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The crystal structure of 4-chloro-thiophenol, C_6H_5ClS

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Abstract

C_6H_5ClS , monoclinic, $P2_1/n$ (no. 14), $a = 5.7461(2)$ Å, $b = 9.7601(4)$ Å, $c = 5.7466(3)$ Å, $\beta = 95.869(2)^\circ$, $V = 320.59(2)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0216$, $wR_{ref}(F^2) = 0.0545$, $T = 200$ K.

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The molecular structure 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

The compound was obtained commercially (Fluka). Crystals suitable for the diffraction study were obtained upon repeated slow sublimation and resublimation of the compound in a closed vessel kept at room temperature.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.55 \times 0.33 \times 0.16$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.80 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2752, 795, 0.012
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 740
$N(\text{param})_{\text{refined}}$:	54
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

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	0.37593 (19)	0.59088 (10)	0.62410 (19)	0.0267 (2)
C2	0.28114 (19)	0.54565 (11)	0.40579 (19)	0.0292 (3)
H2	0.134751	0.576427	0.343306	0.035*
C3	0.40571 (19)	0.45433 (11)	0.28115 (19)	0.0291 (3)
H3	0.343171	0.423547	0.134799	0.035*
Cl1 ^a	0.2180 (4)	0.7058 (2)	0.7821 (3)	0.0273 (5)
S1 ^a	0.2173 (7)	0.7058 (4)	0.7826 (6)	0.0556 (13)
H1A ^b	0.354 (12)	0.724 (6)	0.942 (12)	0.037 (15)*
H1B ^b	0.044 (11)	0.716 (6)	0.661 (11)	0.030 (14)*

^aOccupancy: 0.5, ^bOccupancy: 0.25.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

The sulfur-bound H atom was located on a difference Fourier map and refined freely. It shows orientational disorder over two positions.

The molecule shows pseudo-centrosymmetry due to the almost identical number of electrons for sulfur and chlorine.

Comment

While phenol and its core-substituted derivatives as well as the pertaining deprotonated species have received considerable

attention as ligands in main group and transition metal chemistry and found to exhibit a variety of coordination modes (e.g., monodentate towards tin [7], bidentate towards tantalum [8], bridging tridentate towards zinc [9, 10] and bridging tetradentate towards sodium [11]) considerable less information is at hand for comparable thiophenols. It is especially surprising to find that structural information about the simplest thiophenol derivatives is scant and limited to, e.g., thiophenol as such [12] as well as the 4-methyl-substituted [13] and perchlorinated derivatives [14]. In continuation of our interest in halogenated derivatives of phenols and thiophenols [15, 16] we determined the molecular and crystal structure of the title compound.

The title compound is the *para*-chlorinated derivative of thiophenol. Due to the similarity in the number of electrons for the two heteroatoms, the molecule shows pseudo-centrosymmetry with the chlorine and sulfur atom sites being superimposed. The C–S bond length of 1.758(4) Å as well as the C–Cl bond length of 1.753(2) Å are in very good agreement with the values reported for the corresponding bonds in the Cambridge Structural Database [17] for two other thiophenol derivatives featuring this bonding pattern [18, 19]. The C–C–C angles cover a narrow range of 119.69(10)–120.61(10)° only. The hydrogen atom of the thiol group shows orientational disorder over two positions.

In the crystal, hydrogen bonds supported by the thiol group can be observed. The superposition of the two heteroatoms on grounds of the pseudo-centrosymmetric nature of the title compound as well as the orientational disorder of the sulfur-bound hydrogen atom allows for the interpretation of these hydrogen bonds of being either of the S–H⋯Cl type or the cooperative S–H⋯S type. While both interpretations see the molecules connected to infinite chains along [1 0 1], a graph-set analysis [20, 21] would require a C₁(2) descriptor at the unitary level in case of the cooperative interpretation and a C₁(7) descriptor at the unitary level in case of the chlorine atom acting as acceptor.

While one could discuss the presence of dispersive interactions between the halogen atom and the aromatic system, π -stacking is not a prominent feature in the crystal structure of the title compound.

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