3,6-Dichlorobenzene-1,2,4,5-tetraol

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Abstract: The X-ray structure of the title compound as the monohydrate has been determined and shows a complex structure with two independent molecules each of the compound and water and eleven distinct hydrogen bonding interactions. Its melting point has also been recorded for the first time.

Keywords: X-ray structure; hydrogen bonding; melting point

1. Introduction

The title compound 1 was first reported in 1868 when it was prepared by reduction of the corresponding quinone, chloranilic acid 2, itself readily available by treatment of chloranil 3 with potassium hydroxide (Scheme 1) [1].

![Scheme 1. Synthesis of compound 1 from 3 via 2 [1].](https://doi.org/10.3390/m14151334)

Since then, the compound has been little studied, although it was used to prepare the corresponding tetrakis(2,2-dichloropropionate ester) patented as a herbicide, fungicide and insecticide in 1957 [2]. An early polarographic study on the reaction of 1 with germanic acid (Ge(OH)₄) [3] was followed by careful kinetic studies on its formation from 2 in aqueous solutions of low-valent metal salts including salts of Ge(II), Sn(II) and In(I) [4], Ti(II) [5], and Ti(III) [6]. More recently, compound 1 has been used as a convenient source of chloranilate, the tetradentate dianian of 2, for the formation of a wide range of metal complexes. In these studies, a solution of compound 1 is simply allowed to undergo air oxidation in the presence of appropriate metals salts, and examples include binuclear complexes of Ga(III) and/or Cr(III) [7], and coordination polymers involving Mn(II) [8], lanthanide(III) complexes [9], zinc and iron complexes with large pore size of interest for gas absorption [10], and similar macrocyclic iron, manganese and cadmium complexes of interest for their magnetic and other properties [11,12].

Although X-ray diffraction has been used to study many of the metal complexes involving 2 and also a wide range of donor–acceptor complexes, particularly between 2 and basic nitrogen-containing heterocycles with over 80 structures in the Cambridge Structural Database as of July 2022, these inevitably involve either anions of 2 where the protons are completely removed or complexes where the protons in 2 are involved in hydrogen bonding with the basic donor. Interesting patterns of hydrogen bonding inherent to compound 2 have however been revealed in recent X-ray studies both of anhydrous 2 [13,14] and...
its dihydrate [15,16]. By way of contrast, the only reported X-ray structure containing a molecule of 1 is the tetrathiophenalene complex of formula (TTF)2 (22-) (I) formed in 20% yield by the reaction of 2 with TTF in acetonitrile [17]. In this paper, we report the X-ray structure of 3,6-dichlorobenzene-1,2,4,5-tetraol 1 as a monohydrate.

2. Results

Compound 1 was prepared as previously described [1,11], by the reduction of 2 with tin in hydrochloric acid, and was obtained directly as colourless needles suitable for X-ray diffraction. Its 13C NMR spectrum in d6-acetone showed two signals at δ 135.8 (C–OH) and 109.0 (C–Cl) in agreement with literature data [11]. Rather remarkably for a crystalline compound known for over 150 years, we have been unable to find any record of its melting point and so have determined this as 55–57 °C. It should be noted that compound 1 is highly sensitive towards air oxidation.

In the X-ray structure, the unit cell contained two closely similar molecules and two molecules of water (Supplementary Materials, Figure 1). The bond lengths and angles are unremarkable and show good agreement with those observed in the TTF complex [17].

![Figure 1. Structure of the four independent molecules showing numbering (thermal ellipsoids at 50% level).](image)

A view of the four independent molecules along the a axis shows that they are all connected together by hydrogen bonding in an 11-membered ring, R4,4(11) in terms of the Etter–Bernstein [18] graph set description (Figure 2 (Left)). Within this portion of the structure, we can see that water O(21) acts as both a donor and acceptor, while water O(22) is a two-fold hydrogen bond acceptor. However, considering the whole structure gives a considerably more complex picture with no fewer than eleven separate hydrogen-bonding interactions (Figure 2 (Right), Table 1). By considering the whole structure, it can be seen that water O(21) is involved in two donor and one acceptor interactions, while water O(22) has both two donor and two acceptor interactions, one of the latter with water O(21) as donor.

