

## Hydrogen-bonded network in the trichloroacetate salts of 2-amino-5-chloropyridinium and 2-methyl-5-nitroanilinium monohydrate

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Received 23 April 2009

Accepted 5 June 2009

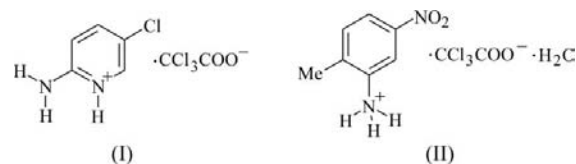
Online 13 June 2009

In the crystal structures of 2-amino-5-chloropyridinium trichloroacetate,  $C_5H_6ClN_2^+ \cdot C_2Cl_3O_2^-$ , (I), and 2-methyl-5-nitroanilinium trichloroacetate monohydrate,  $C_7H_9N_2O_2^+ \cdot C_2Cl_3O_2^- \cdot H_2O$ , (II), the protonated planar 2-amino-5-chloropyridinium [in (I)] and 2-methyl-5-nitroanilinium [in (II)] cations interact with the oppositely charged trichloroacetate anions to form hydrogen-bonded one-dimensional chains in (I) and, together with water molecules, a three-dimensional network in (II). The crystals of (I) exhibit nonlinear optical properties. The second harmonic generation efficiency in relation to potassium dihydrogen phosphate is 0.77. This work demonstrates the usefulness of trichloroacetic acid in crystal engineering for obtaining new materials for nonlinear optics.

### Comment

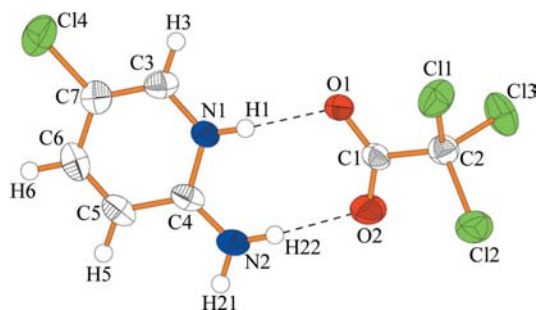
The hybrid crystals of base–acid interactions are potentially good materials for exhibiting nonlinear optical properties (Chemla & Zyss, 1987; Marchewka *et al.*, 2003). In these materials, the anion is responsible for favourable chemical and mechanical properties as a result of directional and relatively strong hydrogen-bond interactions, while the organic base, owing to its relatively high hyperpolarizability, is mainly responsible for the nonlinear optical properties (Bhattacharya *et al.*, 1994; Blagden & Seddon, 1999; Głowiak *et al.*, 2001). Continuing our studies on the characterization of acid–base hybrid crystals exhibiting nonlinear properties, as well as hydrogen-bond interactions and molecular recognition in the solid-state (Janczak & Perpétuo, 2007; Perpétuo & Janczak, 2007), in the present work we investigate the solid-state structures of two salts, namely 2-amino-5-chloropyridinium trichloroacetate, (I), and 2-methyl-5-nitroanilinium trichloroacetate monohydrate, (II).

The asymmetric unit of (I) consists of a 2-amino-5-chloropyridinium cation protonated at the ring N atom and a trichloroacetate anion joined together by two almost linear  $N-H \cdots O$  hydrogen bonds (Fig. 1). Oppositely charged hydrogen-bonded 2-amino-5-chloropyridinium and trichloroacetate units related by a *c*-glide plane interact with one another *via* an additional pair of symmetry-equivalent  $N-H \cdots O$  hydrogen bonds (Table 1) between the amine group of



