

## 5-Carboxy-2,4-dihydroxyanilinium chloride dihydrate

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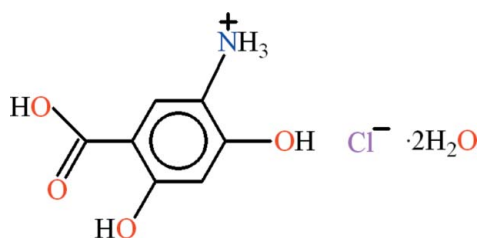
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.115; data-to-parameter ratio = 18.3.

In the title compound,  $\text{C}_7\text{H}_8\text{NO}_4^+\cdot\text{Cl}^-\cdot 2\text{H}_2\text{O}$ , the organic molecule is almost planar with an r.m.s. deviation of 0.0164 Å for all non-H atoms. An  $S(6)$  ring motif is formed due to an intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond. In the crystal, the molecules are linked into a three-dimensional network by  $\text{N}-\text{H}\cdots\text{Cl}$ ,  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{O}-\text{H}\cdots\text{Cl}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds.

### Related literature

For a related structure, see: Naz *et al.* (2010). For graph-set notation, see: Bernstein *et al.* (1995).



### Experimental

#### Crystal data

$\text{C}_7\text{H}_8\text{NO}_4^+\cdot\text{Cl}^-\cdot 2\text{H}_2\text{O}$

$M_r = 241.63$

Triclinic,  $P\bar{1}$

$a = 6.0285$  (8) Å

$b = 7.9597$  (8) Å

$c = 10.9570$  (13) Å

$\alpha = 100.135$  (5)°

$\beta = 97.162$  (4)°

$\gamma = 92.921$  (5)°

$V = 512.10$  (11) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 0.38$  mm<sup>-1</sup>

$T = 296$  K

$0.28 \times 0.15 \times 0.10$  mm

#### Data collection

Bruker Kappa APEXII CCD diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.935$ ,  $T_{\max} = 0.965$

8850 measured reflections

2548 independent reflections

1853 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.115$

$S = 1.03$

2548 reflections

139 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O6}$	0.82	1.88	2.6945 (19)	171
$\text{O3}-\text{H3}\cdots\text{O2}$	0.82	1.96	2.672 (2)	145
$\text{O4}-\text{H4A}\cdots\text{Cl1}^{\text{i}}$	0.82	2.21	3.0097 (15)	164
$\text{N1}-\text{H1A}\cdots\text{O6}^{\text{ii}}$	0.89	2.02	2.903 (2)	169
$\text{N1}-\text{H1B}\cdots\text{O5}^{\text{iii}}$	0.89	1.96	2.853 (2)	178
$\text{N1}-\text{H1C}\cdots\text{Cl1}^{\text{iv}}$	0.89	2.35	3.1950 (18)	157
$\text{O5}-\text{H5A}\cdots\text{O2}^{\text{v}}$	0.86	2.16	2.935 (2)	149
$\text{O5}-\text{H5B}\cdots\text{Cl1}$	0.85	2.41	3.1494 (15)	146
$\text{O6}-\text{H6A}\cdots\text{Cl1}$	0.88	2.27	3.1386 (16)	174
$\text{O6}-\text{H6B}\cdots\text{O5}^{\text{vi}}$	0.86	1.99	2.850 (2)	173

Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $x - 1, y, z + 1$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $x + 1, y, z$ ; (vi)  $-x + 1, -y, -z$ .

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2650).

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## supporting information

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## 5-Carboxy-2,4-dihydroxyanilinium chloride dihydrate

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### S1. Comment

Recently we have reported the crystal structure of 5-carboxy-2,4-dihydroxyanilinium chloride (Naz *et al.*, 2010). The title compound (I, Fig. 1) has been prepared in a slightly different way.

In (I), the organic group (C1—C7/O1—O4/N1) is planar with r. m. s. deviation of 0.0164 Å. In the organic part, there exist a strong intramolecular H-bond of O—H $\cdots$ O type (Table 1, Fig. 1) completing an S(6) ring motif (Bernstein *et al.*, 1995). In the title compound, the Cl<sup>-</sup> anion is penta coordinated due to H-bondings of N—H $\cdots$ Cl and O—H $\cdots$ Cl types (Table 1, Fig. 2). The NH<sub>3</sub><sup>+</sup> ion makes H-bonding with the both water molecules and the Cl<sup>-</sup> ion. Due to these strong H-bondings the molecules are stabilized in the form of three-dimensional polymeric network (Table 1, Fig. 2). There does not exist any  $\pi\cdots\pi$  or C—H $\cdots\pi$  interaction.

