Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Hydrazinediium bis(3,5,6-tricarboxypyrazine-2-carboxylate) hexahydrate

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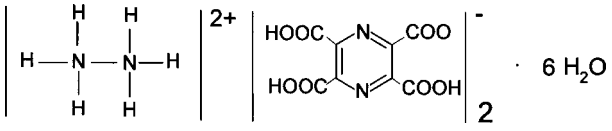
Received 19 July 2007; accepted 2 August 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.138; data-to-parameter ratio = 14.6.

The triclinic unit cell of the title compound, $N_2H_6^{2+}\cdot 2C_8H_3N_2O_8^{-}\cdot 6H_2O$, contains one doubly protonated hydrazine cation which lies on an inversion centre, two symmetry-related singly deprotonated 3,5,6-tricarboxypyrazine-2-carboxylate anions and six solvent water molecules. In the crystal structure, a three-dimensional hydrogen-bonded network is constructed between the protonated carboxylate O atoms, protonated hydrazine cations and solvent water molecules.

Related literature

For the crystal structures of the title anion combined with metal cations, see: Marioni *et al.* (1994); Gryz *et al.* (2005).



Experimental

Crystal data

$N_2H_6^{2+}\cdot 2C_8H_3N_2O_8^{-}\cdot 6H_2O$
M_r = 652.41
Triclinic, $P\overline{1}$
a = 7.3871 (15) Å
b = 9.3453 (19) Å
c = 9.4942 (19) Å
α = 82.93 (3)°
β = 83.73 (3)°
γ = 72.24 (3)°
V = 617.7 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 293 (2) K
0.30 × 0.12 × 0.07 mm

Data collection

Kuma KM-4 four-circle diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2000)
T_{min} = 0.975, T_{max} = 0.985
3809 measured reflections
3606 independent reflections
2606 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
3 standard reflections
every 200 reflections
intensity decay: 0.4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.138
S = 1.05
3606 reflections
247 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H121···O11	0.90 (2)	1.95 (2)	2.8212 (19)	162 (2)
N3—H31···O4	1.00 (3)	2.04 (3)	3.015 (2)	162 (2)
N3—H31···O8	1.00 (3)	2.20 (3)	2.7064 (18)	109.4 (19)
N3—H33···O10^{i}	0.93 (2)	1.93 (2)	2.8031 (19)	155 (2)
N3—H33···O8^{ii}	0.93 (2)	2.30 (2)	2.8627 (19)	118.0 (17)
O10—H101···O4^{iii}	0.81 (3)	1.94 (3)	2.7461 (18)	171 (2)
O10—H102···N2	0.77 (3)	2.18 (3)	2.9066 (17)	156 (3)
O10—H102···O7	0.77 (3)	2.51 (3)	3.0884 (17)	132 (3)
O11—H112···O2^{iii}	0.83 (3)	2.43 (3)	3.125 (2)	141 (3)
O11—H112···O2^{iv}	0.83 (3)	2.46 (3)	3.007 (2)	124 (2)
O1—H1···O10^{v}	0.81 (4)	1.82 (4)	2.6252 (17)	173 (3)
O12—H122···N1^{vi}	0.66 (2)	2.79 (2)	2.9458 (19)	97 (2)
O12—H122···O1^{vi}	0.66 (2)	2.79 (2)	2.929 (2)	95 (2)
N3—H32···O11	1.10 (3)	1.67 (3)	2.742 (2)	164 (2)
O5—H5···O4^{vii}	0.99 (4)	1.58 (4)	2.5736 (16)	177 (4)
O11—H111···O3^{ii}	0.91 (3)	1.90 (3)	2.7744 (19)	161 (3)
O7—H7···O12	0.83 (4)	1.67 (4)	2.4865 (18)	169 (4)

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

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2467).