the 2-amino-5-chloropyridinium cation and an O atom of the trichloroacetate anion [ $N2-H21 \cdots O1^i$ ; symmetry code:  $(i) x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ], forming a one-dimensional chain in the [101] direction. The hydrogen-bonded chains, related by a translation along the *a* axis, form sheets located parallel to the (010) crystallographic plane at  $b = \frac{1}{2}$  and  $\frac{3}{4}$  (Fig. 2). No hydrogen bonds are present between the sheets; they interact only through van der Waals forces. The C–O bond lengths of the  $COO^-$  group of the trichloroacetate anion are slightly different [ $C1-O1 = 1.236(2) \text{ \AA}$  and  $C1-O2 = 1.220(2) \text{ \AA}$ ] and correlate well with the number and strength of the hydrogen bonds in which they are involved as acceptors. The O atom with the longer C–O bond is involved in two hydrogen bonds and that with the shorter C–O bond in only one hydrogen bond.

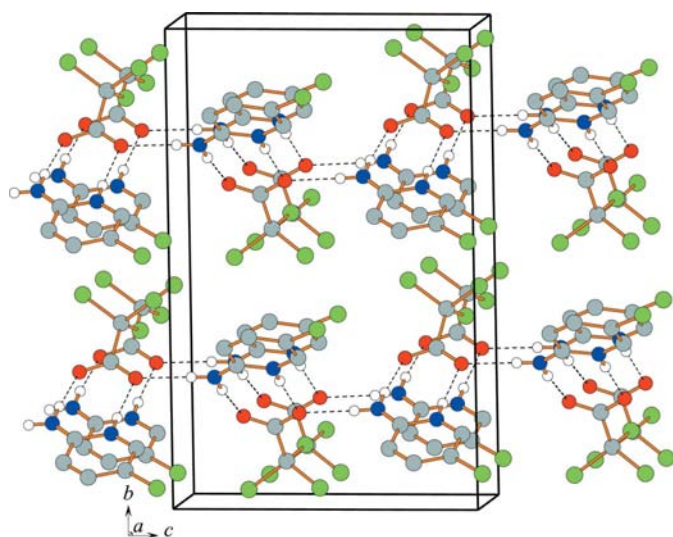
The asymmetric unit of (II) consists of a 2-methyl-5-nitroanilinium cation, a trichloroacetate anion and a water molecule joined together *via*  $N-H \cdots O$  hydrogen bonds (Fig. 3). All H atoms of the protonated amine group are involved in  $N-H \cdots O$  hydrogen bonds, with neighbouring trichloroacetate anions and the water molecule as acceptors. The water molecule, besides the  $N-H \cdots O(\text{water})$  hydrogen bond in which it acts as an acceptor, also acts as a donor in two  $O-H \cdots O$  hydrogen bonds linking two trichloroacetate anions (Table 2). Hydrogen-bonded aggregates related by an inver-



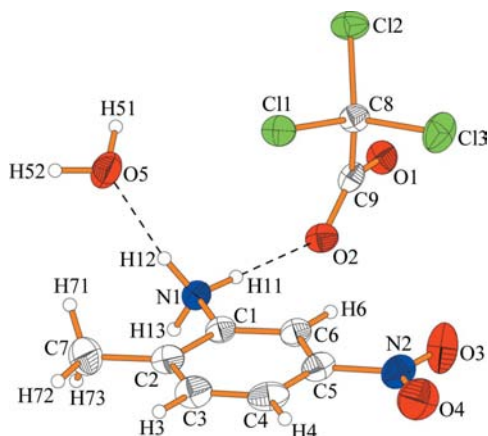
**Figure 1**  
A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii. Dashed lines indicate  $N-H \cdots O$  hydrogen bonds.

sion center form a stacking structure along the *a* axis. The aromatic rings of the 2-methyl-5-nitroanilinium cations are slipped and separated by a distance of 3.408 (3) Å, pointing to  $\pi$ - $\pi$  interactions between the rings, since the value is comparable to the sum of the van der Waals radii of the C atoms of the interacting ring systems (Pauling, 1960; Janiak, 2000; Hunter *et al.*, 2001). The oppositely charged 2-methyl-5-nitroanilinium and trichloroacetate units are interconnected *via* N—H $\cdots$ O hydrogen bonds, together with a much weaker C4—H41 $\cdots$ Cl1<sup>iv</sup> [symmetry code: (iv)  $-x + 1, -y + 1, -z + 2$ ] hydrogen bond, and form double chains that are interconnected *via* hydrogen bonds with water molecules into a three-dimensional network (Fig. 4).

