(1)	−0.005(1)
C(13)	4*e*	0.2740(4)	0.5374(1)	0.0606(3)	0.042(2)	0.035(2)	0.038(2)	0.000(1)	−0.003(1)	0.002(1)
C(14)	4*e*	0.3617(3)	0.5783(1)	0.1652(3)	0.040(2)	0.029(1)	0.042(2)	0.001(1)	−0.000(1)	−0.002(1)

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References

1. Datta, R. L.; Mitter, H. K.: Halogenation. XIX. The Replacement of Sulfonic Groups by Chlorine and the Preparation of Organic Chloro-Derivatives. J. Am. Chem. Soc. **41** (1919) 2028-2038.
2. Li, X.; Zou, Y.-Q.: Crystal structure of tetraaquabis(μ_4-fumarato)-μ_2-oxalatodiyttrium hydrate, $[Y_2(C_2O_4)(C_4H_2O_4)_2(H_2O)_4] \cdot H_2O$. Z. Kristallogr. NCS **220** (2005) 169-170.
3. Zaman, M. B.; Udachin, K. A.; Ripmeester, J. A.: Supramolecular Grid and Layer Architectures. Hydrogen Bonds and Halogen-Halogen Interactions Influenced by Bromo-, Chloro-, and Cyano-Substituted Anilic Acids. Cryst. Growth Des. **4** (2004) 586-589.
4. Boyle, P. D.; Davidson, S. E.; Godfrey, S. M.; Pritchard, R. G.: The structure of *N*-methylbenzothiazole-2-selone dichloride: a novel 'zipper' arrangement of *T*-shaped molecules linked via intermolecular Cl-Cl contacts. Inorg. Chim. Acta **325** (2001) 211-214.
5. Janiak, C.: A critical account on π-π stacking in metal complexes with aromatic nitrogen-containing ligands. J. Chem. Soc., Dalton Trans. (2000) 3885-3896.
6. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.