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Hydrogen Bonding in Two Forms of Bis(diethylenetriammonium) Trioxalate Tetrahydrate

J. C. Barnes and **T. J. R. Weakley**

Abstract

Bis(diethylenetriammonium) trioxalate tetrahydrate, $(C_4H_{16}N_3{}^{3+})_2\cdot(C_2O_4{}^{2-})_3\cdot 4H_2O$, is polymorphic. The all-*trans* conformation of the cation in the monoclinic form of the title compound leads to a less compact hydrogen bond network and an increase in unit cell volume of 5% compared with the triclinic form in which the cation adopts a *trans*-*gauche* conformation.

Comment

As part of our study of hydrogen bonding in carboxylate salts (Barnes and Barnes, 1996, Barnes and Weakley, 1997), diethylene triamine, A, was co-crystallized with oxalic acid, yielding the title compound. This is a neutral oxalate salt, rather than the hydrogen oxalates found from similar reactions with other amines such as ethylene diamine and trimethylene diamine (Barnes and Weakley, 1997). As with the trimethylene diamine system, two forms of the same stoichiometry were obtained containing different conformational isomers of the cation. The structures refined to R1 0.034 (I, triclinic) and *R* 0.063 (II, monoclinic). In both forms the asymmetric unit contains an H_3dien cation (N1—C2—C3—N4—C5—C6—N7), an unconstrained oxalate (B1) (O11,O12—C13—C14—O15,O16), half of a centrosymmetric oxalate (B2) (O18,O19—C20) and two water molecules (O21,O22).

Román, Guzmán-Miralles, Luque and Beitia (1997) recently reported the structure of I. They obtained R1 0.072 from yellow crystals. Yellow or brown degradation products are common impurities in polyamine compounds. Our refinement based on white crystals confirms the molecular architecture from the earlier work and describes the extended hydrogen bond network not discussed in that paper.

In I the H_3dien cation has the terminal N atoms *trans* (N1) and *gauche* (N7) respectively whereas in II the cation has an all *trans* conformation giving zigzag cations which require a more open structure. The volume per asymmetric unit in II is 5% greater than in I.

Hydrogen Bonding.

In I the *gauche* arrangement at N7 allows closed, centrosymmetric, hydrogen- bonded clusters with a 26-membered ring of two amines and two oxalate (B2) groups (C19—O18.·N1–N4–N7.·O17'-C19')$_2$, capped by oxalate (B1) ions (N1.·O16–O11(.·N4').·N7'). (Symmetry relationships are given in the Tables.) These clusters share oxalate (B2) ions along the *bc* diagonal and are connected in the b direction by N1.·O16'' hydrogen bonds.

In II, the hydrogen bonding produces a honeycomb made up of two kinds of fused open columns perpendicular to b. Centrosymmetrically related 23-membered rings B2—A—B1—A'-B2 (–C19—C19'-O17'.·N7–N4.·O11–O16.·N1''–N4''–N7''.·O18—C19-) are connected by centrosymmetric 20-membered rings (–C3—N4.·O11—C13—C14—O16.·N1—C2-)$_2$. (Symmetry relationships are given in the Tables.) Further hydrogen bonds in the b-direction assemble these rings into columns.

In I and II the water molecules are involved in the hydrogen bonding but do not play the pivotal role seen in the diamine/hydrogen oxalate structures. (Barnes and Weakley, 1997). In I both hydrogen bonded water molecules are highly ordered. O21 lies within the large hydrogen bonded cluster and O22 outside. In II the water molecules occupy well defined sites within the larger columns. The hydrogen atoms associated with O21 are well resolved as part of a tetrahedral hydrogen bonding scheme but no satisfactory positions were found for H atoms near O22. It seems likely that this water molecule is slightly disordered in position and can adopt more than one hydrogen bonding scheme.

Experimental

Aqueous solutions of amine (2 mmol) and oxalic acid (3 mmol) were mixed and allowed to crystallize at room temperature. The sample contained I and II as morphologically different forms.