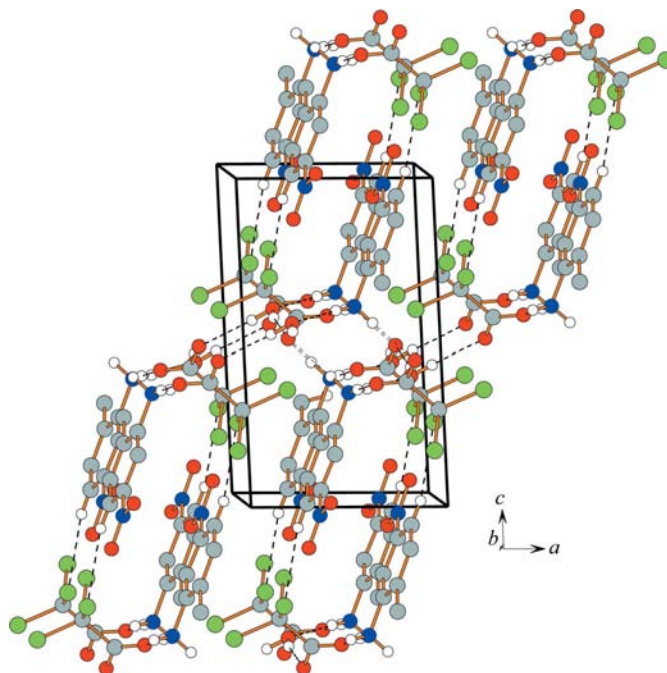
This study illustrates the utility of trichloroacetic acid in crystal engineering for developing supramolecular structures in solids. One of the investigated crystals exhibits nonlinear optical properties. The structures illustrate that weak  $\pi$ - $\pi$



**Figure 2**  
A view of the crystal packing of (I), showing the N—H $\cdots$ O hydrogen-bonded chains.



**Figure 3**  
A view of the molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Dashed lines indicate hydrogen-bond interactions.



**Figure 4**  
A view of the hydrogen-bonded three-dimensional network of (II).

aromatic interactions between slipped rings modulated by stronger hydrogen bonds play a significant role in assembling the components of the supramolecular systems. In (I), the components interact *via* an  $R_2^2(8)$  hydrogen-bond motif between the  $\text{COO}^-$  group and the 2-amino-5-chloropyridinium cation, whereas in (II), the O atoms of the  $\text{COO}^-$  group are involved as acceptors with two 2-methyl-5-nitroanilinium cations. Thus, the different topology of the hydrogen-bonding interactions between the components is reflected in the dimensionality of the formed hydrogen-bonding networks.

## Experimental

Suitable crystals of (I) and (II) were obtained by slow evaporation of a solution of 2-amino-5-chloropyridine or 2-methyl-5-nitroaniline in 5% trichloroacetic acid. An SHG (second harmonic generation) experiment was carried out using the Kutz–Perry powder technique (Kutz & Perry, 1968). Samples of 2-amino-5-chloropyridinium trichloroacetate were irradiated at 1064 nm with an Nd:YAG laser and the second harmonic beam power diffused by the sample at 532 nm was measured as a function of the fundamental beam power. The SHG efficiency in relation to potassium dihydrogen phosphate (KDP) is 0.77 [ $d_{\text{eff}} = 0.77d_{\text{eff}}(\text{KDP})$ ].

