Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Chloroanilinium hydrogen (2*R*,3*R*)-tartrate monohydrate

Graham Smith,[a]* Urs D. Wermuth[b] and Jonathan M. White[c]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, [b]School of Biomolecular and Physical Sciences, Griffith University, Nathan, Queensland 4111, Australia, and [c]BIO-21 Molecular Science and Biotechnology, University of Melbourne, Parkville, Victoria 3052, Australia
Correspondence e-mail: g.smith@qut.edu.au

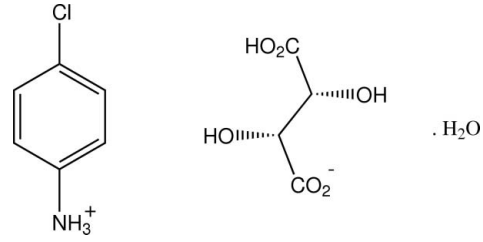
Received 2 July 2007; accepted 3 July 2007

Key indicators: single-crystal X-ray study; T = 130 K; mean σ(C–C) = 0.010 Å; R factor = 0.076; wR factor = 0.197; data-to-parameter ratio = 12.3.

In the structure of the hydrated 1:1 compound of 4-chloroaniline with L-tartaric acid, $C_6H_7ClN^+\cdot C_4H_5O_6^-\cdot H_2O$, determined at 130 K, the asymmetric unit comprises two 4-chloroanilinium cations, two hydrogen tartrate anions and two water molecules of solvation, and forms a two-dimensional duplex substructure comprising head-to-tail $C_1^1(7)$ hydrogen-bonded hydrogen tartrate anions and water molecules. The π-associated 4-chloroanilinium cation pairs [ring centroid separation = 3.576 (4) Å; inter-ring dihedral angle = 0.5 (1)°] are accommodated within the channels of the substructure and are hydrogen-bonded to it peripherally.

Related literature

The structure of the title compound is different from those of the L-tartrates of the parent aniline (Chen *et al.*, 2005), *p*-toluidine and *m*-anisidine (Renuka *et al.*, 1995). For related literature, see: Aakeröy *et al.* (1992); Bijvoet *et al.* (1951); Bott *et al.* (1993); Fuller *et al.* (1995); Manivannan *et al.* (1995); Smith *et al.* (2006).



Experimental

Crystal data

$C_6H_7ClN^+\cdot C_4H_5O_6^-\cdot H_2O$
M_r = 295.67
Monoclinic, $P2_1$
a = 7.3437 (15) Å
b = 10.850 (2) Å
c = 15.971 (3) Å
β = 97.880 (4)°
V = 1260.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 130 (2) K
0.45 × 0.15 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.93, T_{max} = 0.98
6196 measured reflections
4197 independent reflections
3319 reflections with $I > 2\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.197
S = 1.06
4197 reflections
342 parameters
1 restraint
H-atom parameters not refined
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}
Absolute structure: Flack (1983), 1857 Friedel pairs
Flack parameter: 0.02 (6)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H11A···O12C	0.91	2.40	3.131 (7)	137
N1A—H11A···O21C	0.91	1.91	2.731 (7)	149
N1A—H12A···O21D^{i}	0.92	1.889	2.765 (8)	160
N1A—H13A···O12D^{ii}	0.90	1.98	2.855 (7)	165
N1B—H11B···O42D	0.90	2.14	2.747 (7)	124
N1B—H12B···O31C	0.88	2.02	2.884 (7)	166
N1B—H12B···O41C	0.88	2.52	2.868 (7)	104
N1B—H13B···O31D^{iii}	0.91	2.13	2.768 (7)	126
N1B—H13B···O41C	0.91	2.43	2.868 (7)	109
O11C—H11C···O42C^{iv}	0.90	1.71	2.609 (6)	179
O11D—H11D···O41D^{iv}	0.90	1.62	2.521 (6)	179
O21C—H21C···O2W	0.85	1.78	2.527 (7)	145
O31C—H31C···O1W	0.84	1.86	2.672 (7)	163
O21D—H21D···O31D	0.74	2.54	2.936 (7)	115
O21D—H21D···O42C^{v}	0.74	2.09	2.768 (7)	151
O31D—H31D···O1W	0.94	2.19	2.798 (7)	121
O31D—H31D···O42D	0.94	1.87	2.554 (6)	127
O1W—H11W···O42C^{v}	0.90	2.02	2.923 (7)	179
O1W—H12W···O41C^{iv}	0.90	1.84	2.702 (7)	161
O2W—H21W···O12C^{iii}	0.82	1.91	2.674 (8)	153
O2W—H22W···O12D^{ii}	0.89	1.92	2.810 (8)	179

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the School of Physical and Chemical Sciences (Queensland University of Technology), the School of Biomolecular and Physical Sciences, Griffith University and the School of Chemistry, University of Melbourne.

 © 2007 International Union of Crystallography doi:10.1107/S1600536807032473

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2426).

References

Aakeröy, C. B., Hitchcock, P. B. & Seddon, K. R. (1992). *J. Chem. Soc. Chem. Commun.* pp. 553–555.

Bijvoet, J. M., Peerdeman, A. F. & van Bommel, A. J. (1951). *Nature (London)*, **168**, 271–272.

Bott, R. C., Sagatys, D. S., Lynch, D. E., Smith, G. & Kennard, C. H. L. (1993). *Acta Cryst.* C**49**, 1150–1152.

Bruker (1999). *SADABS* (Version 2.03) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SMART* (Version 5.55). Bruker AXS Inc., Madison, Wisconsin, USA.

Chen, W., Zheng, J.-M. & Che, Y.-X. (2005). *Rengong Jingti Xuebao*, **34**, 265–269.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fuller, J., Carlin, R. T., Simpson, L. J. & Furtak, T. E. (1995). *Chem. Mater.* **7**, 909–915.