### S2. Experimental

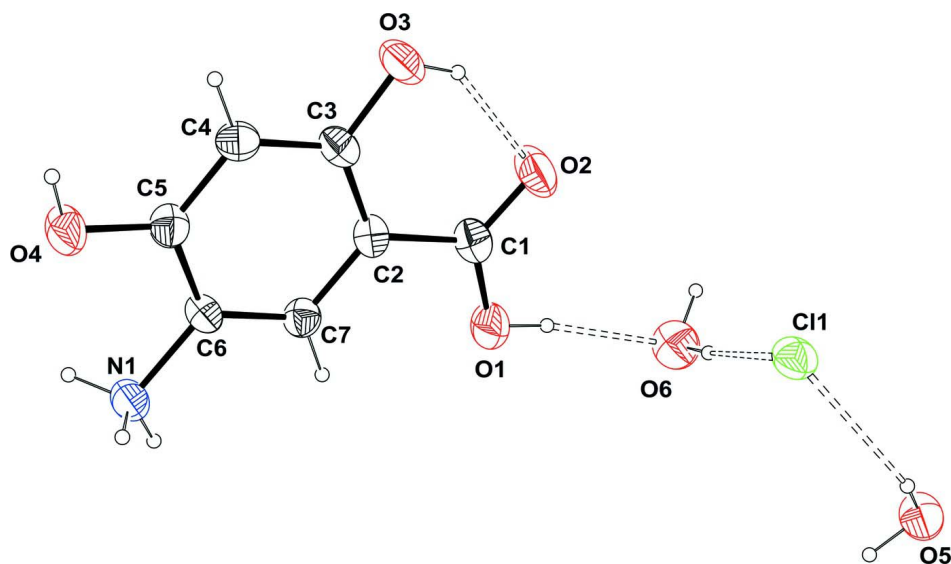
Concentrated nitric acid (2 mL, 67%) was added drop by drop to  $\beta$ -resorcylic acid (1 g, 97%, 6.3 mmol) in a round bottom flask. The mixture was protected from moisture by CaCl<sub>2</sub> (anhydrous) tube and was allowed to stand for 12 h at room temperature. Then reaction mixture was diluted with water. The crude material was filtered and recrystallized from water to afford the 5-nitro- $\beta$ -resorcylic acid.

Then a mixture of 5-nitro- $\beta$ -resorcylic acid (1.5 g, 7.5 mmol), tin (3 g, 25 mmol) and absolute ethanol (5 ml) were taken in a 100 ml round bottom flask and passed HCl gas under reflux with stirring for 1 h. The completion of reaction was monitored by TLC. The reaction mixture was filtered to remove any unreacted tin. Filtrate was kept for seven days to afford light brown needles of (I).