Computing details

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989) for (jcb14bI); *CAD-4 Software* (Enraf-Nonius, 1989) for (jcb14aII). Cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989) for (jcb14bI); *CAD-4 Software* (Enraf-Nonius, 1989) for (jcb14aII). For both compounds, data reduction: *XCAD4* (Harms & Woclado, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997)

Diethylenetriammonium oxalate hydrate (2:3:4)

Crystal data

$C_4H_{16}N_3^{3+}\cdot1.5C_2O_4^{2-}\cdot2H_2O$	$\gamma = 86.618\ (10)°$
$M_r = 274.26$	$V = 640.58\ (12)$ Å^3
Triclinic, $P\overline{1}$	$Z = 2$
$a = 8.5553\ (11)$ Å	Mo $K\alpha$
$b = 9.2494\ (11)$ Å	$\mu = 0.13$ mm^{-1}
$c = 9.3431\ (8)$ Å	$T = 293\ (2)$ K
$\alpha = 66.011\ (9)°$	0.36 × 0.22 × 0.09 mm
$\beta = 72.016\ (9)°$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.009$
Absorption correction: none	3 standard reflections
2405 measured reflections	every 60 min
2242 independent reflections	intensity decay: 4%
1733 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	223 parameters

$wR(F^2) = 0.103$

$S = 0.91$

2242 reflections

Only H-atom coordinates refined

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}

$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °)

N1—C2	1.480 (2)	O12—C13	1.222 (2)
C2—C3	1.494 (3)	C13—C14	1.550 (2)
C3—N4	1.483 (2)	C14—O16	1.243 (2)
N4—C5	1.480 (2)	C14—O15	1.250 (2)
C5—C6	1.500 (3)	O17—C19	1.242 (2)
C6—N7	1.486 (2)	O18—C19	1.257 (2)
O11—C13	1.253 (2)	C19—C19$^{\rm i}$	1.553 (4)
N1—C2—C3	109.63 (15)	O11—C13—C14	116.95 (15)
N4—C3—C2	110.30 (15)	O16—C14—O15	125.62 (16)
C5—N4—C3	111.99 (14)	O16—C14—C13	116.99 (15)
N4—C5—C6	112.93 (16)	O15—C14—C13	117.39 (14)
N7—C6—C5	112.34 (17)	O17—C19—O18	125.83 (17)
O12—C13—O11	125.26 (17)	O17—C19—C19$^{\rm i}$	118.29 (19)
O12—C13—C14	117.78 (16)	O18—C19—C19$^{\rm i}$	115.88 (19)
O11—C13—C14—O15	16.1 (3)	C3—N4—C5—C6	−177.29 (17)
N1—C2—C3—N4	−178.07 (15)	N4—C5—C6—N7	−76.9 (2)
C2—C3—N4—C5	−173.55 (17)		

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

Table 2

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O16	0.93 (2)	1.98 (2)	2.834 (2)	152.4 (19)
N1—H1A···O12	0.93 (2)	2.30 (2)	2.965 (2)	128.6 (17)
N1—H1B···O16$^{\rm ii}$	0.94 (2)	1.86 (2)	2.770 (2)	164.1 (19)
N1—H1C···O18	0.90 (2)	1.95 (2)	2.837 (2)	168.3 (19)
N4—H4A···O15$^{\rm iii}$	0.86 (2)	1.91 (2)	2.728 (2)	157 (2)
N4—H4B···O11$^{\rm iv}$	0.90 (2)	1.92 (2)	2.805 (2)	165.3 (19)
N4—H4A···O11$^{\rm iii}$	0.86 (2)	2.40 (2)	2.986 (2)	125.6 (18)
N7—H7A···O21	0.92 (3)	1.84 (3)	2.732 (2)	160 (2)
N7—H7B···O17$^{\rm iv}$	0.93 (3)	1.88 (3)	2.809 (2)	175 (2)
N7—H7C···O11$^{\rm iv}$	0.93 (3)	1.98 (3)	2.881 (2)	164 (2)
O21—H21A···O18$^{\rm v}$	0.84 (3)	1.85 (3)	2.684 (2)	172 (3)
O21—H21B···O15$^{\rm vi}$	0.87 (3)	1.86 (3)	2.7228 (19)	171 (2)
O22—H22A···O12	0.91 (4)	2.15 (4)	2.946 (3)	145 (3)
O22—H22B···O18	0.82 (4)	2.23 (4)	3.006 (3)	158 (4)

Symmetry codes: (ii) $-x+1, -y+1, -z+2$; (iii) $x+1, y, z$; (iv) $-x+1, -y, -z+2$; (v) $-x+2, -y, -z+2$; (vi) $-x+1, -y, -z+3$.

