*Acta Cryst.* (1987). C**43**, 1175–1177

# Structure of Ammonium Trichloroacetate–Water (1/2·5)

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(*Received* 28 *October* 1986; *accepted* 26 *January* 1987)

**Abstract.** $NH_4^+.C_2Cl_3O_2^-.2{\cdot}5H_2O$, $M_r = 225{\cdot}45$, orthorhombic, *Pbam*, $a = 17{\cdot}983\ (2)$, $b = 9{\cdot}040\ (1)$, $c = 11{\cdot}524\ (1)$ Å, $V = 1873{\cdot}6\ (3)$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}60\ (1)$, $D_x = 1{\cdot}60$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}95$ mm$^{-1}$, $F(000) = 920$, $T = 292$ K, $R = 0{\cdot}068$ for 1318 observed reflections. Two independent trichloroacetate ions lie on the mirror planes parallel to (001) at $z = 0$ and $z = \frac{1}{2}$. The ammonium ions, water molecules and carboxylate ions are linked together by N—H···O and O—H···O hydrogen bonds, forming a three-dimensional network.

**Introduction.** Some hydrated carboxylate salts, *e.g.* copper(II) formate tetrahydrate, exhibit dielectric anomalies or protonic conduction closely related to their hydrogen-bonded systems (Kiriyama, 1962). The present study was undertaken to establish the hydrogen-bonding scheme in the title compound which contains ammonium ions, water molecules and carboxylate oxygen atoms and to ascertain the structural character for proton conduction.

**Experimental.** The title compound was prepared by adding a half-equimolar amount of ammonium carbonate to an aqueous solution of trichloroacetic acid and recrystallized from water as colorless needles. Crystal 0·3 × 0·3 × 0·25 mm sealed in a capillary because of its efflorescence nature, m.p. 307·6 K. Density measured by pycnometry with petroleum at 292 K. Rigaku AFC-4, graphite-monochromated Mo $K\alpha$ radiation, 40 kV, 200 mA; unit-cell parameters determined from least squares of setting angles of 25 reflections in $2\theta$ range 20–32°; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}65$ Å$^{-1}$ ($2\theta < 55°$), range of $h$, $k$, $l$: 0→23, −11→11, 0→15; standard reflections 080, 008 and 440, intensity variations <4%, 4145 reflections measured, 2254 unique, $R_{\text{int}} = 0{\cdot}044$ based on $F$, 936 reflections with $|F_o| < 3\sigma(F_o)$ regarded as unobserved. Corrections for Lorentz and polarization factors, not for absorption because $\mu R < 0{\cdot}4$. Systematic absences: $h0l$ for $h = 2n+1$, $0kl$ for $k = 2n+1$, space group *Pbam* or *Pba*2. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares on $F$ with anisotropic thermal parameters for non-hydrogen atoms in both *Pbam* and *Pba*2. Refinement based on space group *Pba*2 failed to converge satisfactorily, $R = 0{\cdot}135$, while $R = 0{\cdot}074$ for *Pbam*. The space group *Pbam* was therefore chosen as the correct one. The four peaks assignable to the N atom of the $NH_4^+$ ion and three O($W$) atoms of 2·5 $H_2O$ molecules in the electron density map were distinguished with the aid of symmetry and chemical considerations. One of these positions corresponds to the 4($e$) site of *Pbam* and the others to 8($i$) sites. The former was necessarily assigned to the water oxygen O($W$1) to satisfy the stoichiometric relation. Two sites of the latter three each have close neighbors related by mirror symmetry at distances of *ca* 2·8 Å. Water molecules are electrically neutral and capable of forming hydrogen bonds as hydrogen donors and/or acceptors, unlike $NH_4^+$ ions. On these grounds, two 8($i$) sites were assigned to the water oxygen atoms, O($W$2) and O($W$3), and the remaining 8($i$) site to the N atom. Nine H atoms were located on difference Fourier maps and refined isotropically. In these calculations the occupancy of H(7) was fixed at 0·5 for the reason described later. Final $R = 0{\cdot}068$ and $wR = 0{\cdot}054$, $S = 1{\cdot}08$ for 142 variables, $w = 1/[\sigma^2(F_o) + 0{\cdot}1219|F_o| - 0{\cdot}00096|F_o|^2]$, $(\Delta/\sigma)_{\max} = 0{\cdot}05$, max. and min. height in final difference Fourier synthesis 0·60 and −0·54 e Å$^{-3}$ in the vicinity of some Cl atoms. Scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974), programs used: *The Universal Crystallographic Computing System–Osaka* (1979).