Manivannan, S., Dhanuskodi, S., Kirchbaum, K. & Tiwari, S. K. (1995). *Cryst. Growth Des.* **6**, 1285–1290.

Renuka, K., Row, T. N. G., Prasad, B. R., Subramanian, C. K. & Bhattacharya, S. (1995). *New J. Chem.* **19**, 83–89.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Smith, G., Wermuth, U. D. & White, J. M. (2006). *Acta Cryst.* C**62**, o694–o698.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2007). E**63**, o3432-o3433 [**doi:10.1107/S1600536807032473**]

4-Chloroanilinium hydrogen (2*R*,3*R*)-tartrate monohydrate

G. Smith, U. D. Wermuth and J. M. White

Comment

The utility of *L*-tartaric acid as an agent for the introduction of chirality in organic compounds for the generation of crystalline materials with potentially useful nonlinear optical properties has been recognized (Aakeröy *et al.*, 1992; Fuller *et al.*, 1995; Renuka *et al.*, 1995; Chen *et al.*, 2005; Manivannan *et al.*, 1995). The product from the 1:1 reaction with aniline (Chen *et al.*, 2005), *p*-toluidine and *m*-anisidine (a monohydrate) (Renuka *et al.*, 1995) have been determined so that our similar reaction of *L*-tartaric acid with 4-chloroaniline in aqueous propan-2-ol not unexpectedly gave good crystals of the proton-transfer compound 4-chloroanilinium hydrogen (2*R*,3*R*)-tartrate monohydrate $C_6H_7ClN^+ C_4H_5O_6^- \cdot H_2O$, (I) and the structure is reported here.

In (I), the asymmetric unit comprises two 4-chloroanilinium cations (A and B), two hydrogen *L*-tartarate anions (C and D) and two water molecules of solvation (O1W and O2W) (Fig. 1). The two hydrogen tartrate anions and the water molecules form duplex hydrogen-bonded substructures through homomeric A and B chain carboxylate interactions with other tartrate carboxylic acid and hydroxyl groups as well as with the water molecules (Table 1). These include the $C_1^1(7)$ head-to-tail carboxylic acid–carboxylate associations (O11–H11···O42) which extend down the *a* cell direction in the unit cell (Figs. 2, 3). These carboxyl associations typify the hydrogen-bonded framework substructures in the majority of the anhydrous hydrogen tartrates (Aakeröy *et al.*, 1992). The two independent 4-chloroanilinium cations in (I) form a π-associated dimer through partial overlapping of the offset benzene rings [ring centroid separation, 3.576 (4) Å; inter-ring dihedral angle, 0.5 (1)°]. However, the inter-dimer separation down the *a* cell direction [4.242 (4) Å] does not give stacks such as is found in the structure of quinolinium hydrogen-*L*-tartrate (Smith *et al.*, 2006). In (I), these dimers are accommodated between the substructures and are peripherally hydrogen-bonded to them through aminium N^+—H···O interactions with water and both carboxyl and hydroxyl O acceptors of the anions, including the $R^3_4(8)$ cyclic system seen in the asymmetric unit in Fig. 1. The result is a two-dimensional network structure.

The accepted (2*R*,3*R*) absolute configuration for the *L*-tartrate residues in (I) (Bijvoet *et al.*, 1951) was assumed and both anions C and D adopt the common extended conformation. The intramolecular hydroxyl *O–H···O*(carboxyl) hydrogen bond which is also common in hydrogen tartrates is absent in the C anion but present in the D anion [O···O, [2.554 (6) Å]. In addition, in the D anion there is an unusual intramolecular hydroxyl–hydroxyl O–H···O contact [O···O, 2.936 (7) Å]. However, there are no significant conformational differences in the two anions, the O21–C2–C3–O31 torsion angles being −61.7 (7) ° (C) and −69.5 (6) ° (D), comparing with −66.8 (2) ° in sodium hydrogen *L*-tartrate monohydrate (Bott *et al.*, 1993).

Experimental

Compound (I) was synthesized by heating for 10 min under reflux, 1 mmol quantities of *L*-tartaric acid and 4-chloroaniline in 50 ml of 50% 2-propanol-water. Colourless needles (m.p. 443 K) were obtained after partial room-temperature evaporation of solvent.

Refinement

Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined but these were constrained in the final refinement cycles. Other H atoms were included at calculated positions [C—H (aromatic) = 0.95 Å and C—H (aliphatic) = 0.98–1.00 Å] and treated as riding with U_{iso}(H) = 1.2U_{eq}(C). The absolute configuration determined for the parent *L*-(+)-tartaric acid (2*R*,3*R*) (Bijvoet *et al.*, 1951) was invoked.

Figures

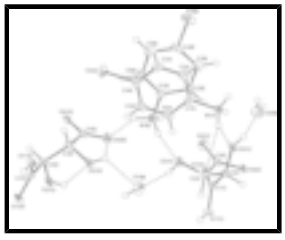


Fig. 1. The molecular configuration and atom-numbering scheme for the two 4-chloroanilinium cations (A and B), the two hydrogen *L*-tartrate anions (C and D) and the two water molecules of solvation in the asymmetric unit of (I). Inter- species hydrogen bonds are shown as dashed lines. Non-H atoms are shown as 40% probability displacement ellipsoids.