CIF access

Diethylenetriammonium oxalate hydrate (2:3:4)

Crystal data

$C_4H_{16}N_3^{3+}\cdot 1.5C_2O_4^{2-}\cdot 2H_2O$

$M_r = 274.26$

Monoclinic, $P2_1/c$

$a = 19.3069\ (16)$ Å

$b = 6.6698\ (9)$ Å

$c = 12.0449\ (9)$ Å

$\beta = 120.166\ (7)°$

$V = 1341.0\ (2)$ Å^3

$Z = 4$

Mo $K\alpha$

$\mu = 0.12$ mm^{-1}

$T = 293\ (2)$ K

0.36 × 0.14 × 0.04 mm

Data collection

Enraf-Nonius CAD-4 diffractometer

Absorption correction: none

2483 measured reflections

2356 independent reflections

1206 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.028$

3 standard reflections

every 60 min

intensity decay: 13%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$

$wR(F^2) = 0.218$

$S = 0.97$

2356 reflections

217 parameters

Only H-atom coordinates refined

$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}

$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O12	0.89 (5)	1.85 (5)	2.727 (5)	165 (4)
N1—H1B···O11$^{\rm i}$	1.12 (5)	1.65 (5)	2.769 (5)	174 (4)
N1—H1C···O12$^{\rm ii}$	0.96 (5)	1.99 (5)	2.827 (5)	145 (4)
N1—H1C···O16$^{\rm ii}$	0.96 (5)	2.20 (5)	2.930 (5)	132 (4)
N4—H4A···O11$^{\rm iii}$	0.83 (5)	2.12 (5)	2.866 (4)	149 (5)
N4—H4A···O15$^{\rm iii}$	0.83 (5)	2.16 (5)	2.807 (5)	135 (4)
N4—H4B···O16$^{\rm iv}$	1.15 (5)	1.61 (5)	2.749 (5)	169 (4)
N7—H7A···O18$^{\rm v}$	0.93 (5)	1.84 (6)	2.765 (5)	174 (5)
N7—H7B···O17$^{\rm vi}$	0.91 (5)	1.93 (6)	2.793 (5)	156 (5)
N7—H7C···O17$^{\rm vii}$	0.93 (5)	2.03 (6)	2.847 (5)	145 (4)
N7—H7C···O18	0.93 (5)	2.15 (5)	2.867 (5)	133 (4)
O21—H21A···O22	1.00 (9)	1.87 (9)	2.840 (7)	162 (7)
O21—H21B···O15	0.95 (9)	1.81 (9)	2.753 (5)	173 (7)

Symmetry codes: (i) $-x+1, y-1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, -y, -z+2$; (v) $-x, -y+1, -z+1$; (vi) $x, -y+1/2, z+1/2$; (vii) $-x, -y, -z+1$.

References

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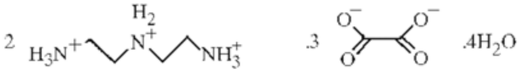
CIF access

Scheme 1



supplementary materials

Diethylenetriammonium oxalate hydrate (2:3:4)

Crystal data

$C_4H_{16}N_3^{3+}\cdot 1.5C_2O_4^{2-}\cdot 2H_2O$

$M_r = 274.26$

Triclinic, $P\bar{1}$

$a = 8.5553$ (11) Å

$b = 9.2494$ (11) Å

$c = 9.3431$ (8) Å

$\alpha = 66.011$ (9)°

$\beta = 72.016$ (9)°

$\gamma = 86.618$ (10)°

$V = 640.58$ (12) Å^3

$Z = 2$

$F_{000} = 294$

$D_x = 1.422$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Cell parameters from 25 reflections