References

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  doi:10.1107/S1600536807038135

supplementary materials

Acta Cryst. (2007). E**63**, o3734 [**doi:10.1107/S1600536807038135**]

Hydrazinediium bis(3,5,6-tricarboxypyrazine-2-carboxylate) hexahydrate

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Comment

The molecular structure of the title compound contains one doubly- protonated hydrazine cation having its geometrical centre on an inversion centre at 1/2,1/2,0, two symmetry related singly-deprotonated pyrazine- 2,3, 5,6-tetracarboxylate anions and three pairs of symmetry related solvent water molecules. Fig.1. shows the asymmetric unit with atom labelling scheme. Atoms forming the pyrazine ring are coplanar (r.m.s. 0.0032 Å). Carboxylate groups form the following angles with the plane of the pyrazine ring: 11.3 (2)° (C7/O1/O2), 58.5 (2)° (C8/O3/O4), 82.1 (2)° (C9/O5/O6) and 23.5 (2)° (C10/O7/O8). Bond lengths and bond angles within the pyrazine ring do not differ from those reported in other ionic metal complexes with the title ligand (Gryz *et al.*, 2005; Marioni *et al.*, 1994). In the crystal structure, an extended hydrogen bond network is constructed (Fig. 2) *via* protonated carboxylate O atoms of the anions acting as donors in strong bonds [2.480 (2)- 2.626 (2) Å] to solvent water and non-protonated carboxylate O atoms. Hydrazine N atoms also act as also donors in hydrogen bonds bonds to non-protonated carboxylate and solvent water O atoms, the latter donate their O atoms to weak bonds linking them to carboxylate O atoms.

Experimental

The title compound was obtained unintentionally in the course of attempts to obtain single crystals of a zinc complex with pyrazine-2,3,5,6-tetracarboxylic ligand. Pale-yellow single crystals of the title compound were separated from a mass of polycrystalline material, washed with cold water and dried in the air. Hydrazine was used to maintain the acidity of the initial solution.

Refinement

All H atoms were located in a difference map and refined with isotropic displacement parameters.

Figures

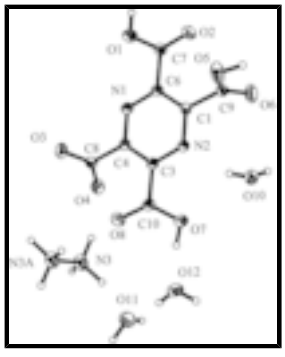


Fig. 1. The asymmetric unit with atom labels and 50% probability displacement ellipsoids for non-H atoms. The hydrazine cation is symmetry complete (symmetry code: (A) −*x* + 1, −*y* + 1, −*z*).

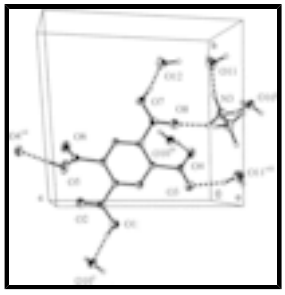


Fig. 2. A fragment of the hydrogen bond network in the structure. For clarity, only bonds with d<2.8Å are indicated. Symmetry code: (i)*x*,*y*,*z* − 1; (ii)-*x* + 1,-*y* + 1,*z*; (iii)-*x*-*y* + 1,-*z* + 1; (iv)*x*,*y* + 1,*z* − 1; (v)*x*,*y* − 1,*z*; (vi)*x*,*y* + 1,*z*; (vii)*x*.*y*,*z* + 1; (viii)-*x* + 1,-*y*,-*z*.

Hydrazinediium bis(3,5,6-tricarboxypyrazine-2-carboxylate) hexahydrate

Crystal data

$N_2H_6^{2+}\cdot 2C_8H_3N_2O_8^-\cdot 6H_2O$	$Z = 1$
$M_r = 652.41$	$F_{000} = 338$
Triclinic, $P\bar{1}$	$D_x = 1.754$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.3871$ (15) Å	Cell parameters from 25 reflections
$b = 9.3453$ (19) Å	$\theta = 6$–15°
$c = 9.4942$ (19) Å	$\mu = 0.17$ mm^{-1}
$\alpha = 82.93$ (3)°	$T = 293$ (2) K
$\beta = 83.73$ (3)°	Rectangular blocks, pale yellow
$\gamma = 72.24$ (3)°	0.30 × 0.12 × 0.07 mm
$V = 617.7$ (2) Å^3	

