Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3,7-Bis(dimethylamino)phenothiazin-5-ium nitrate dihydrate

Savaridasson Jose Kavitha,[a] Mani Mohan Raj,[a] Krishnaswamy Panchanatheswaran[a] and Daniel E. Lynch[b]*

[a]Department of Chemistry, Bharathidasan University, Tiruchirappalli 24, India, and [b]School of Science and the Environment, Coventry University, Coventry CV1 5FB, England

Correspondence e-mail: apx106@coventry.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.068
wR factor = 0.206
Data-to-parameter ratio = 16.0

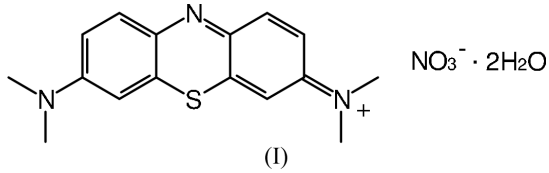
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 24 June 2004
Accepted 14 July 2004
Online 24 July 2004

The reaction of 3,7-bis(dimethylamino)phenothiazin-5-ium chloride pentahydrate (methylene blue) with silver nitrate in a 1:2 molar ratio in water yielded the title compound, $C_{16}H_{18}N_3S^+\cdot NO_3^-\cdot 2H_2O$, as one of the products. The cationic dye molecules are planar and stacked in an antiparallel fashion, exhibiting π–π associations at a distance of 3.7040 (18) Å. The nitrate anion and the two water molecules are involved in a hydrogen-bonding network that also includes the phenothiazinium N atom.

Comment

Methylene blue (MB) is an important cationic dye with various colorimetric uses (Tuite & Kelly, 1993). It is marketed as its chloride salt. Other forms, such as the cyanide and nitrate [the title compound, (I)] salts exhibit anti-methemoglobinemic, antiseptic and disinfectant properties (The Merck Index, 2001). The Cambridge Structural Database (Version 5.25, April 2004 update; Allen, 2002) includes four MB crystal structures containing the phenothiazinium moiety, as chloride pentahydrate (Marr *et al.*, 1973), triiodide (Endres *et al.*, 1977), thiocyanate (Kahn-Harari *et al.*, 1973), urate hexahydrate (Sours *et al.*, 2002) and bis(maleonitriledithiolato)cuprate(II) (Snaathorst *et al.*, 1981) salts. In each case, the bond distances in the MB cations indicate a resonance structure in which the positive charge is delocalized over the two dimethylamine N atoms, with conjugation through the phenothiazinium N atom, although the MB cation is sometimes represented as aromatic with a positive S atom. The addition of $AgNO_3$ to aqueous MB chloride solution does not precipitate silver chloride, yet the IR spectrum of the product shows features very different from that of the starting materials. Further investigations are currently underway to determine the nature of the resultant soluble silver product but here we report the structure of the precipitated product.



(I)

The asymmetric unit of (I) consists of an MB cation, a nitrate anion and two water molecules (Fig. 1). The MB cation displays a typical MB resonance structure, as evident from the pronounced shortening of the C1—C2, C4—C12, C8—C9 and C6—C13 bonds compared with other C—C bonds (Table 1). The two C—S bonds are equal in length, indicating that

