Kina Muller, Eric C. Hosten and Richard Betz*

The crystal structure of 4-hydroxybenzene-1,3-diaminium dichloride, $C_6H_{10}Cl_2N_2O$

Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	$0.52 \times 0.19 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.71 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7218, 2091, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2025
$N(\text{param})_{\text{refined}}$:	104
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

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Abstract

$C_6H_{10}Cl_2N_2O$, triclinic, $P\bar{1}$ (no. 2), $a = 4.8274(4)$ Å, $b = 8.0556(7)$ Å, $c = 12.0648(10)$ Å, $\alpha = 71.237(4)^\circ$, $\beta = 78.739(4)^\circ$, $\gamma = 72.950(4)^\circ$, $V = 422.06(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0225$, $wR_{\text{ref}}(F^2) = 0.0614$, $T = 190$ 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 (Merck). Crystals were taken directly from the provided product.

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South) University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za.
<https://orcid.org/0000-0002-5730-2152>

Kina Muller and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South) University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa.
<https://orcid.org/0000-0003-4173-2550> (E.C. Hosten)

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.36516 (9)	0.80272 (5)	0.40539 (3)	0.02232 (10)
Cl2	0.79378 (8)	0.87456 (5)	0.90263 (3)	0.02083 (9)
O1	0.2879 (3)	0.81061 (16)	0.71567 (10)	0.0231 (2)
H1	0.149226	0.816630	0.769655	0.035*
N1	0.7883 (3)	0.78913 (17)	0.57529 (11)	0.0193 (3)
H1A	0.975252	0.769081	0.540352	0.029*
H1B	0.743485	0.891981	0.598160	0.029*
H1C	0.665146	0.801648	0.523216	0.029*
N2	1.1613 (3)	0.17191 (17)	0.82886 (11)	0.0192 (3)
H2A	1.309917	0.173963	0.769399	0.029*
H2B	1.083291	0.077823	0.837510	0.029*
H2C	1.230354	0.158224	0.897076	0.029*
C1	0.4947 (3)	0.6551 (2)	0.75050 (13)	0.0171 (3)
C2	0.7577 (3)	0.6362 (2)	0.67816 (12)	0.0160 (3)
C3	0.9794 (3)	0.4806 (2)	0.70059 (13)	0.0163 (3)
H3	1.155594	0.468649	0.649111	0.020*
C4	0.9365 (3)	0.3419 (2)	0.80084 (12)	0.0162 (3)
C5	0.6817 (4)	0.3589 (2)	0.87694 (13)	0.0188 (3)
H5	0.659323	0.263498	0.946316	0.023*
C6	0.4599 (3)	0.5149 (2)	0.85182 (13)	0.0188 (3)
H6	0.284057	0.526528	0.903527	0.023*

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 H atoms of the ammonium groups were allowed to rotate with a fixed angle around the N–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program [3]), with $U(\text{H})$ set to $1.5U_{\text{eq}}(\text{N})$. The H atom of the hydroxyl groups was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program [3]), with $U(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$. The compound was refined as a twin with a ratio of 83.2:16.8 (Twin law: 1 0 0 1 –1 0 1 0 –1).

Comment

The effect of size and steric pretense of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades. Among the many effects that can be attributed to the spatial requirements of counterions have been the glass transition temperature in ionomers [7], surfactant modifying properties [8], the charge transfer in radical ions [9] and polymer-modified electrodes [10] as well as the structural and vibrational spectroscopic behaviour of DNA building blocks [11]. Furthermore, the benefit of choosing the adequate size of counterions to crystallize ionic compounds has been confirmed on many occasions [12]. In continuation of our interest in metrical features of large cations [13–15] the title structure has been determined. Furthermore, the molecular and crystal structure of meta-phenylene diamine has been determined earlier [16].

The structure shows the presence of a hydroxy-substituted meta-phenylenediamine with the latter being present as its diammonium cation. The charge is counterbalanced by two chloride ions. C–N bond lengths are found at 1.4598(18) Å and 1.4634(19) Å which is in good agreement with other anilinium derivatives deposited with the Cambridge Structural Database [17]. Intracyclic C–C–C angles cover a range of 118.75(14)–122.22(13)° with the largest angle found on the ammonium-group bearing carbon atom in ortho position to the hydroxyl group and the smallest angle present on the carbon atom in between the two ammonium-group bearing carbon atom. The molecule is essentially planar with the least-squares plane as defined by all non-hydrogen atoms showing the largest deviation for the oxygen atom with only –0.057(1) Å.

In the crystal, classical hydrogen bonds of the O–H...Cl and the N–H...Cl type are observed next to C–H...Cl contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. The classical hydrogen bonds involve all hydrogen

atoms bonded to the heteroatoms as donors and both chloride anions as acceptors. In terms of graph-set analysis [18], the descriptor for these contacts is DDDDDDD on the unary level. The C–H...Cl contacts are supported by both C–H groups and employ the two different chloride anions present in the asymmetric unit as acceptors. Their graph-set descriptor on the unary level is determined as DD. In total, the entities of the crystal structure are connected to a three-dimensional network.

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