$\theta = 14$–15°

$\mu = 0.13$ mm^{-1}

$T = 293$ (2) K

Block, colourless

0.36 × 0.22 × 0.09 mm

Data collection

Enraf-Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

ω–2θ scans

Absorption correction: none

2405 measured reflections

2242 independent reflections

1733 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$

$\theta_{\text{max}} = 25.0$°

$\theta_{\text{min}} = 2.5$°

$h = 0\rightarrow10$

$k = -10\rightarrow10$

$l = -10\rightarrow11$

3 standard reflections

every 60 min

intensity decay: 4%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.103$

$S = 0.91$

2242 reflections

223 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.2535P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.010$

$\Delta\rho_{\text{max}} = 0.25$ e Å^{-3}

$\Delta\rho_{\text{min}} = -0.19$ e Å^{-3}

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\text{sigma}(F^2)$ 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}
N1	0.64582 (19)	0.40348 (19)	0.8417 (2)	0.0307 (3)
H1A	0.535 (3)	0.369 (3)	0.896 (3)	0.046*
H1B	0.669 (3)	0.495 (3)	0.853 (3)	0.046*
H1C	0.667 (3)	0.424 (2)	0.734 (3)	0.046*
C2	0.7501 (2)	0.2803 (2)	0.9155 (2)	0.0357 (4)
H2A	0.859 (3)	0.333 (3)	0.874 (3)	0.054*
H2B	0.746 (3)	0.196 (3)	0.886 (3)	0.054*
C3	0.6876 (2)	0.2217 (2)	1.0991 (2)	0.0353 (4)
H3A	0.579 (3)	0.169 (3)	1.143 (3)	0.053*
H3B	0.684 (3)	0.305 (3)	1.134 (3)	0.053*
N4	0.79425 (18)	0.10207 (18)	1.17477 (17)	0.0287 (3)
H4A	0.891 (3)	0.148 (3)	1.146 (3)	0.043*
H4B	0.805 (3)	0.025 (3)	1.137 (3)	0.043*
C5	0.7261 (3)	0.0277 (2)	1.3569 (2)	0.0393 (4)
H5A	0.619 (3)	−0.027 (3)	1.384 (3)	0.059*
H5B	0.711 (3)	0.109 (3)	1.392 (3)	0.059*
C6	0.8359 (3)	−0.0882 (2)	1.4366 (3)	0.0404 (5)
H6A	0.950 (3)	−0.045 (3)	1.384 (3)	0.061*
H6B	0.800 (3)	−0.116 (3)	1.555 (3)	0.061*
N7	0.8258 (2)	−0.24197 (19)	1.4236 (2)	0.0376 (4)
H7A	0.893 (3)	−0.309 (3)	1.477 (3)	0.056*
H7B	0.716 (3)	−0.284 (3)	1.473 (3)	0.056*
H7C	0.858 (3)	−0.226 (3)	1.314 (3)	0.056*
O11	0.12423 (16)	0.14982 (17)	0.92222 (17)	0.0468 (4)
O12	0.38788 (19)	0.1709 (3)	0.8931 (3)	0.0802 (6)
C13	0.2440 (2)	0.1934 (2)	0.9494 (2)	0.0336 (4)
C14	0.2050 (2)	0.2799 (2)	1.0664 (2)	0.0302 (4)
O15	0.05879 (15)	0.26865 (18)	1.15455 (18)	0.0472 (4)
O16	0.32244 (15)	0.35381 (16)	1.06522 (17)	0.0440 (4)
O17	0.50902 (17)	0.35068 (17)	0.42873 (18)	0.0478 (4)
O18	0.68761 (15)	0.42554 (18)	0.52006 (17)	0.0457 (4)
C19	0.5559 (2)	0.4351 (2)	0.4847 (2)	0.0328 (4)
O21	0.99347 (18)	−0.41521 (18)	1.63597 (18)	0.0436 (4)
H21A	1.096 (4)	−0.418 (3)	1.594 (3)	0.065*
H21B	0.983 (3)	−0.376 (3)	1.709 (3)	0.065*
O22	0.6824 (3)	0.0719 (3)	0.7011 (3)	0.0800 (6)
H22A	0.593 (5)	0.059 (5)	0.791 (5)	0.120*
H22B	0.667 (5)	0.161 (5)	0.641 (5)	0.120*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0285 (8)	0.0357 (8)	0.0313 (8)	−0.0002 (6)	−0.0101 (6)	−0.0159 (7)
C2	0.0355 (10)	0.0400 (10)	0.0347 (10)	0.0072 (8)	−0.0111 (8)	−0.0188 (8)
C3	0.0323 (10)	0.0394 (10)	0.0344 (10)	0.0067 (8)	−0.0100 (8)	−0.0160 (8)
N4	0.0255 (8)	0.0319 (8)	0.0313 (8)	0.0011 (6)	−0.0075 (6)	−0.0163 (7)
C5	0.0444 (11)	0.0428 (11)	0.0309 (10)	0.0070 (9)	−0.0086 (8)	−0.0181 (9)
C6	0.0500 (12)	0.0409 (11)	0.0366 (10)	0.0011 (9)	−0.0195 (9)	−0.0173 (9)
N7	0.0379 (9)	0.0389 (9)	0.0392 (9)	0.0009 (7)	−0.0157 (8)	−0.0160 (8)
O11	0.0401 (8)	0.0637 (9)	0.0526 (8)	−0.0050 (7)	−0.0113 (6)	−0.0406 (8)
O12	0.0350 (9)	0.1233 (16)	0.1198 (16)	0.0039 (9)	−0.0037 (9)	−0.1008 (14)
C13	0.0314 (10)	0.0355 (9)	0.0350 (9)	−0.0051 (7)	−0.0042 (8)	−0.0191 (8)
C14	0.0282 (9)	0.0320 (9)	0.0343 (9)	0.0000 (7)	−0.0095 (7)	−0.0171 (8)
O15	0.0289 (7)	0.0677 (9)	0.0583 (9)	−0.0057 (6)	−0.0013 (6)	−0.0466 (8)
O16	0.0303 (7)	0.0548 (8)	0.0619 (9)	−0.0044 (6)	−0.0095 (6)	−0.0408 (7)
O17	0.0426 (8)	0.0575 (9)	0.0625 (9)	0.0069 (6)	−0.0200 (7)	−0.0408 (8)
O18	0.0291 (7)	0.0731 (10)	0.0505 (8)	0.0153 (6)	−0.0187 (6)	−0.0373 (8)
C19	0.0271 (9)	0.0439 (10)	0.0291 (9)	0.0027 (8)	−0.0082 (7)	−0.0170 (8)
O21	0.0325 (7)	0.0631 (9)	0.0461 (8)	0.0070 (6)	−0.0120 (6)	−0.0336 (7)
O22	0.1126 (17)	0.0730 (13)	0.0602 (12)	0.0285 (12)	−0.0247 (11)	−0.0373 (10)