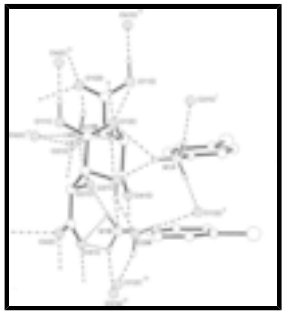


Fig. 2. The homomeric $C_1^1(7)$ hydrogen-bonded extension of the C– and D-anion structures in the two-dimensional duplex-chain substructure of (I), viewed perpendicular to the *a* axial direction. Hydrogen-bonding interactions are shown as dashed lines and non-interactive hydrogen atoms are omitted. For symmetry codes, see Table 1.

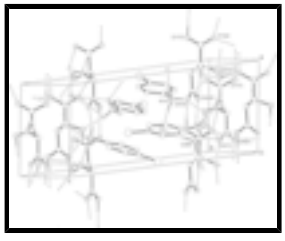


Fig. 3. A perspective view of the packing of the two-dimensional structure of (I) in the unit cell showing the extension of the substructure along the *a* cell direction.

4-chloroanilinium hydrogen (2*R*,3*R*)-tartrate monohydrate

Crystal data

$C_6H_7ClN^+·C_4H_5O_6^-·H_2O$	F_{000} = 616
M_r = 295.67	D_x = 1.558 Mg m^{-3}
Monoclinic, $P2_1$	Melting point: 443 K
Hall symbol: P 2yb	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 7.3437 (15) Å	Cell parameters from 1450 reflections
b = 10.850 (2) Å	θ = 2.9–22.5º
c = 15.971 (3) Å	μ = 0.33 mm^{-1}

β = 97.880 (4)º	T = 130 (2) K
V = 1260.5 (4) Å^3	Needle, colourless
Z = 4	0.45 × 0.15 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer	4197 independent reflections
Radiation source: sealed tube	3319 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.087
T = 130(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 1.3º
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$h = -8 \rightarrow 8$
T_{min} = 0.93, T_{max} = 0.98	$k = -12 \rightarrow 11$
6196 measured reflections	$l = -18 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.076	$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.197	$(\Delta/\sigma)_{max} < 0.001$
S = 1.06	$\Delta\rho_{max}$ = 0.79 e Å^{-3}
4197 reflections	$\Delta\rho_{min}$ = −0.59 e Å^{-3}
342 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 1857 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.02 (6)
Secondary atom site location: difference Fourier map	

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl4A	0.9564 (3)	0.55789 (17)	0.48663 (12)	0.0366 (6)

N1A	0.6345 (8)	0.9058 (5)	0.2194 (3)	0.0197 (17)
C1A	0.7105 (9)	0.8202 (7)	0.2862 (4)	0.0203 (19)
C2A	0.7486 (10)	0.8612 (6)	0.3678 (5)	0.026 (2)
C3A	0.8266 (10)	0.7810 (6)	0.4301 (4)	0.024 (2)
C4A	0.8612 (10)	0.6607 (6)	0.4076 (4)	0.024 (2)
C5A	0.8207 (9)	0.6193 (6)	0.3260 (4)	0.025 (2)
C6A	0.7471 (9)	0.6994 (6)	0.2644 (4)	0.022 (2)
Cl4B	0.3364 (3)	0.82187 (19)	0.47195 (13)	0.0439 (7)
N1B	0.3270 (7)	0.4358 (5)	0.2080 (3)	0.0192 (17)
C1B	0.3282 (9)	0.5305 (6)	0.2730 (4)	0.020 (2)
C2B	0.2610 (10)	0.6462 (6)	0.2512 (5)	0.024 (2)
C3B	0.2671 (10)	0.7368 (7)	0.3126 (5)	0.028 (3)
C4B	0.3326 (10)	0.7061 (7)	0.3945 (5)	0.027 (3)
C5B	0.3993 (10)	0.5903 (7)	0.4180 (5)	0.031 (3)
C6B	0.3935 (10)	0.5014 (6)	0.3561 (5)	0.027 (2)
O11D	1.3279 (6)	0.1806 (4)	0.3335 (3)	0.0205 (14)
O12D	1.2998 (6)	0.0308 (4)	0.2370 (3)	0.0227 (16)
O21D	0.9331 (6)	0.0562 (5)	0.2059 (3)	0.0213 (16)
O31D	1.0026 (6)	0.3206 (4)	0.2331 (3)	0.0255 (16)
O41D	0.6701 (6)	0.1617 (4)	0.3335 (3)	0.0240 (16)
O42D	0.6568 (6)	0.3134 (5)	0.2385 (3)	0.0280 (17)
C1D	1.2342 (9)	0.1077 (6)	0.2827 (4)	0.0173 (19)
C2D	1.0252 (8)	0.1109 (6)	0.2818 (4)	0.0146 (17)
C3D	0.9500 (9)	0.2378 (6)	0.2957 (4)	0.0197 (19)
C4D	0.7397 (9)	0.2382 (6)	0.2880 (4)	0.020 (2)
O11C	0.7704 (6)	0.7011 (4)	−0.0581 (3)	0.0223 (14)
O12C	0.8064 (6)	0.7839 (5)	0.0707 (3)	0.0281 (16)
O21C	0.4577 (6)	0.8208 (5)	0.0689 (3)	0.0251 (17)
O31C	0.5071 (6)	0.5544 (5)	0.0801 (3)	0.0248 (17)
O41C	0.1507 (6)	0.5520 (5)	0.0570 (3)	0.0273 (16)
O42C	0.1257 (6)	0.6830 (4)	−0.0542 (3)	0.0197 (12)
C1C	0.7086 (9)	0.7465 (6)	0.0082 (4)	0.018 (2)
C2C	0.5001 (9)	0.7479 (6)	0.0013 (4)	0.0174 (17)
C3C	0.4269 (9)	0.6155 (6)	0.0054 (4)	0.0209 (19)
C4C	0.2190 (10)	0.6152 (6)	0.0028 (4)	0.021 (2)
O1W	0.8354 (7)	0.4453 (5)	0.0895 (3)	0.0276 (17)
O2W	0.1433 (8)	0.8814 (5)	0.1023 (4)	0.042 (2)
H2A	0.7218	0.9438	0.3816	0.032*
H3A	0.8558	0.8078	0.4869	0.029*
H5A	0.8435	0.5360	0.3125	0.030*
H6A	0.7213	0.6729	0.2073	0.026*
H11A	0.617	0.865	0.169	0.035*
H12A	0.714	0.970	0.215	0.036*
H13A	0.526	0.934	0.231	0.030*
H2B	0.2108	0.6637	0.1944	0.029*
H3B	0.2269	0.8183	0.2983	0.033*
H5B	0.4475	0.5725	0.4750	0.037*
H6B	0.4343	0.4201	0.3705	0.032*
H11B	0.375	0.366	0.233	0.029*