Data collection

Kuma KM-4 four-circle diffractometer	$R_{int} = 0.010$
Radiation source: fine-focus sealed tube	$\theta_{max} = 30.1^\circ$
Monochromator: graphite	$\theta_{min} = 2.2^\circ$
$T = 293(2)$ K	$h = -9\rightarrow10$
profile data from ω/–2θ scans	$k = 0\rightarrow12$
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2000)	$l = -13\rightarrow13$
$T_{min} = 0.975$, $T_{max} = 0.985$	3 standard reflections
3809 measured reflections	every 200 reflections
3606 independent reflections	intensity decay: 0.4%
2606 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	All H-atom parameters refined

$wR(F^2) = 0.138$	$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2 + 0.1092P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3606 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
247 parameters	$\Delta\rho_{min} = -0.36$ 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. 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}
N2	0.20465 (16)	0.36376 (12)	0.60373 (11)	0.0189 (2)
N1	0.24160 (17)	0.10473 (12)	0.47527 (11)	0.0202 (2)
C9	0.11430 (19)	0.26486 (15)	0.83419 (13)	0.0205 (3)
C4	0.27719 (19)	0.22494 (14)	0.40009 (13)	0.0182 (2)
C1	0.16787 (18)	0.24388 (14)	0.67820 (13)	0.0178 (2)
C6	0.18665 (19)	0.11358 (14)	0.61342 (13)	0.0187 (2)
C10	0.32009 (19)	0.48649 (14)	0.38932 (13)	0.0200 (2)
C7	0.1434 (2)	−0.02063 (15)	0.69872 (14)	0.0222 (3)
C3	0.26019 (18)	0.35528 (14)	0.46594 (13)	0.0178 (2)
C8	0.3337 (2)	0.20828 (15)	0.24250 (13)	0.0200 (3)
O7	0.24607 (19)	0.61045 (12)	0.45014 (12)	0.0327 (3)
O3	0.47317 (18)	0.10377 (13)	0.21073 (12)	0.0337 (3)
O2	0.06495 (19)	−0.01124 (13)	0.81724 (12)	0.0334 (3)
O12	0.3699 (3)	0.82052 (15)	0.33870 (14)	0.0375 (3)
O5	0.26197 (18)	0.20910 (17)	0.90837 (12)	0.0382 (3)
O6	−0.04224 (17)	0.33557 (15)	0.87695 (12)	0.0347 (3)
O8	0.43073 (17)	0.47009 (12)	0.28463 (11)	0.0289 (2)
O1	0.1973 (2)	−0.14131 (13)	0.62962 (12)	0.0353 (3)
O11	0.33128 (19)	0.83427 (15)	0.04456 (14)	0.0350 (3)
O10	0.16102 (17)	0.61037 (12)	0.77595 (12)	0.0260 (2)
H121	0.378 (3)	0.833 (3)	0.243 (3)	0.036 (5)*
N3	0.39902 (19)	0.53719 (17)	0.00114 (14)	0.0297 (3)
O4	0.22560 (17)	0.30338 (13)	0.15643 (10)	0.0288 (2)
H31	0.342 (4)	0.470 (3)	0.071 (3)	0.050 (6)*
H33	0.353 (3)	0.547 (3)	−0.088 (2)	0.037 (5)*