**Discussion.** The final positional and thermal parameters are listed in Table 1‡ and selected interatomic distances and angles in Table 2.

Two crystallographically nonequivalent $CCl_3COO^-$ ions lie on the mirror planes parallel to (001) at $z = 0$

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43750 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates and isotropic temperature factors* (Å$^2$) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cl(1) | 0·3854 (1) | 0·3898 (3) | 0 | 4·90 (6) |
| Cl(2) | 0·4099 (1) | 0·1198 (2) | 0·1238 (2) | 7·36 (5) |
| Cl(3) | 0·1977 (1) | 0·2661 (2) | 0·5 | 4·85 (5) |
| Cl(4) | 0·0628 (1) | 0·3222 (2) | 0·3748 (2) | 7·17 (5) |
| O(1) | 0·5478 (2) | 0·2752 (4) | 0·0967 (3) | 3·21 (6) |
| O(2) | 0·1444 (2) | 0·5929 (4) | 0·4039 (3) | 3·61 (6) |
| O(*W*1) | 0 | 0 | 0·2510 (5) | 3·79 (9) |
| O(*W*2) | 0·2012 (2) | 0·2433 (5) | 0·1230 (4) | 3·91 (7) |
| O(*W*3) | 0·3741 (2) | 0·3976 (4) | 0·3772 (4) | 3·66 (7) |
| N | 0·2522 (2) | 0·4937 (5) | 0·2462 (4) | 2·38 (6) |
| C(1) | 0·4350 (4) | 0·2199 (8) | 0 | 2·71 (12) |
| C(2) | 0·5189 (4) | 0·2599 (7) | 0 | 2·20 (11) |
| C(3) | 0·1136 (4) | 0·3681 (8) | 0·5 | 2·81 (13) |
| C(4) | 0·1352 (4) | 0·5367 (8) | 0·5 | 2·54 (13) |
| H(1) | 0·261 (3) | 0·556 (6) | 0·203 (5) | 2·5 (14)* |
| H(2) | 0·218 (3) | 0·511 (6) | 0·282 (4) | 1·1 (12)* |
| H(3) | 0·225 (4) | 0·403 (8) | 0·200 (7) | 7·9 (26)* |
| H(4) | 0·285 (5) | 0·478 (10) | 0·291 (8) | 10·3 (31)* |
| H(5) | 0·012 (3) | 0·089 (6) | 0·197 (5) | 3·4 (16)* |
| H(6) | 0·145 (4) | 0·226 (7) | 0·139 (6) | 4·2 (18)* |
| H(7)† | 0·222 (5) | 0·250 (11) | 0·060 (8) | 1·1 (23)* |
| H(8) | 0·374 (4) | 0·286 (7) | 0·394 (6) | 4·8 (19)* |
| H(9) | 0·425 (4) | 0·442 (7) | 0·346 (6) | 5·3 (20)* |

* Isotropic temperature factor, $B_{iso}$.
† Occupancy factor was fixed at 0·5 (see text).

Table 2. *Interatomic distances* (Å) *and angles* (°)

(1) $CCl_3COO^-$ ions

| | | | |
|---|---|---|---|
| Cl(1)–C(1) | 1·776 (5) | Cl(3)–C(3) | 1·771 (5) |
| Cl(2)–C(1) | 1·748 (5) | Cl(4)–C(3) | 1·757 (5) |
| C(1)–C(2) | 1·551 (7) | C(3)–C(4) | 1·573 (7) |
| C(2)–O(1) | 1·237 (6) | C(4)–O(2) | 1·230 (6) |
| Cl(1)–C(1)–Cl(2) | 108·5 (3) | Cl(3)–C(3)–Cl(4) | 108·7 (3) |
| Cl(2)–C(1)–Cl(2) | 109·3 (3) | Cl(4)–C(3)–Cl(4) | 110·4 (3) |
| Cl(2)–C(1)–C(2) | 111·8 (3) | Cl(4)–C(3)–C(4) | 110·9 (3) |
| Cl(1)–C(1)–C(2) | 106·7 (3) | Cl(3)–C(3)–C(4) | 107·1 (3) |
| C(1)–C(2)–O(1) | 115·7 (4) | C(3)–C(4)–O(2) | 115·7 (4) |
| O(1)–C(2)–O(1) | 128·5 (4) | O(2)–C(4)–O(2) | 128·5 (5) |