H12B	0.390	0.460	0.168	0.031*
H13B	0.209	0.424	0.183	0.033*
H2D	0.9973	0.0583	0.3298	0.018*
H3D	1.0024	0.2678	0.3532	0.024*
H11D	1.450	0.174	0.334	0.060*
H21D	0.908	0.108	0.176	0.070*
H31D	0.890	0.360	0.215	0.041*
H2C	0.4472	0.7867	−0.0534	0.021*
H3C	0.4585	0.5688	−0.0446	0.025*
H11C	0.893	0.695	−0.056	0.042*
H21C	0.345	0.842	0.058	0.051*
H31C	0.609	0.525	0.073	0.060*
H11W	0.847	0.364	0.079	0.062*
H12W	0.948	0.478	0.091	0.061*
H21W	0.031	0.873	0.099	0.040*
H22W	0.193	0.928	0.145	0.052*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl4A	0.0468 (12)	0.0268 (10)	0.0363 (11)	0.0033 (9)	0.0056 (9)	0.0137 (9)
N1A	0.021 (3)	0.016 (3)	0.024 (3)	−0.002 (2)	0.010 (2)	−0.002 (2)
C1A	0.020 (3)	0.017 (3)	0.023 (4)	−0.003 (3)	0.000 (3)	−0.001 (3)
C2A	0.034 (4)	0.018 (4)	0.028 (4)	−0.010 (3)	0.007 (3)	0.000 (3)
C3A	0.028 (4)	0.023 (4)	0.021 (4)	−0.007 (3)	0.005 (3)	−0.003 (3)
C4A	0.023 (4)	0.020 (4)	0.027 (4)	0.000 (3)	0.002 (3)	0.009 (3)
C5A	0.026 (4)	0.013 (3)	0.038 (4)	−0.004 (3)	0.011 (3)	−0.002 (3)
C6A	0.019 (4)	0.017 (4)	0.030 (4)	−0.004 (3)	0.007 (3)	−0.009 (3)
Cl4B	0.0475 (13)	0.0352 (11)	0.0515 (13)	−0.0046 (10)	0.0158 (10)	−0.0212 (10)
N1B	0.019 (3)	0.013 (3)	0.026 (3)	−0.003 (2)	0.005 (2)	0.001 (2)
C1B	0.019 (3)	0.019 (4)	0.022 (4)	−0.009 (3)	0.008 (3)	−0.001 (3)
C2B	0.033 (4)	0.019 (4)	0.024 (4)	−0.001 (3)	0.014 (3)	0.004 (3)
C3B	0.028 (4)	0.016 (4)	0.043 (5)	−0.001 (3)	0.017 (3)	−0.003 (3)
C4B	0.021 (4)	0.024 (4)	0.038 (5)	−0.006 (3)	0.012 (3)	−0.014 (3)
C5B	0.031 (4)	0.037 (5)	0.023 (4)	0.004 (3)	0.002 (3)	0.001 (3)
C6B	0.031 (4)	0.014 (3)	0.036 (4)	0.002 (3)	0.007 (3)	0.001 (3)
O11D	0.011 (2)	0.024 (2)	0.027 (3)	0.002 (2)	0.0040 (19)	−0.006 (2)
O12D	0.015 (2)	0.020 (3)	0.035 (3)	0.004 (2)	0.010 (2)	−0.003 (2)
O21D	0.020 (3)	0.014 (2)	0.028 (3)	0.002 (2)	−0.003 (2)	−0.005 (2)
O31D	0.029 (3)	0.011 (2)	0.039 (3)	0.002 (2)	0.014 (2)	0.000 (2)
O41D	0.026 (3)	0.016 (2)	0.032 (3)	0.007 (2)	0.011 (2)	0.001 (2)
O42D	0.023 (3)	0.026 (3)	0.036 (3)	0.004 (2)	0.008 (2)	0.006 (3)
C1D	0.025 (4)	0.014 (3)	0.013 (3)	−0.003 (3)	0.003 (3)	0.002 (3)
C2D	0.018 (3)	0.013 (3)	0.013 (3)	−0.004 (3)	0.003 (3)	−0.004 (3)
C3D	0.021 (3)	0.011 (3)	0.027 (4)	−0.001 (3)	0.003 (3)	−0.005 (3)
C4D	0.025 (4)	0.012 (3)	0.025 (4)	0.002 (3)	0.006 (3)	−0.003 (3)
O11C	0.021 (2)	0.025 (3)	0.022 (2)	−0.001 (2)	0.007 (2)	−0.006 (2)
O12C	0.016 (2)	0.044 (3)	0.024 (3)	−0.001 (2)	0.002 (2)	−0.009 (2)