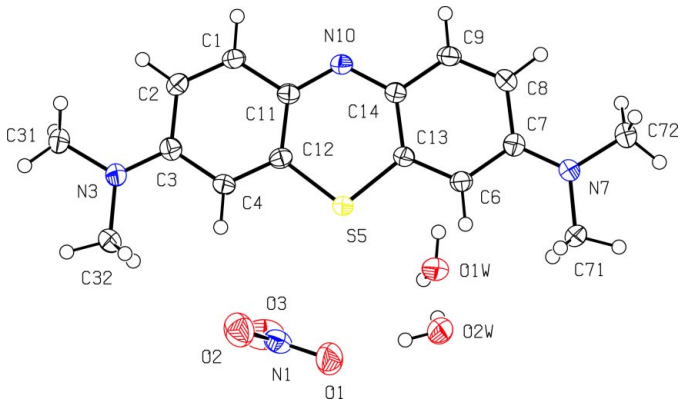


Figure 1
Molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

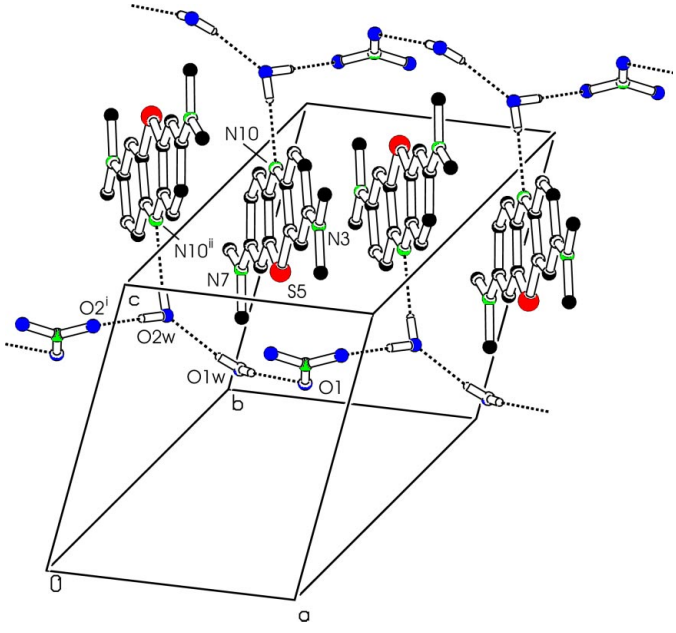


Figure 2
Packing diagram for (I). For clarity, the non-essential H atoms have been omitted. [Symmetry codes: (i) $-1+x, y, z$; (ii) $-x, -y+1, -z+2$.]

conjugation occurs *via* N10. The MB cation is thus planar and the cations are stacked in an antiparallel fashion, exhibiting π–π associations at a distance of 3.7040 (18) Å. In contrast to MB chloride, which crystallizes with five lattice water molecules, the degree of hydration of the MB nitrate is lower. This difference may be due in part to the hydrogen-bonding network and the fact that more hydrogen-bond acceptor atoms are available on the nitrate ion than for a chloride anion. Hydrogen-bonding associations are listed in Table 2 and indicate that all of the strong hydrogen-bond donor atoms are utilized, although this is not the case for the strong hydrogen-bond acceptor atoms. Only one hydrogen-bond acceptor atom from the phenothiazinium moiety, N10, is involved in the hydrogen-bond network, along with two nitrate O atoms and one water O atom. The nitrate ion and the water molecules form a one-dimensional hydrogen-bonded chain in the *a* cell direction (Fig. 2). There are close contacts between the S atom and the nitrate N atom [3.369 (4) Å] and also between atom O3 and both N3 [2.906 (4) Å; symmetry code: $(1-x, -y, 2-z)$] and C32 [2.962 (4) Å; symmetry code: $(1-x, -y, 2-z)$], although for the latter there is no appropriate H atom to construct a C—H···O association. These close contacts for O3 may explain why there is no strong hydrogen-bonding interaction with this atom. Two unassigned areas of electron density, 0.64 and 0.59 e Å^{-3}, exist approximately equidistant, 1.94 and 1.96 Å, respectively, from atom S5, which may be the cause of the higher than expected *R* values.

Experimental

Methylene blue (1 mmol) was dissolved with silver nitrate (2 mmol) in water (10 ml). Crystals of the title compound were obtained by the slow evaporation of this reaction mixture.

Crystal data

$C_{16}H_{18}N_3S^+\cdot NO_3^-\cdot 2H_2O$
$M_r = 382.44$
Triclinic, $P\overline{1}$
$a = 7.6985$ (3) Å
$b = 10.9638$ (3) Å
$c = 11.3244$ (4) Å
$\alpha = 87.081$ (2)°
$\beta = 76.032$ (2)°
$\gamma = 73.524$ (2)°
$V = 889.33$ (5) Å^3
$Z = 2$
$D_x = 1.428$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 187 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.22$ mm^{-1}
$T = 120$ (2) K
Prism, red
0.42 × 0.36 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.836$, $T_{max} = 0.952$
17 489 measured reflections
4077 independent reflections
3225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 27.6°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.206$
$S = 1.13$
4077 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 1.7607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—C2	1.359 (4)	C6—C7	1.415 (4)
C1—C11	1.430 (4)	C7—N7	1.340 (4)
C2—C3	1.439 (4)	C7—C8	1.436 (4)
C3—N3	1.335 (4)	C8—C9	1.361 (4)
C3—C4	1.416 (4)	C9—C14	1.424 (4)
C4—C12	1.373 (4)	N10—C11	1.335 (4)
S5—C13	1.728 (3)	N10—C14	1.344 (4)
S5—C12	1.728 (3)	C11—C12	1.438 (4)
C6—C13	1.376 (4)	C13—C14	1.432 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H11W···O2^{i}	0.88 (5)	1.91 (5)	2.789 (4)	174 (4)
O1W—H12W···N10^{ii}	0.84 (5)	2.10 (5)	2.929 (4)	172 (4)
O2W—H21W···O1	0.81 (6)	2.14 (6)	2.886 (5)	154 (5)
O2W—H22W···O1W	0.75 (5)	2.05 (5)	2.792 (4)	171 (5)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, 2-z$.