(2) Ammonium ion, water molecules and hydrogen bonds

| *A*—H···*B* | *A*···*B* | *A*—H | H···*B* | *A*—H···*B* |
|---|---|---|---|---|
| N–H(1)···O($W2^{i}$) | 2·794 (6) | 0·77 (6) | 2·05 (6) | 165 (6) |
| N–H(2)···O(2) | 2·804 (6) | 0·75 (5) | 2·07 (5) | 165 (5) |
| N–H(3)···O(*W*2) | 2·825 (6) | 1·10 (8) | 1·74 (8) | 167 (7) |
| N–H(4)···O(*W*3) | 2·800 (6) | 0·80 (9) | 2·02 (9) | 166 (9) |
| O(*W*1)–H(5)···O($1^{ii}$) | 2·834 (4) | 1·04 (6) | 1·80 (6) | 170 (5) |
| O(*W*2)–H(6)···O($1^{ii}$) | 2·781 (5) | 1·04 (7) | 1·82 (7) | 153 (6) |
| O(*W*2)–H(7)···O($W2^{iii}$) | 2·835 (6) | 0·83 (9) | 2·14 (9) | 142 (9) |
| O(*W*3)–H(8)···O($2^{i}$) | 2·791 (5) | 1·02 (7) | 1·79 (7) | 167 (6) |
| O(*W*3)–H(9)···O($W1^{i}$) | 2·846 (4) | 1·07 (7) | 1·81 (7) | 162 (6) |
| O(*W*3)···O($W3^{iv}$) | 2·830 (5) | | | |

| | | | |
|---|---|---|---|
| H(1)–N–H(2) | 112 (6) | H(5)–O(*W*1)–H(5) | 106 (5) |
| H(1)–N–H(3) | 108 (6) | H(6)–O(*W*2)–H(7) | 128 (7) |
| H(1)–N–H(4) | 114 (8) | H(8)–O(*W*3)–H(9) | 115 (5) |
| H(2)–N–H(3) | 93 (6) | | |
| H(2)–N–H(4) | 106 (7) | | |
| H(3)–N–H(4) | 121 (8) | | |

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

and $z = \frac{1}{2}$. The Cl atoms of both $CCl_3$ groups are in contact with the Cl atoms of the adjacent anions with van der Waals distances of Cl(2)···Cl(2) 3·897 (3), Cl(4)···Cl(4) 3·929 (3), and Cl(2)···Cl(4) 3·981 (3) Å. The bond lengths and angles in $CCl_3COO^-$ ions agree well with those reported for $NH_4H(CCl_3CO_2)_2$ (Golič & Lazarini, 1975). The influence of the substitution of Cl for H atoms in acetate groups is recognized in the C—C bond lengths and O—C—O angles. The C—C distances are longer by *ca* 0·06 Å and the O—C—O angles are larger by *ca* 5° than those found in the crystal structure of sodium acetate trihydrate (Wei & Ward, 1977). Each CCOO plane is planar within ±0·02 Å and the dihedral angles between ClCC and CCO planes are 89·3 (4), 29·2 (5) and 152·1 (4)° for the $CCl_3COO^-$ ion including Cl(1) and Cl(2) atoms, and 88·1 (5), 30·3 (5) and 153·4 (4)° for the other including Cl(3) and Cl(4).

Three kinds of water molecules, one of which lies on the twofold axis, one ammonium ion, and two carboxylic groups of $CCl_3COO^-$ ions are linked together by hydrogen bonds with donor–acceptor distances of 2·781 (5)–2·846 (4) Å, forming a three-dimensional network as shown in Figs. 1 and 2. In this hydrogen-bonding scheme, the $NH_4^+$ ion evidently donates four H

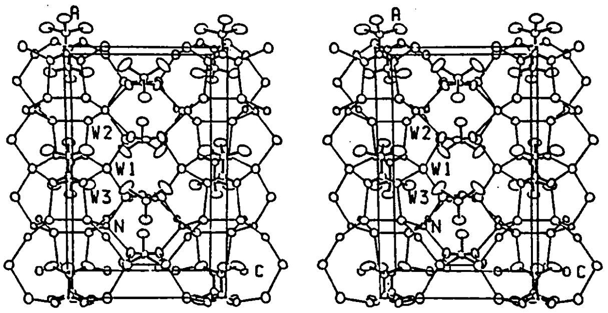

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the crystal structure viewed along the *b* axis.