O21C	0.020 (3)	0.026 (3)	0.030 (3)	0.010 (2)	0.006 (2)	−0.008 (2)
O31C	0.021 (3)	0.024 (3)	0.031 (3)	0.006 (2)	0.009 (2)	0.007 (2)
O41C	0.020 (2)	0.030 (3)	0.032 (3)	−0.006 (2)	0.004 (2)	0.005 (2)
O42C	0.018 (2)	0.021 (2)	0.019 (2)	0.004 (2)	−0.0018 (19)	−0.003 (2)
C1C	0.025 (4)	0.014 (3)	0.018 (4)	0.004 (3)	0.013 (3)	0.003 (3)
C2C	0.020 (3)	0.014 (3)	0.020 (3)	0.005 (3)	0.009 (3)	−0.005 (3)
C3C	0.029 (4)	0.018 (3)	0.017 (3)	0.006 (3)	0.008 (3)	0.001 (3)
C4C	0.032 (4)	0.011 (3)	0.021 (4)	0.000 (3)	0.011 (3)	−0.006 (3)
O1W	0.022 (3)	0.027 (3)	0.034 (3)	−0.004 (2)	0.005 (2)	0.001 (2)
O2W	0.036 (3)	0.044 (4)	0.045 (4)	−0.001 (3)	0.007 (3)	−0.002 (3)

Geometric parameters (Å, °)

Cl4A—C4A	1.756 (7)	N1B—H11B	0.90
Cl4B—C4B	1.760 (8)	C1A—C2A	1.369 (10)
O11C—C1C	1.305 (8)	C1A—C6A	1.392 (10)
O12C—C1C	1.217 (8)	C2A—C3A	1.385 (10)
O21C—C2C	1.407 (8)	C3A—C4A	1.387 (9)
O31C—C3C	1.420 (8)	C4A—C5A	1.372 (9)
O41C—C4C	1.261 (8)	C5A—C6A	1.367 (9)
O42C—C4C	1.292 (8)	C2A—H2A	0.9500
O11C—H11C	0.90	C3A—H3A	0.9500
O21C—H21C	0.85	C5A—H5A	0.9500
O31C—H31C	0.84	C6A—H6A	0.9500
O11D—C1D	1.267 (8)	C1B—C6B	1.384 (10)
O12D—C1D	1.248 (8)	C1B—C2B	1.376 (9)
O21D—C2D	1.433 (8)	C2B—C3B	1.385 (11)
O31D—C3D	1.436 (8)	C3B—C4B	1.371 (11)
O41D—C4D	1.257 (8)	C4B—C5B	1.382 (11)
O42D—C4D	1.237 (8)	C5B—C6B	1.378 (11)
O11D—H11D	0.90	C2B—H2B	0.9500
O21D—H21D	0.74	C3B—H3B	0.9500
O31D—H31D	0.94	C5B—H5B	0.9500
O1W—H11W	0.90	C6B—H6B	0.9500
O1W—H12W	0.90	C1C—C2C	1.520 (9)
N1A—C1A	1.466 (9)	C2C—C3C	1.538 (9)
N1A—H11A	0.91	C3C—C4C	1.522 (10)
N1A—H13A	0.90	C2C—H2C	1.0000
N1A—H12A	0.92	C3C—H3C	1.0000
O2W—H21W	0.82	C1D—C2D	1.533 (9)
O2W—H22W	0.89	C2D—C3D	1.511 (9)
N1B—C1B	1.460 (8)	C3D—C4D	1.532 (9)
N1B—H13B	0.91	C2D—H2D	1.0000
N1B—H12B	0.88	C3D—H3D	1.0000
C1C—O11C—H11C	117	C4B—C5B—C6B	117.8 (7)
C2C—O21C—H21C	108	C1B—C6B—C5B	120.1 (6)
C3C—O31C—H31C	110	C3B—C2B—H2B	120.00
C1D—O11D—H11D	114	C1B—C2B—H2B	120.00
C2D—O21D—H21D	106	C4B—C3B—H3B	121.00