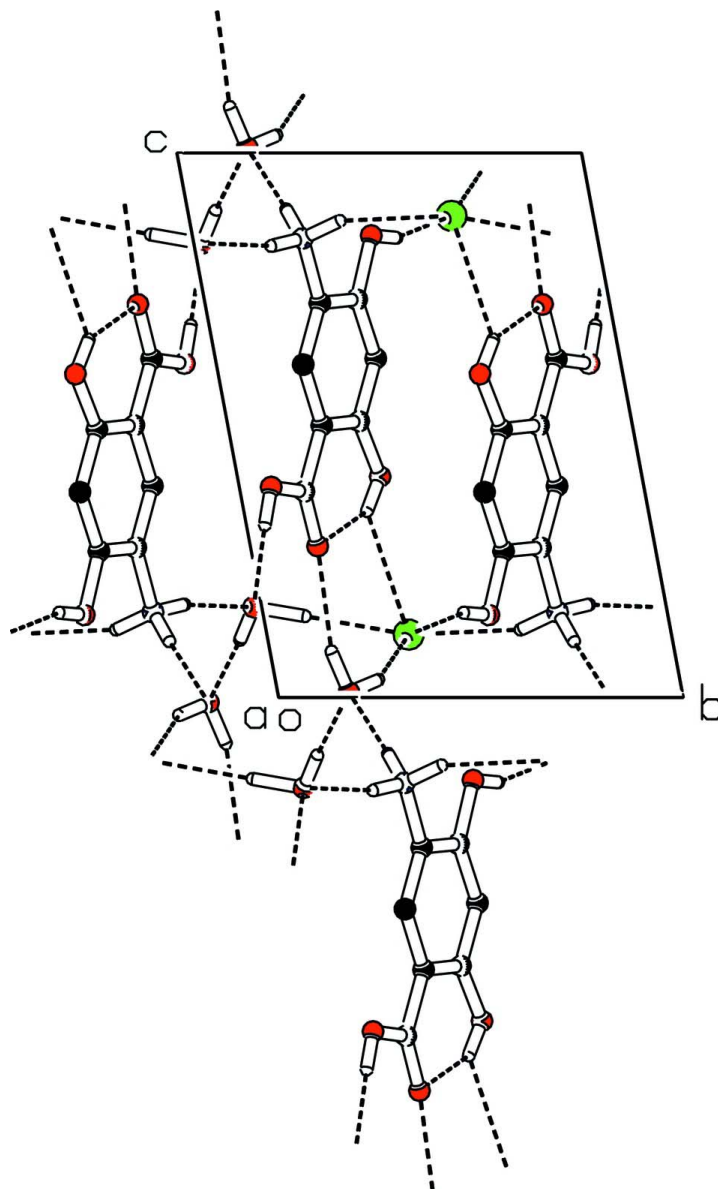
### S3. Refinement

All H atoms attached to C atoms, N atom and hydroxyl O atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (C), N—H = 0.89 Å and

O—H = 0.82 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$ . H atoms of water molecules were located in difference Fourier maps and included in the subsequent refinement using restraints (O—H = 0.85 (1) Å and H $\cdots$ H = 1.40 (2) Å) with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . In the last cycles of refinement, they were treated as riding on their parent O atoms.

**Figure 1**

View of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary radii. The dotted line represents the intramolecular H-bonding.



**Figure 2**

The partial packing (*PLATON*; Spek, 2009) which shows that molecules form various ring motifs and molecules are interlinked through H-bondings to form three dimensional polymeric network.

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#### Crystal data

$C_7H_8NO_4^+ \cdot Cl^- \cdot 2H_2O$

$M_r = 241.63$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 6.0285\ (8)\ \text{\AA}$

$b = 7.9597\ (8)\ \text{\AA}$

$c = 10.9570\ (13)\ \text{\AA}$

$\alpha = 100.135\ (5)^\circ$

$\beta = 97.162\ (4)^\circ$

$\gamma = 92.921\ (5)^\circ$

$V = 512.10\ (11)\ \text{\AA}^3$

$Z = 2$

$F(000) = 252$

$D_x = 1.567\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1853 reflections

$\theta = 1.9\text{--}28.4^\circ$

$\mu = 0.38\ \text{mm}^{-1}$

$T = 296$  K  $0.28 \times 0.15 \times 0.10$  mm  
 Needle, brown

*Data collection*

Bruker Kappa APEXII CCD diffractometer	8850 measured reflections
Radiation source: fine-focus sealed tube	2548 independent reflections
Graphite monochromator	1853 reflections with $I > 2\sigma(I)$
Detector resolution: $7.50$ pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.039$
$\omega$ scans	$\theta_{\text{max}} = 28.4^\circ$ , $\theta_{\text{min}} = 1.9^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.935$ , $T_{\text{max}} = 0.965$	$k = -10 \rightarrow 8$
	$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.0225P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2548 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
139 parameters	$\Delta\rho_{\text{max}} = 0.40 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2807 (3)	0.0789 (2)	0.38672 (13)	0.0395 (4)
H1	0.3127	0.0453	0.3164	0.059*
O2	-0.0155 (3)	0.1663 (2)	0.27792 (13)	0.0454 (4)
O3	-0.2957 (3)	0.35281 (19)	0.40596 (13)	0.0401 (4)
H3	-0.2501	0.3044	0.3424	0.060*
O4	-0.1327 (3)	0.4424 (2)	0.84841 (13)	0.0415 (4)
H4A	-0.2380	0.5033	0.8442	0.062*
N1	0.2345 (3)	0.2711 (2)	0.84317 (14)	0.0306 (4)
H1A	0.3302	0.1906	0.8294	0.046*
H1B	0.1449	0.2439	0.8965	0.046*
H1C	0.3104	0.3712	0.8755	0.046*
C1	0.0937 (4)	0.1574 (2)	0.37826 (18)	0.0303 (5)
C2	0.0302 (3)	0.2322 (2)	0.50004 (17)	0.0268 (4)
C3	-0.1622 (4)	0.3252 (2)	0.50731 (18)	0.0284 (4)