H101	0.049 (4)	0.627 (3)	0.802 (2)	0.036 (6)*
H102	0.192 (4)	0.558 (3)	0.715 (3)	0.055 (7)*
H112	0.216 (5)	0.878 (4)	0.040 (3)	0.059 (8)*
H1	0.184 (5)	−0.214 (4)	0.681 (4)	0.077 (10)*
H122	0.277 (3)	0.851 (3)	0.336 (2)	0.024 (6)*
H32	0.362 (4)	0.651 (3)	0.037 (3)	0.062 (8)*
H5	0.248 (6)	0.243 (4)	1.005 (5)	0.101 (12)*
H111	0.395 (4)	0.873 (3)	−0.030 (3)	0.056 (7)*
H7	0.294 (5)	0.673 (5)	0.404 (4)	0.089 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0276 (5)	0.0150 (5)	0.0157 (5)	−0.0084 (4)	0.0005 (4)	−0.0036 (4)
N1	0.0307 (6)	0.0160 (5)	0.0155 (5)	−0.0090 (4)	−0.0007 (4)	−0.0031 (4)
C9	0.0289 (6)	0.0180 (5)	0.0155 (5)	−0.0089 (5)	0.0024 (4)	−0.0030 (4)
C4	0.0256 (6)	0.0149 (5)	0.0143 (5)	−0.0060 (4)	−0.0006 (4)	−0.0028 (4)
C1	0.0228 (5)	0.0167 (5)	0.0144 (5)	−0.0063 (4)	−0.0003 (4)	−0.0035 (4)
C6	0.0263 (6)	0.0155 (5)	0.0154 (5)	−0.0079 (4)	−0.0014 (4)	−0.0019 (4)
C10	0.0275 (6)	0.0174 (6)	0.0171 (5)	−0.0090 (5)	−0.0028 (4)	−0.0021 (4)
C7	0.0303 (6)	0.0181 (6)	0.0197 (6)	−0.0102 (5)	−0.0011 (5)	−0.0011 (4)
C3	0.0246 (6)	0.0147 (5)	0.0150 (5)	−0.0068 (4)	−0.0012 (4)	−0.0026 (4)
C8	0.0302 (6)	0.0184 (6)	0.0139 (5)	−0.0106 (5)	0.0009 (4)	−0.0042 (4)
O7	0.0537 (7)	0.0179 (5)	0.0287 (5)	−0.0169 (5)	0.0115 (5)	−0.0076 (4)
O3	0.0418 (6)	0.0269 (5)	0.0242 (5)	0.0005 (5)	0.0055 (4)	−0.0055 (4)
O2	0.0485 (7)	0.0267 (5)	0.0239 (5)	−0.0142 (5)	0.0098 (5)	−0.0008 (4)
O12	0.0590 (10)	0.0221 (5)	0.0329 (6)	−0.0176 (6)	0.0082 (6)	−0.0039 (4)
O5	0.0341 (6)	0.0552 (8)	0.0193 (5)	0.0003 (5)	−0.0050 (4)	−0.0132 (5)
O6	0.0315 (6)	0.0386 (6)	0.0279 (5)	−0.0020 (5)	0.0057 (4)	−0.0093 (4)
O8	0.0380 (6)	0.0266 (5)	0.0230 (5)	−0.0135 (4)	0.0068 (4)	−0.0036 (4)
O1	0.0641 (8)	0.0193 (5)	0.0270 (5)	−0.0216 (5)	0.0077 (5)	−0.0050 (4)
O11	0.0343 (6)	0.0357 (6)	0.0341 (6)	−0.0114 (5)	0.0001 (5)	0.0003 (5)
O10	0.0317 (5)	0.0235 (5)	0.0252 (5)	−0.0119 (4)	0.0049 (4)	−0.0085 (4)
N3	0.0286 (6)	0.0354 (7)	0.0229 (6)	−0.0072 (5)	−0.0004 (5)	−0.0018 (5)
O4	0.0371 (6)	0.0302 (5)	0.0162 (4)	−0.0044 (4)	−0.0038 (4)	−0.0039 (4)

Geometric parameters (Å, °)

N2—C3	1.3321 (16)	C8—O3	1.2234 (18)
N2—C1	1.3333 (17)	C8—O4	1.2753 (18)
N1—C6	1.3349 (16)	O7—H7	0.83 (4)
N1—C4	1.3351 (17)	O12—H121	0.90 (2)
C9—O6	1.1983 (18)	O12—H122	0.66 (2)
C9—O5	1.2993 (18)	O5—H5	0.99 (4)
C9—C1	1.5115 (17)	O1—H1	0.81 (4)
C4—C3	1.4026 (17)	O11—H112	0.83 (3)
C4—C8	1.5226 (17)	O11—H111	0.91 (3)
C1—C6	1.3939 (17)	O10—H101	0.81 (3)
C6—C7	1.5063 (18)	O10—H102	0.77 (3)