C3D—O31D—H31D	101	C2B—C3B—H3B	121.00
H11W—O1W—H12W	106	C6B—C5B—H5B	121.00
H12A—N1A—H13A	110	C4B—C5B—H5B	121.00
H11A—N1A—H13A	109	C1B—C6B—H6B	120.00
H11A—N1A—H12A	108	C5B—C6B—H6B	120.00
C1A—N1A—H11A	109	O11C—C1C—C2C	113.8 (5)
C1A—N1A—H12A	111	O12C—C1C—C2C	122.1 (6)
C1A—N1A—H13A	109	O11C—C1C—O12C	124.1 (6)
H21W—O2W—H22W	115	O21C—C2C—C3C	112.1 (5)
H12B—N1B—H13B	107	C1C—C2C—C3C	110.0 (5)
C1B—N1B—H11B	108	O21C—C2C—C1C	106.1 (5)
C1B—N1B—H12B	111	C2C—C3C—C4C	110.9 (5)
H11B—N1B—H12B	111	O31C—C3C—C4C	108.7 (5)
H11B—N1B—H13B	111	O31C—C3C—C2C	111.4 (5)
C1B—N1B—H13B	109	O41C—C4C—C3C	118.3 (6)
N1A—C1A—C2A	119.6 (6)	O41C—C4C—O42C	124.8 (7)
N1A—C1A—C6A	118.8 (6)	O42C—C4C—C3C	116.8 (6)
C2A—C1A—C6A	121.5 (6)	C1C—C2C—H2C	110.00
C1A—C2A—C3A	119.3 (6)	C3C—C2C—H2C	110.00
C2A—C3A—C4A	118.5 (6)	O21C—C2C—H2C	109.00
C3A—C4A—C5A	122.1 (6)	C4C—C3C—H3C	109.00
Cl4A—C4A—C5A	119.2 (5)	O31C—C3C—H3C	109.00
Cl4A—C4A—C3A	118.7 (5)	C2C—C3C—H3C	109.00
C4A—C5A—C6A	119.2 (6)	O12D—C1D—C2D	118.4 (6)
C1A—C6A—C5A	119.3 (6)	O11D—C1D—C2D	116.6 (6)
C3A—C2A—H2A	120.00	O11D—C1D—O12D	124.9 (6)
C1A—C2A—H2A	120.00	O21D—C2D—C1D	110.8 (5)
C4A—C3A—H3A	121.00	C1D—C2D—C3D	113.9 (5)
C2A—C3A—H3A	121.00	O21D—C2D—C3D	111.2 (5)
C6A—C5A—H5A	120.00	C2D—C3D—C4D	112.1 (5)
C4A—C5A—H5A	120.00	O31D—C3D—C4D	107.9 (5)
C5A—C6A—H6A	120.00	O31D—C3D—C2D	109.2 (5)
C1A—C6A—H6A	120.00	O41D—C4D—C3D	115.9 (6)
C2B—C1B—C6B	121.0 (6)	O42D—C4D—C3D	117.1 (6)
N1B—C1B—C6B	119.3 (6)	O41D—C4D—O42D	127.0 (6)
N1B—C1B—C2B	119.7 (6)	C1D—C2D—H2D	107.00
C1B—C2B—C3B	119.5 (7)	C3D—C2D—H2D	107.00
C2B—C3B—C4B	118.4 (7)	O21D—C2D—H2D	107.00
Cl4B—C4B—C3B	117.8 (6)	C4D—C3D—H3D	109.00
C3B—C4B—C5B	123.0 (7)	O31D—C3D—H3D	109.00
Cl4B—C4B—C5B	119.2 (6)	C2D—C3D—H3D	109.00
N1A—C1A—C2A—C3A	−177.7 (6)	O12C—C1C—C2C—O21C	12.0 (9)
C6A—C1A—C2A—C3A	0.5 (11)	O12C—C1C—C2C—C3C	−109.5 (7)
N1A—C1A—C6A—C5A	179.0 (6)	O21C—C2C—C3C—O31C	−61.7 (7)
C2A—C1A—C6A—C5A	0.8 (10)	O21C—C2C—C3C—C4C	59.6 (7)
C1A—C2A—C3A—C4A	−0.9 (11)	C1C—C2C—C3C—O31C	56.1 (7)
C2A—C3A—C4A—Cl4A	−178.9 (6)	C1C—C2C—C3C—C4C	177.3 (5)
C2A—C3A—C4A—C5A	0.0 (11)	O31C—C3C—C4C—O41C	−8.5 (8)
Cl4A—C4A—C5A—C6A	−179.8 (5)	O31C—C3C—C4C—O42C	169.8 (5)

C3A—C4A—C5A—C6A	1.3 (11)	C2C—C3C—C4C—O41C	−131.2 (6)
C4A—C5A—C6A—C1A	−1.7 (10)	C2C—C3C—C4C—O42C	47.1 (7)
N1B—C1B—C2B—C3B	−178.2 (6)	O11D—C1D—C2D—O21D	161.6 (5)
C6B—C1B—C2B—C3B	3.2 (11)	O11D—C1D—C2D—C3D	35.4 (8)
N1B—C1B—C6B—C5B	178.6 (6)	O12D—C1D—C2D—O21D	−21.6 (8)
C2B—C1B—C6B—C5B	−2.8 (11)	O12D—C1D—C2D—C3D	−147.8 (6)
C1B—C2B—C3B—C4B	−3.1 (11)	O21D—C2D—C3D—O31D	−69.5 (6)
C2B—C3B—C4B—Cl4B	−179.1 (6)	O21D—C2D—C3D—C4D	49.9 (7)
C2B—C3B—C4B—C5B	2.6 (12)	C1D—C2D—C3D—O31D	56.5 (7)
Cl4B—C4B—C5B—C6B	179.6 (6)	C1D—C2D—C3D—C4D	175.9 (5)
C3B—C4B—C5B—C6B	−2.1 (11)	O31D—C3D—C4D—O41D	173.8 (5)
C4B—C5B—C6B—C1B	2.2 (11)	O31D—C3D—C4D—O42D	−6.5 (8)
O11C—C1C—C2C—O21C	−168.5 (5)	C2D—C3D—C4D—O41D	53.6 (7)
O11C—C1C—C2C—C3C	70.0 (7)	C2D—C3D—C4D—O42D	−126.8 (6)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1A—H11A···O12C	0.91	2.40	3.131 (7)	137
N1A—H11A···O21C	0.91	1.91	2.731 (7)	149
N1A—H12A···O21D^{i}	0.92	1.889	2.765 (8)	160
N1A—H13A···O12D^{ii}	0.90	1.98	2.855 (7)	165
N1B—H11B···O42D	0.90	2.14	2.747 (7)	124
N1B—H12B···O31C	0.88	2.02	2.884 (7)	166
N1B—H12B···O41C	0.88	2.52	2.868 (7)	104
N1B—H13B···O31D^{iii}	0.91	2.13	2.768 (7)	126
N1B—H13B···O41C	0.91	2.43	2.868 (7)	109
O11C—H11C···O42C^{iv}	0.90	1.71	2.609 (6)	179
O11D—H11D···O41D^{iv}	0.90	1.62	2.521 (6)	179
O21C—H21C···O2W	0.85	1.78	2.527 (7)	145
O31C—H31C···O1W	0.84	1.86	2.672 (7)	163
O21D—H21D···O31D	0.74	2.54	2.936 (7)	115
O21D—H21D···O42C^{v}	0.74	2.09	2.768 (7)	151
O31D—H31D···O1W	0.94	2.19	2.798 (7)	121
O31D—H31D···O42D	0.94	1.87	2.554 (6)	127
O1W—H11W···O42C^{v}	0.90	2.02	2.923 (7)	179
O1W—H12W···O41C^{iv}	0.90	1.84	2.702 (7)	161
O2W—H21W···O12C^{iii}	0.82	1.91	2.674 (8)	153
O2W—H22W···O12D^{ii}	0.89	1.92	2.810 (8)	179
C2A—H2A···O41D^{i}	0.95	2.50	3.343 (8)	148
C2B—H2B···O41C	0.95	2.49	3.261 (9)	138
C3B—H3B···O12D^{ii}	0.95	2.59	3.431 (9)	148