## Salt (I)

### Crystal data

$\text{C}_5\text{H}_6\text{ClN}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^-$   
 $M_r = 291.94$   
 Monoclinic, *Cc*  
 $a = 5.6426(11)$  Å  
 $b = 17.512(3)$  Å  
 $c = 11.323(2)$  Å  
 $\beta = 94.36(1)^\circ$

$V = 1115.6(4)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.04$  mm<sup>-1</sup>  
 $T = 295$  K  
 $0.32 \times 0.24 \times 0.16$  mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector  
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction Poland, 2008)  
 $T_{\min} = 0.732$ ,  $T_{\max} = 0.851$

7423 measured reflections  
2699 independent reflections  
1817 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.047$   
 $S = 1.00$   
2699 reflections  
145 parameters  
2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{\AA}^{-3}$   
Absolute structure: Flack (1983), 1226 Friedel pairs  
Flack parameter: 0.10 (5)

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1	0.83 (2)	1.98 (2)	2.806 (3)	174 (2)
N2—H21...O1 <sup>i</sup>	0.87 (2)	2.03 (1)	2.893 (3)	176 (3)
N2—H22...O2	0.87 (2)	1.96 (2)	2.821 (3)	175 (2)

Symmetry code: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

Salt (II)

Crystal data

$\text{C}_7\text{H}_9\text{N}_2\text{O}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^- \cdot \text{H}_2\text{O}$   
 $M_r = 333.55$   
Triclinic,  $P\bar{1}$   
 $a = 6.9810$  (14)  $\text{\AA}$   
 $b = 8.3611$  (17)  $\text{\AA}$   
 $c = 12.229$  (2)  $\text{\AA}$   
 $\alpha = 103.74$  (1)  $^\circ$   
 $\beta = 92.29$  (1)  $^\circ$

$\gamma = 94.77$  (1)  $^\circ$   
 $V = 689.6$  (2)  $\text{\AA}^3$   
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.68 \text{ mm}^{-1}$   
 $T = 295 \text{ K}$   
 $0.34 \times 0.30 \times 0.16 \text{ mm}$

Data collection

Kuma KM-4 diffractometer with a CCD area detector  
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction Poland, 2008)  
 $T_{\min} = 0.811$ ,  $T_{\max} = 0.908$

7531 measured reflections  
3305 independent reflections  
2306 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.131$   
 $S = 1.01$   
3305 reflections  
189 parameters  
2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.42 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.46 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H11...O2	0.86 (4)	1.95 (4)	2.810 (4)	179 (6)
N1—H12...O5	0.88 (4)	1.90 (4)	2.772 (4)	169 (4)
N1—H13...O1 <sup>i</sup>	0.86 (4)	2.04 (4)	2.903 (4)	177 (4)
N1—H13...O2 <sup>i</sup>	0.86 (4)	2.52 (4)	3.066 (3)	122 (3)
O5—H51...O1 <sup>ii</sup>	0.92 (4)	2.26 (4)	3.175 (4)	178 (4)
O5—H52...O1 <sup>iii</sup>	0.92 (4)	1.96 (4)	2.851 (4)	165 (5)

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

H atoms involved in hydrogen bonding were located in difference Fourier maps and their positions refined. C-bound H atoms were introduced at calculated positions [ $\text{C—H} = 0.93$  (aromatic) or  $0.96 \text{ \AA}$  (methyl)] and refined as riding on their carrier atoms.  $U_{\text{iso}}(\text{H})$  values were constrained as  $1.5U_{\text{eq}}$  of the carrier atoms for water and amine groups, and  $1.2U_{\text{eq}}$  otherwise. For (I), the N2—H21 and N2—H22 bond lengths, and for (II), the O5—H51 and O5—H52 bond lengths, were all restrained to  $0.87$  (2)  $\text{\AA}$ .

For both salts, data collection: *CrysAlis CCD* (Oxford Diffraction Poland, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction Poland, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3318). Services for accessing these data are described at the back of the journal.

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