Geometric parameters (Å, °)

N1—C2	1.480 (2)	O12—C13	1.222 (2)
C2—C3	1.494 (3)	C13—C14	1.550 (2)
C3—N4	1.483 (2)	C14—O16	1.243 (2)
N4—C5	1.480 (2)	C14—O15	1.250 (2)
C5—C6	1.500 (3)	O17—C19	1.242 (2)
C6—N7	1.486 (2)	O18—C19	1.257 (2)
O11—C13	1.253 (2)	C19—C19$^{\mathrm{i}}$	1.553 (4)
N1—C2—C3	109.63 (15)	O11—C13—C14	116.95 (15)
N4—C3—C2	110.30 (15)	O16—C14—O15	125.62 (16)
C5—N4—C3	111.99 (14)	O16—C14—C13	116.99 (15)
N4—C5—C6	112.93 (16)	O15—C14—C13	117.39 (14)
N7—C6—C5	112.34 (17)	O17—C19—O18	125.83 (17)
O12—C13—O11	125.26 (17)	O17—C19—C19$^{\mathrm{i}}$	118.29 (19)
O12—C13—C14	117.78 (16)	O18—C19—C19$^{\mathrm{i}}$	115.88 (19)
O11—C13—C14—O15	16.1 (3)	C3—N4—C5—C6	−177.29 (17)
N1—C2—C3—N4	−178.07 (15)	N4—C5—C6—N7	−76.9 (2)
C2—C3—N4—C5	−173.55 (17)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O16	0.93 (2)	1.98 (2)	2.834 (2)	152.4 (19)