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*−1, *y*+1, *z*; (iii) *x*−1, *y*, *z*; (iv) *x*+1, *y*, *z*; (v) −*x*+1, *y*−1/2, −*z*.

Fig. 1

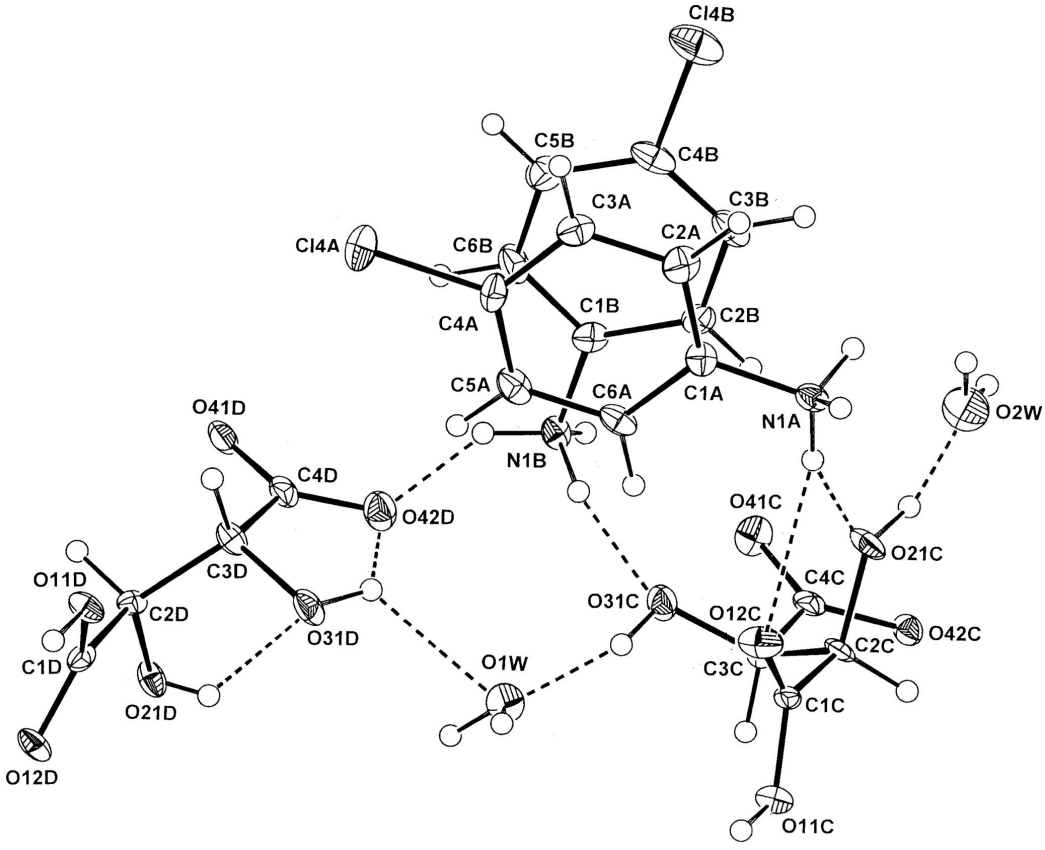
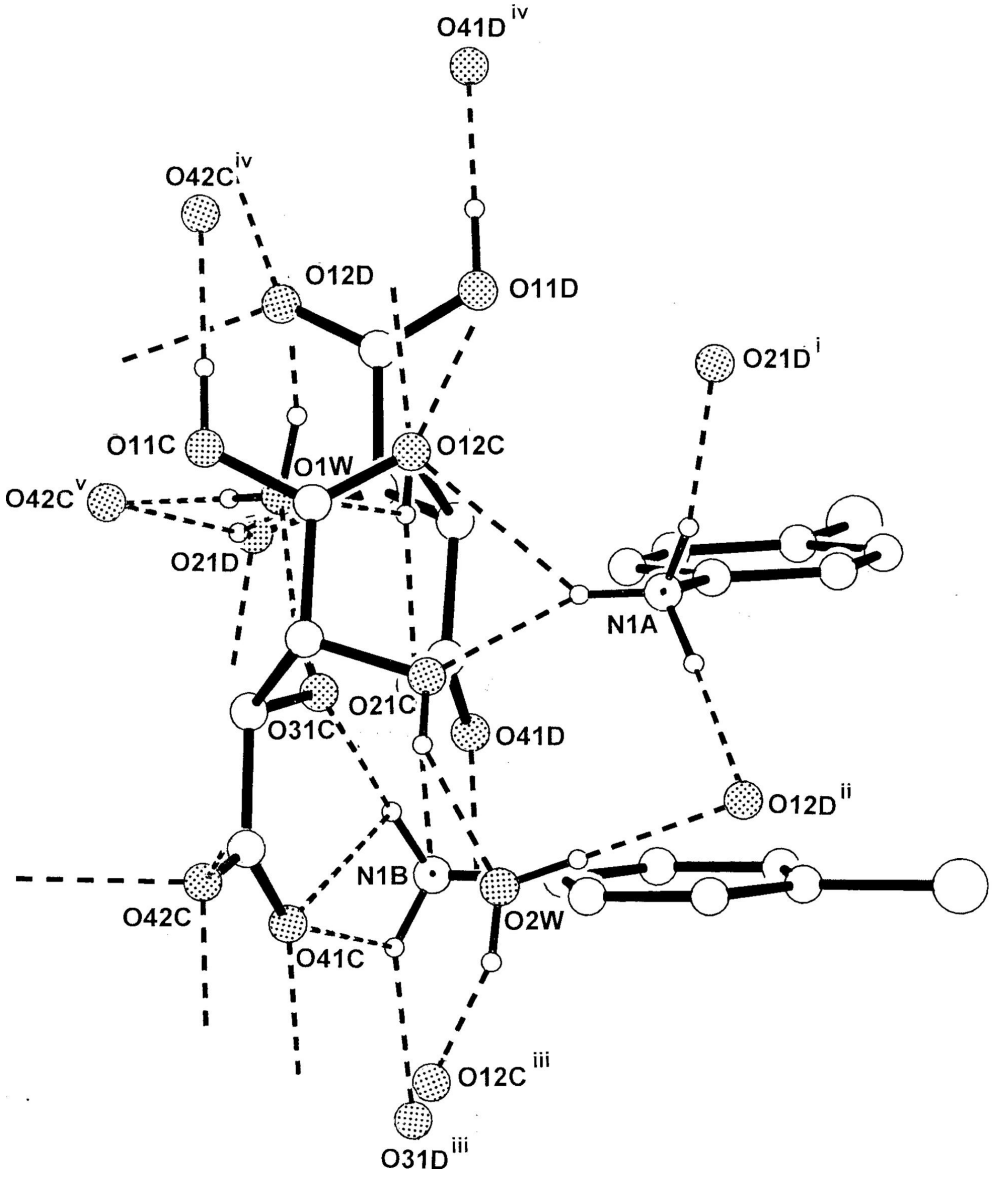