C4	-0.2215 (3)	0.3963 (2)	0.62285 (18)	0.0303 (5)
H4	-0.3489	0.4570	0.6270	0.036*
C5	-0.0912 (3)	0.3766 (2)	0.73114 (18)	0.0286 (5)
C6	0.0990 (3)	0.2839 (2)	0.72445 (17)	0.0248 (4)
C7	0.1595 (3)	0.2145 (2)	0.61147 (17)	0.0259 (4)
H7	0.2879	0.1547	0.6086	0.031*
O5	0.9425 (3)	0.17641 (17)	0.00957 (13)	0.0372 (4)
H5A	0.9959	0.1488	0.0794	0.056*
H5B	0.8641	0.2602	0.0303	0.056*
O6	0.4319 (3)	-0.02049 (19)	0.16590 (14)	0.0427 (4)
H6A	0.4697	0.0818	0.1525	0.064*
H6B	0.3236	-0.0641	0.1078	0.064*
Cl1	0.53107 (9)	0.35035 (6)	0.11554 (5)	0.03442 (17)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0407 (10)	0.0515 (9)	0.0269 (8)	0.0127 (7)	0.0097 (7)	0.0025 (7)
O2	0.0577 (11)	0.0566 (10)	0.0220 (8)	0.0189 (8)	0.0017 (7)	0.0056 (7)
O3	0.0422 (10)	0.0517 (9)	0.0257 (8)	0.0121 (7)	-0.0042 (7)	0.0093 (7)
O4	0.0478 (10)	0.0534 (10)	0.0251 (8)	0.0274 (8)	0.0074 (7)	0.0035 (7)
N1	0.0326 (10)	0.0357 (9)	0.0231 (9)	0.0089 (7)	0.0018 (7)	0.0043 (7)
C1	0.0377 (13)	0.0276 (10)	0.0255 (11)	0.0000 (9)	0.0033 (9)	0.0058 (8)
C2	0.0325 (12)	0.0258 (9)	0.0229 (10)	0.0025 (8)	0.0059 (9)	0.0050 (8)
C3	0.0319 (12)	0.0284 (10)	0.0246 (11)	0.0018 (8)	-0.0012 (9)	0.0081 (8)
C4	0.0282 (11)	0.0322 (10)	0.0323 (12)	0.0097 (8)	0.0035 (9)	0.0086 (9)
C5	0.0327 (12)	0.0271 (10)	0.0271 (11)	0.0052 (8)	0.0059 (9)	0.0062 (8)
C6	0.0289 (11)	0.0242 (9)	0.0205 (10)	0.0036 (8)	0.0000 (8)	0.0038 (8)
C7	0.0272 (11)	0.0251 (9)	0.0261 (11)	0.0037 (8)	0.0049 (8)	0.0047 (8)
O5	0.0415 (9)	0.0386 (8)	0.0343 (8)	0.0153 (7)	0.0085 (7)	0.0085 (7)
O6	0.0468 (10)	0.0400 (8)	0.0408 (9)	0.0073 (7)	0.0065 (8)	0.0045 (7)
Cl1	0.0335 (3)	0.0385 (3)	0.0323 (3)	0.0111 (2)	0.0022 (2)	0.0086 (2)

*Geometric parameters (Å, °)*

O1—C1	1.317 (2)	C2—C7	1.397 (3)
O1—H1	0.8200	C2—C3	1.410 (3)
O2—C1	1.225 (2)	C3—C4	1.390 (3)
O3—C3	1.346 (2)	C4—C5	1.376 (3)
O3—H3	0.8199	C4—H4	0.9300
O4—C5	1.358 (2)	C5—C6	1.397 (3)
O4—H4A	0.8200	C6—C7	1.365 (3)
N1—C6	1.470 (2)	C7—H7	0.9300
N1—H1A	0.8900	O5—H5A	0.8616
N1—H1B	0.8900	O5—H5B	0.8517
N1—H1C	0.8900	O6—H6A	0.8764
C1—C2	1.467 (3)	O6—H6B	0.8647

C1—O1—H1	109.5	O3—C3—C2	123.24 (18)
C3—O3—H3	109.5	C4—C3—C2	120.50 (18)
C5—O4—H4A	109.5	C5—C4—C3	119.87 (18)
C6—N1—H1A	109.5	C5—C4—H4	120.1
C6—N1—H1B	109.5	C3—C4—H4	120.1
H1A—N1—H1B	109.5	O4—C5—C4	124.58 (17)
C6—N1—H1C	109.5	O4—C5—C6	115.57 (17)
H1A—N1—H1C	109.5	C4—C5—C6	119.85 (18)
H1B—N1—H1C	109.5	C7—C6—C5	120.75 (18)
O2—C1—O1	122.79 (18)	C7—C6—N1	121.88 (16)
O2—C1—C2	123.65 (19)	C5—C6—N1	117.31 (16)
O1—C1—C2	113.56 (17)	C6—C7—C2	120.62 (17)
C7—C2—C3	118.40 (17)	C6—C7—H7	119.7
C7—C2—C1	120.94 (18)	C2—C7—H7	119.7
C3—C2—C1	120.67 (18)	H5A—O5—H5B	104.7
O3—C3—C4	116.25 (17)	H6A—O6—H6B	106.8

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
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N1—H1C $\cdots$ C11 <sup>iv</sup>	0.89	2.35	3.1950 (18)	157
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