C10—O8	1.2096 (17)	N3—N3^{i}	1.440 (3)
C10—O7	1.2976 (17)	N3—H31	1.00 (3)
C10—C3	1.5065 (18)	N3—H33	0.93 (2)
C7—O2	1.2087 (17)	N3—H32	1.10 (3)
C7—O1	1.3083 (17)		
C3—N2—C1	118.13 (11)	O1—C7—C6	112.71 (12)
C6—N1—C4	118.09 (11)	N2—C3—C4	121.16 (12)
O6—C9—O5	126.47 (13)	N2—C3—C10	116.41 (11)
O6—C9—C1	122.20 (13)	C4—C3—C10	122.20 (11)
O5—C9—C1	111.05 (12)	O3—C8—O4	126.48 (12)
N1—C4—C3	120.52 (11)	O3—C8—C4	117.62 (12)
N1—C4—C8	115.17 (11)	O4—C8—C4	115.86 (12)
C3—C4—C8	124.31 (11)	C10—O7—H7	106 (3)
N2—C1—C6	120.85 (11)	H121—O12—H122	87 (2)
N2—C1—C9	113.15 (11)	C9—O5—H5	116 (2)
C6—C1—C9	125.95 (11)	C7—O1—H1	111 (2)
N1—C6—C1	121.25 (12)	H112—O11—H111	108 (3)
N1—C6—C7	118.50 (11)	H101—O10—H102	112 (3)
C1—C6—C7	120.25 (11)	N3^{i}—N3—H31	103.8 (15)
O8—C10—O7	126.14 (13)	N3^{i}—N3—H33	111.9 (14)
O8—C10—C3	120.78 (12)	H31—N3—H33	111 (2)
O7—C10—C3	113.04 (12)	N3^{i}—N3—H32	111.7 (15)
O2—C7—O1	126.05 (13)	H31—N3—H32	111 (2)
O2—C7—C6	121.23 (12)	H33—N3—H32	107 (2)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H121···O11	0.90 (2)	1.95 (2)	2.8212 (19)	162 (2)
N3—H31···O4	1.00 (3)	2.04 (3)	3.015 (2)	162 (2)
N3—H31···O8	1.00 (3)	2.20 (3)	2.7064 (18)	109.4 (19)
N3—H33···O10^{ii}	0.93 (2)	1.93 (2)	2.8031 (19)	155 (2)
N3—H33···O8^{i}	0.93 (2)	2.30 (2)	2.8627 (19)	118.0 (17)
O10—H101···O4^{iii}	0.81 (3)	1.94 (3)	2.7461 (18)	171 (2)
O10—H102···N2	0.77 (3)	2.18 (3)	2.9066 (17)	156 (3)
O10—H102···O7	0.77 (3)	2.51 (3)	3.0884 (17)	132 (3)
O11—H112···O2^{iii}	0.83 (3)	2.43 (3)	3.125 (2)	141 (3)
O11—H112···O2^{iv}	0.83 (3)	2.46 (3)	3.007 (2)	124 (2)
O1—H1···O10^{v}	0.81 (4)	1.82 (4)	2.6252 (17)	173 (3)
O12—H122···N1^{vi}	0.66 (2)	2.79 (2)	2.9458 (19)	97 (2)
O12—H122···O1^{vi}	0.66 (2)	2.79 (2)	2.929 (2)	95 (2)
N3—H32···O11	1.10 (3)	1.67 (3)	2.742 (2)	164 (2)
O5—H5···O4^{vii}	0.99 (4)	1.58 (4)	2.5736 (16)	177 (4)
O11—H111···O3^{i}	0.91 (3)	1.90 (3)	2.7744 (19)	161 (3)
O7—H7···O12	0.83 (4)	1.67 (4)	2.4865 (18)	169 (4)