N1—H1A···O12	0.93 (2)	2.30 (2)	2.965 (2)	128.6 (17)
N1—H1B···O16^{ii}	0.94 (2)	1.86 (2)	2.770 (2)	164.1 (19)
N1—H1C···O18	0.90 (2)	1.95 (2)	2.837 (2)	168.3 (19)
N4—H4A···O15^{iii}	0.86 (2)	1.91 (2)	2.728 (2)	157 (2)
N4—H4B···O11^{iv}	0.90 (2)	1.92 (2)	2.805 (2)	165.3 (19)
N4—H4A···O11^{iii}	0.86 (2)	2.40 (2)	2.986 (2)	125.6 (18)
N7—H7A···O21	0.92 (3)	1.84 (3)	2.732 (2)	160 (2)
N7—H7B···O17^{iv}	0.93 (3)	1.88 (3)	2.809 (2)	175 (2)
N7—H7C···O11^{iv}	0.93 (3)	1.98 (3)	2.881 (2)	164 (2)
O21—H21A···O18^{v}	0.84 (3)	1.85 (3)	2.684 (2)	172 (3)
O21—H21B···O15^{vi}	0.87 (3)	1.86 (3)	2.7228 (19)	171 (2)
O22—H22A···O12	0.91 (4)	2.15 (4)	2.946 (3)	145 (3)
O22—H22B···O18	0.82 (4)	2.23 (4)	3.006 (3)	158 (4)

Symmetry codes: (ii) $-x+1, -y+1, -z+2$; (iii) $x+1, y, z$; (iv) $-x+1, -y, -z+2$; (v) $-x+2, -y, -z+2$; (vi) $-x+1, -y, -z+3$.

Diethylenetriammonium oxalate hydrate (2:3:4)

Crystal data

$C_4H_{16}N_3^{3+}\cdot 1.5C_2O_4^{2-}\cdot 2H_2O$	$F_{000} = 588$
$M_r = 274.26$	$D_x = 1.358$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 19.3069$ (16) Å	Cell parameters from 25 reflections
$b = 6.6698$ (9) Å	$\theta = 14$–15°
$c = 12.0449$ (9) Å	$\mu = 0.12$ mm^{-1}
$\beta = 120.166$ (7)°	$T = 293$ (2) K
$V = 1341.0$ (2) Å^3	Lath, colourless
$Z = 4$	0.36 × 0.14 × 0.04 mm

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{int} = 0.028$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.1$°
Monochromator: graphite	$\theta_{min} = 2.4$°
$T = 293(2)$ K	$h = -22\rightarrow19$
ω–2θ scans	$k = 0\rightarrow7$
Absorption correction: none	$l = 0\rightarrow14$
2483 measured reflections	3 standard reflections
2356 independent reflections	every 60 min
1206 reflections with $I > 2\sigma(I)$	intensity decay: 13%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.063$	Only H-atom coordinates refined
$wR(F^2) = 0.218$	$w = 1/[\sigma^2(F_o^2) + (0.1298P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.040$
2356 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