Cl4B
C5B
C4B
C3A
C3B
Cl4A
C6B
C2A
C4A
C1B
C2B
C5A
C6A
C1A
N1A
O2W
O41D
N1B
C4D
O42D
O41C
O21C
C3D
C4C
O11D
C2D
O31C
O12C
O42C
O31D
O1W
C2C
C1D
C3C
O21D
C1C
O12D
O11C

Fig. 2


O41D iv
O42C iv
O12D
O11D
O21D i
O11C
O1W
O12C
O42C v
O21D
N1A
O21C
O31C
O41D
O12D ii
N1B
O42C
O2W
O41C
O12C iii
O31D iii

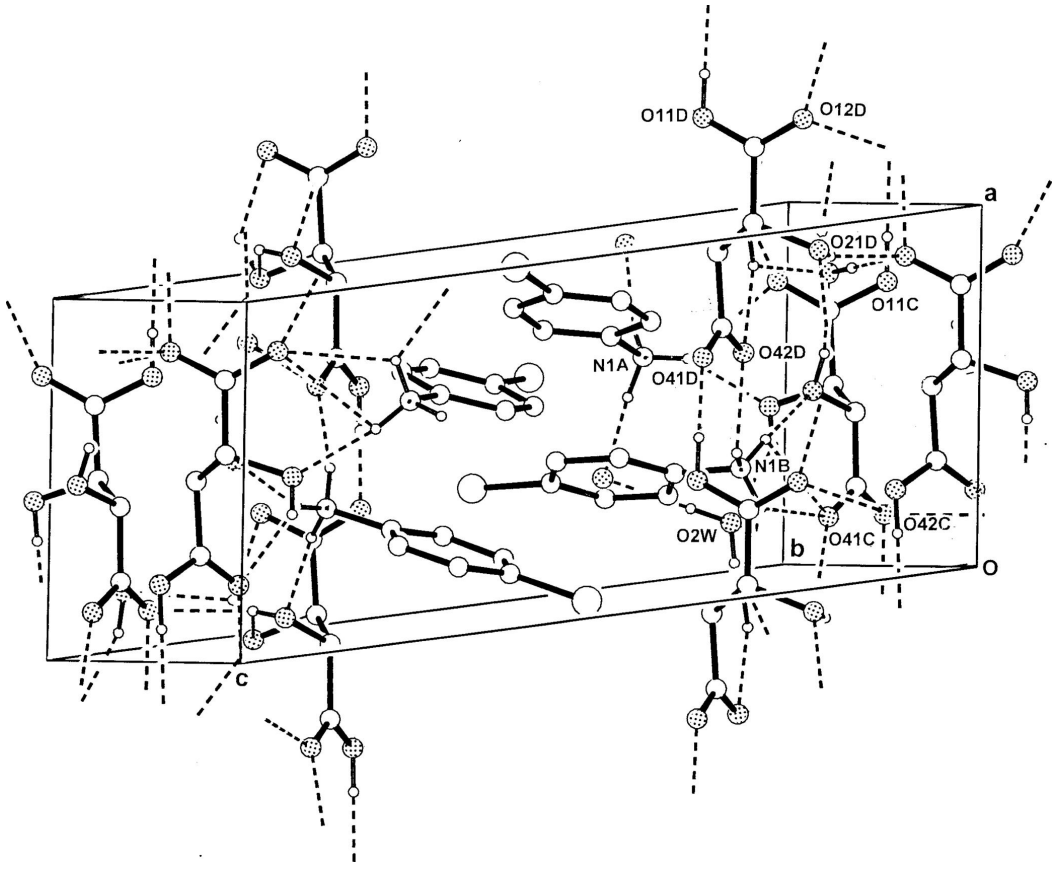



Fig. 3