In order to better understand the arrangement of the molecules of 1, it is helpful to remove the water molecules, and the remaining structure of just the tetraol molecules shows a regular two-dimensional network in which each molecule of type 1 is surrounded by and hydrogen bonded to four of type 2 and vice versa (Figure 3). The apparent 20-membered ring cavities bounded only by OH groups, either O(5,6,12,13) or O(2,3,15,16) are those that are filled with two water molecules each, as shown in Figure 2, while the centre of the chlorine-containing rings involving O(2,16,6,12) or O(3,15,5,13) is essentially filled by the chlorine atoms. These are 24-membered rings, R4,4(24) in terms of the Etter–Bernstein [18] graph set description, each made up of two seven-atom bis(donors) and two five-atom bis(acceptors).
Table 1. Hydrogen bonding parameters for 1 (Å, °).

| D—H . . . A | D—H  | H . . . A | D . . . A | D—H . . . A |
|-------------|-------|-----------|-----------|-------------|
| O(2)—H(2) . . . O(16) | 0.977(16) | 2.02(3) | 2.675(2) | 122(3) |
| O(3)—H(3) . . . O(22) | 0.98(2) | 1.71(2) | 2.684(2) | 176(3) |
| O(5)—H(5) . . . O(21) | 0.98(2) | 1.73(2) | 2.695(2) | 166(3) |
| O(6)—H(6) . . . O(12) | 0.977(14) | 2.027(19) | 2.886(2) | 146(2) |
| O(13)—H(13) . . . O(5) | 0.98(2) | 2.01(4) | 2.697(2) | 126(3) |
| O(15)—H(15) . . . O(3) | 0.98(2) | 1.86(2) | 2.787(2) | 158(3) |
| O(16)—H(16) . . . O(21) | 0.98(3) | 1.70(3) | 2.659(3) | 165(3) |
| O(21)—H(21A) . . . O(22) | 0.979(18) | 1.757(18) | 2.734(2) | 175(2) |
| O(21)—H(21B) . . . O(6) | 0.98(2) | 1.89(3) | 2.868(2) | 174(2) |
| O(22)—H(22A) . . . O(13) | 0.98(2) | 1.83(3) | 2.772(3) | 160(3) |
| O(22)—H(22B) . . . O(2) | 0.98(2) | 1.83(2) | 2.799(2) | 171(3) |

In summary, the X-ray crystal structure of the title compound shows a complex two-dimensional network of aromatic tetraol molecules joined by hydrogen bonding with two repeating large-ring structures: a 20-membered ring filled with two water molecules to which there is additional hydrogen bonding and a 24-membered ring filled by four inward-pointing chlorine atoms.

3. Experimental Section

Melting points were recorded on a Reichert hot-stage microscope (Reichert, Vienna, Austria) and are uncorrected. NMR spectra were obtained for $^{13}$C at 75 MHz using a Bruker AV300 instrument (Bruker, Billerica, MA, USA). Spectra were run at 25 °C on solutions in...
CD$_3$COCD$_3$ with the solvent signal as the reference. Chemical shifts are reported in ppm to high frequency of Me$_2$Si.

3,6-Dichlorobenzene-1,2,4,5-tetral (1)

A suspension of chloranilic acid 2 (2.0 g, 9.57 mmol) in concentrated HCl (50 mL) was heated to 100 °C with vigorous stirring. Tin flakes (1.36 g, 11.48 mmol) were added portionwise over 5 min to the red-orange suspension, causing gas evolution. Over a period of 10 min, the red-orange colour bleached out, and the reaction solution became clear and colourless. The hot reaction mixture was removed from the heat and immediately filtered hot through a sintered glass funnel to remove the unreacted tin. The clear filtrate was transferred into a conical flask with a septum and purged with N$_2$ gas, and then cooled down to 4 °C. The product crystallised as long colourless needles, which were isolated by suction filtration, washed with ice-cold water (3 × 50 mL) and dried in vacuo to afford the product 1 (1.23 g, 61%). Mp 55–57 °C; $^{13}$C NMR (126 MHz, CD$_3$COCD$_3$) δ 135.8 (4C, C–OH), 109.0 (2C, C–Cl).

Crystal data for C$_8$H$_4$Cl$_2$O$_5$, $M = 229.02$ g mol$^{-1}$, colourless needle, crystal dimensions 0.10 × 0.01 × 0.01 mm, triclinic, space group P–1 (No. 2), $a = 7.5016(8)$, $b = 9.4933(11)$, $c = 11.6530(11)$ Å, $\alpha = 95.102(9)$, $\beta = 100.354(8)$, $\gamma = 103.689(9)^\circ$, $V = 785.63(15)$ Å$^3$, $Z = 4$, $D_{calc} = 1.936$ g cm$^{-3}$, $T = 93$ K, $R_1 = 0.042$, $R_{W2} = 0.129$ for 2556 reflections with $I > 2\sigma(I)$, and 283 variables. Data were collected using graphite monochromated Mo Kα radiation $\lambda = 0.71073$ Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2169372. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures. The structure was solved by direct methods and refined by full-matrix least-squares against F$^2$ (SHELXL, Version 2018/3 [19]).

Supplementary Materials: The following is available online, cif and check-cif files for 1.

Author Contributions: N.S. prepared the compound; A.M.Z.S. collected the X-ray data and solved the structure; R.A.A. designed the study, analysed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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