Refinement. The hydrogen atoms on the water molecule at O22 are omitted since no satisfactory positions were located.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
N1	0.4279 (2)	0.2973 (6)	0.6808 (3)	0.0324 (9)
H1A	0.481 (3)	0.283 (7)	0.733 (4)	0.049*
H1B	0.401 (3)	0.172 (7)	0.610 (4)	0.049*
H1C	0.415 (3)	0.416 (8)	0.629 (4)	0.049*
C2	0.3903 (3)	0.2963 (9)	0.7612 (4)	0.0438 (12)
H2A	0.415 (3)	0.381 (9)	0.825 (5)	0.066*
H2B	0.401 (3)	0.170 (8)	0.802 (5)	0.066*
C3	0.3016 (2)	0.3302 (8)	0.6806 (4)	0.0373 (11)
H3A	0.285 (3)	0.461 (8)	0.628 (5)	0.056*
H3B	0.272 (3)	0.235 (8)	0.616 (5)	0.056*
N4	0.2657 (2)	0.3373 (5)	0.7646 (3)	0.0307 (9)
H4A	0.287 (3)	0.429 (8)	0.818 (5)	0.046*
H4B	0.283 (2)	0.205 (7)	0.835 (4)	0.046*
C5	0.1775 (3)	0.3651 (8)	0.6911 (4)	0.0368 (11)
H5A	0.159 (3)	0.252 (8)	0.643 (5)	0.055*
H5B	0.168 (3)	0.479 (8)	0.637 (5)	0.055*
C6	0.1460 (3)	0.3957 (8)	0.7821 (4)	0.0418 (11)
H6A	0.174 (3)	0.493 (8)	0.843 (5)	0.063*
H6B	0.159 (3)	0.276 (9)	0.838 (5)	0.063*
N7	0.0595 (2)	0.4298 (6)	0.7097 (4)	0.0365 (9)
H7A	0.046 (3)	0.536 (8)	0.652 (5)	0.055*

H7B	0.039 (3)	0.425 (8)	0.764 (5)	0.055*
H7C	0.034 (3)	0.318 (8)	0.659 (5)	0.055*
O11	0.6280 (2)	0.4819 (4)	0.9920 (3)	0.0543 (10)
O12	0.58148 (17)	0.2144 (5)	0.8667 (3)	0.0467 (9)
C13	0.6245 (2)	0.2975 (6)	0.9723 (4)	0.0333 (10)
C14	0.6771 (2)	0.1642 (7)	1.0883 (4)	0.0350 (10)
O15	0.7182 (3)	0.2475 (6)	1.1912 (3)	0.0887 (16)
O16	0.6776 (2)	−0.0173 (5)	1.0692 (3)	0.0618 (11)
O17	−0.02220 (19)	−0.0150 (5)	0.3407 (3)	0.0431 (8)
O18	−0.0097 (2)	0.2513 (5)	0.4599 (3)	0.0600 (10)
C19	−0.0098 (2)	0.0693 (7)	0.4427 (4)	0.0324 (10)
O21	0.8136 (3)	0.0749 (7)	1.4281 (4)	0.0872 (15)
H21A	0.837 (5)	0.191 (13)	1.489 (8)	0.131*
H21B	0.784 (5)	0.138 (12)	1.347 (9)	0.131*
O22	0.8518 (3)	0.3927 (8)	1.6066 (5)	0.1073 (17)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0340 (19)	0.026 (2)	0.0307 (18)	0.0041 (16)	0.0110 (16)	0.0031 (15)
C2	0.041 (3)	0.055 (3)	0.027 (2)	0.004 (2)	0.011 (2)	0.002 (2)
C3	0.038 (3)	0.039 (3)	0.029 (2)	0.000 (2)	0.0133 (19)	0.001 (2)
N4	0.036 (2)	0.024 (2)	0.0253 (17)	−0.0030 (15)	0.0104 (15)	−0.0034 (14)
C5	0.041 (2)	0.036 (3)	0.029 (2)	0.002 (2)	0.0139 (19)	−0.0041 (19)
C6	0.053 (3)	0.040 (3)	0.034 (2)	0.007 (2)	0.023 (2)	−0.002 (2)
N7	0.051 (2)	0.032 (2)	0.036 (2)	0.0033 (18)	0.0284 (19)	0.0005 (17)
O11	0.080 (2)	0.0208 (18)	0.0429 (19)	0.0026 (16)	0.0165 (17)	0.0004 (14)
O12	0.0453 (17)	0.0341 (18)	0.0369 (17)	0.0071 (14)	0.0030 (14)	−0.0049 (14)
C13	0.038 (2)	0.028 (3)	0.030 (2)	−0.0023 (18)	0.0145 (19)	−0.0020 (18)
C14	0.041 (2)	0.026 (3)	0.032 (2)	−0.0030 (19)	0.0143 (19)	−0.0011 (18)
O15	0.125 (4)	0.035 (2)	0.0327 (19)	0.004 (2)	−0.015 (2)	0.0012 (17)
O16	0.106 (3)	0.023 (2)	0.0361 (18)	0.0082 (17)	0.0203 (19)	0.0046 (14)
O17	0.063 (2)	0.0390 (19)	0.0339 (16)	−0.0030 (15)	0.0289 (15)	−0.0031 (14)
O18	0.098 (3)	0.032 (2)	0.0418 (19)	0.0010 (19)	0.0295 (19)	0.0033 (16)
C19	0.033 (2)	0.036 (3)	0.025 (2)	−0.0014 (19)	0.0126 (17)	0.0027 (19)
O21	0.114 (4)	0.057 (3)	0.060 (3)	0.001 (2)	0.021 (3)	0.015 (2)
O22	0.102 (4)	0.103 (4)	0.096 (3)	−0.016 (3)	0.034 (3)	−0.036 (3)