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

Fig. 1

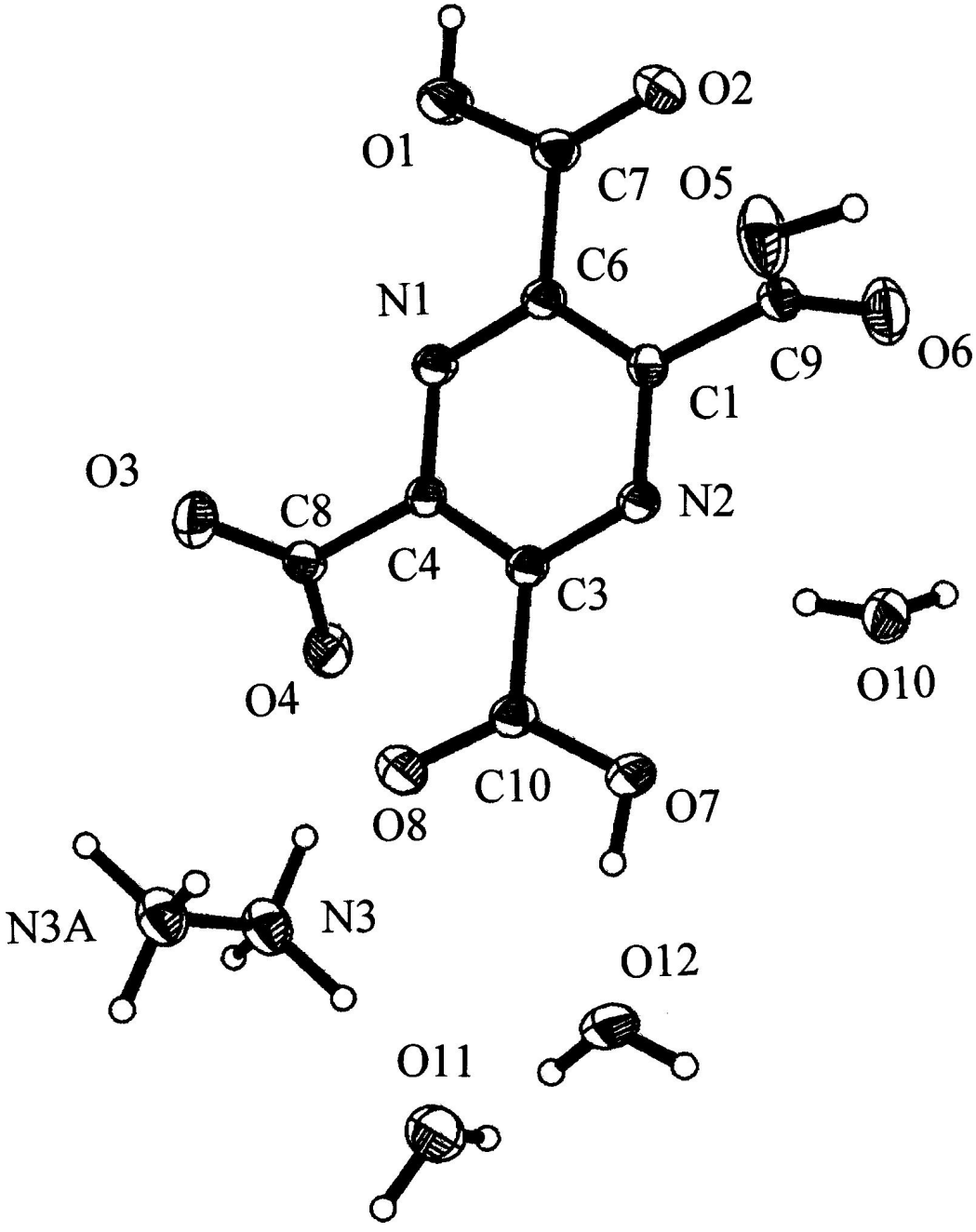