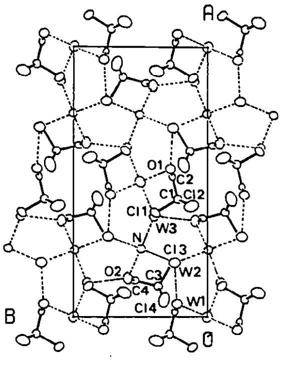

Fig. 2. *ORTEP* drawing (Johnson, 1976) of the crystal structure viewed along the *c* axis. Hydrogen bonds are shown by dotted lines.

atoms to one carboxylic oxygen O(2) and to three water oxygen atoms, 2O(*W*2) and O(*W*3). On the other hand, all the hydrogen atoms of water molecules participate in O—H···O hydrogen bonds. As given in Table 2, the geometries of the hydrogen bonds are reasonable, except for the H(7)···H($7^{iii}$) distance (1·4 Å), which is too short to be accepted. Such an undesirable approach of two H(7) atoms suggests that the water molecule *W*2 must be orientationally disordered with occupancy 0·5 for H(7). The so-called half-hydrogen model was adopted in the final calculations of least-squares refinement and Fourier syntheses, although the remaining half-hydrogen atom could not be located certainly.

The rather large *R* value in the present study may be attributed mainly to the relatively large amplitude of thermal motion of the chlorine atoms. In fact, no $^{35}$Cl NQR signal was detected in the wide temperature region 100–300 K, indicating that all the $CCl_3$ groups are rapidly reorienting about their threefold axes (Hashimoto, 1986). Additionally, molecular motion of the ammonium ion has been confirmed from the $^1$H NMR results.

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*Acta Cryst.* (1987). C**43**, 1177–1179

# Structure of the *E* Isomer of 5-Benzylidene-1-methyl-2,4-imidazolidinedione

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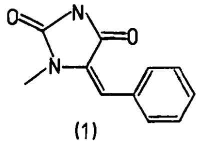
(*Received* 15 *December* 1986; *accepted* 10 *February* 1987)

**Abstract.** $C_{11}H_{10}N_2O_2$, $M_r = 202·22$, orthorhombic, *Pcan*, $a = 7·184$ (7), $b = 20·330$ (9), $c = 13·532$ (9) Å, $V = 1976·4$ Å$^3$, $Z = 8$, $D_m = 1·33$ (3), $D_x = 1·35$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·58$ cm$^{-1}$, $F(000) = 848$, room temperature, final $R = 0·069$ for 868 [$I > 2\sigma(I)$] independent observed reflections. The molecule, also known as 5-benzylidene-1-methylhydantoin, is essentially flat with the two planes of non-H atoms (the 2,4-imidazolidinedione and the benzene rings) at an angle of 5·7 (3)°. As is usual with most hydantoins containing an imine H and two O atoms, hydrogen bonds are observed with N(3)—H(31)···O(14) and H(31)···O(14) at 2·81 (1) and 1·82 (6) Å respectively.

**Introduction.** Compounds of 2,4-imidazolidinedione (also known as hydantoin) are well known (*Kirk-Othmer Encyclopedia of Chemical Technology,* 1980). However, only a few such compounds contain a methylene linkage at the 5-position. In previous structure determinations (Drew, Mok, Ang & Tan, 1987*a,b*) it was reported that the *Z* isomer of 5-[(4-methoxyphenyl)methylene]-2,4-imidazolidinedione was flat within 0·30 Å despite the presence of strain caused by the proximity of two H atoms, while in the *Z* isomer of 5-benzylidene-1-methylhydantoin the five-membered ring was rotated 45·9 (3)° from the plane of the phenyl ring. The structure of the *E* isomer of the latter molecule (1) is now reported.



(1)

**Experimental.** Compound (1) prepared as described elsewhere (Tan, Ang & Fong, 1986). Density measured by flotation in $CCl_4$/ligroin. Space group *Pcan* (non-standard setting of *Pbcn* with $a \rightarrow b$, $b \rightarrow a$, $c \rightarrow \bar{c}$).

0108-2701/87/061177-03$01.50