Geometric parameters (Å, °)

N1—C2	1.474 (6)	O12—C13	1.246 (5)
C2—C3	1.502 (6)	C13—C14	1.532 (6)
C3—N4	1.487 (5)	C14—O15	1.219 (5)
N4—C5	1.485 (6)	C14—O16	1.233 (5)
C5—C6	1.511 (6)	O17—C19	1.259 (5)
C6—N7	1.463 (6)	O18—C19	1.231 (5)
O11—C13	1.248 (5)	C19—C19$^{\text{i}}$	1.543 (8)
N1—C2—C3	110.6 (3)	O11—C13—C14	116.8 (4)

N4—C3—C2	109.5 (3)	O15—C14—O16	125.1 (4)
C5—N4—C3	112.7 (3)	O15—C14—C13	117.2 (4)
N4—C5—C6	110.1 (3)	O16—C14—C13	117.6 (4)
N7—C6—C5	110.1 (4)	O18—C19—O17	126.0 (4)
O12—C13—O11	125.2 (4)	O18—C19—C19^{i}	117.5 (5)
O12—C13—C14	117.9 (4)	O17—C19—C19^{i}	116.5 (5)
N1—C2—C3—N4	−177.6 (4)	N4—C5—C6—N7	178.1 (4)
C2—C3—N4—C5	−178.5 (4)	O12—C13—C14—O15	−179.3 (5)
C3—N4—C5—C6	−173.3 (4)		

Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O12	0.89 (5)	1.85 (5)	2.727 (5)	165 (4)
N1—H1B···O11^{ii}	1.12 (5)	1.65 (5)	2.769 (5)	174 (4)
N1—H1C···O12^{iii}	0.96 (5)	1.99 (5)	2.827 (5)	145 (4)
N1—H1C···O16^{iii}	0.96 (5)	2.20 (5)	2.930 (5)	132 (4)
N4—H4A···O11^{iv}	0.83 (5)	2.12 (5)	2.866 (4)	149 (5)
N4—H4A···O15^{iv}	0.83 (5)	2.16 (5)	2.807 (5)	135 (4)
N4—H4B···O16^{v}	1.15 (5)	1.61 (5)	2.749 (5)	169 (4)
N7—H7A···O18^{vi}	0.93 (5)	1.84 (6)	2.765 (5)	174 (5)
N7—H7B···O17^{vii}	0.91 (5)	1.93 (6)	2.793 (5)	156 (5)
N7—H7C···O17^{i}	0.93 (5)	2.03 (6)	2.847 (5)	145 (4)
N7—H7C···O18	0.93 (5)	2.15 (5)	2.867 (5)	133 (4)
O21—H21A···O22	1.00 (9)	1.87 (9)	2.840 (7)	162 (7)
O21—H21B···O15	0.95 (9)	1.81 (9)	2.753 (5)	173 (7)

Symmetry codes: (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) −*x*+1, −*y*+1, −*z*+2; (v) −*x*+1, −*y*, −*z*+2; (vi) −*x*, −*y*+1, −*z*+1; (vii) *x*, −*y*+1/2, *z*+1/2; (i) −*x*, −*y*, −*z*+1.