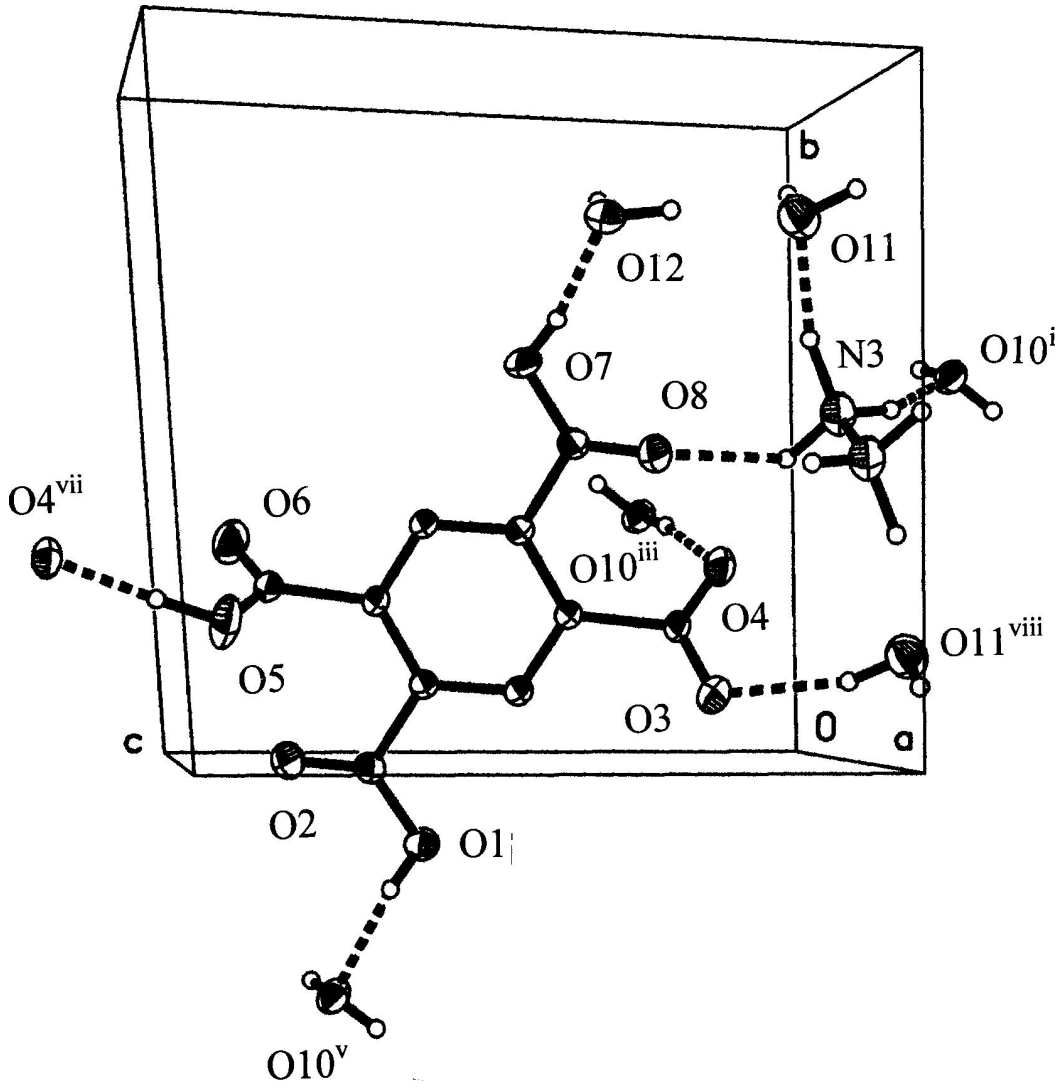


Fig. 2


b
O12
O11
O7
N3
O10i
O8
O4vii
O6
O10iii
O4
O11viii
O5
O3
0
a
c
O2
O1
O10v