All H atoms, except the water H atoms, were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.95 (aromatic H atoms) and 0.98 Å (CH_3 H atoms). The isotropic displacement parameters were set equal to $1.25U_{eq}$ of the carrier atom. The water H atoms were located in difference syntheses and both positional and displacement parameters were refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*, *SCALEPACK* (Otwinowski & Minor, 1997) and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

The authors thank the EPSRC National Crystallography Service (Southampton, England).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Endres, H., Jeromin, G. & Keller, H. J. (1977). *Z. Naturforsch. Teil B*, **32**, 1375–1378.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Kahn-Harari, A., Ballard, R. E. & Norris, E. K. (1973). *Acta Cryst.* B**29**, 1124–1126.
Marr, H. E. III, Stewart, J. M. & Chiu, M. F. (1973). *Acta Cryst.* B**29**, 847–853.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Snaathorst, D., Doesburg, H. M., Perenboom, J. A. A. J. & Keijzers, C. P. (1981). *Inorg. Chem.* **20**, 2526–2532.
Sours, R. E., Fink, D. A. & Swift, J. A. (2002). *J. Am. Chem. Soc.* **124**, 8630–8636.
Spek, A. L. (1997). *PLATON*97. University of Utrecht, The Netherlands.
The Merck Index (2001). 13th ed. Whitehouse Station: Merck and Co. Inc.
Tuite, E. M. & Kelly, J. M. (1993). *J. Photochem. Photobiol. B*, **21**, 103–124.

supporting information

Acta Cryst. (2004). E**60**, o1367–o1369 [https://doi.org/10.1107/S1600536804017222]

3,7-Bis(dimethylamino)phenothiazin-5-ium nitrate dihydrate

Savaridasson Jose Kavitha, Mani Mohan Raj, Krishnaswamy Panchanatheswaran and Daniel E. Lynch

3,7-Bis(dimethylamino)phenothiazin-5-ium nitrate dihydrate

Crystal data

$C_{16}H_{18}N_3S^+\cdot NO_3^-\cdot 2H_2O$
$M_r = 382.44$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.6985$ (3) Å
$b = 10.9638$ (3) Å
$c = 11.3244$ (4) Å
$\alpha = 87.081$ (2)°
$\beta = 76.032$ (2)°
$\gamma = 73.524$ (2)°
$V = 889.33$ (5) Å^3
$Z = 2$
$F(000) = 404$
$D_x = 1.428$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 12187 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.22$ mm^{-1}
$T = 120$ K
Prism, red
0.42 × 0.36 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
$T_{min} = 0.836$, $T_{max} = 0.952$
17489 measured reflections
4077 independent reflections
3225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 27.6°$, $\theta_{min} = 3.0°$
$h = -9\rightarrow 9$
$k = -14\rightarrow 14$
$l = -14\rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.206$
$S = 1.13$
4077 reflections
255 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 1.7607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3039 (4)	0.4163 (3)	1.2264 (3)	0.0253 (6)
H1	0.2291	0.4793	1.2864	0.032*
C2	0.4150 (4)	0.3079 (3)	1.2620 (3)	0.0256 (6)
H2	0.4170	0.2967	1.3455	0.032*
C3	0.5295 (4)	0.2101 (3)	1.1740 (3)	0.0244 (6)
N3	0.6397 (4)	0.1028 (3)	1.2068 (2)	0.0272 (6)
C31	0.6448 (5)	0.0733 (3)	1.3341 (3)	0.0345 (8)
H311	0.6506	0.1483	1.3749	0.043*
H312	0.7550	0.0025	1.3368	0.043*
H313	0.5321	0.0495	1.3756	0.043*
C32	0.7498 (5)	0.0020 (3)	1.1173 (3)	0.0356 (8)
H321	0.6679	−0.0213	1.0738	0.045*
H322	0.8106	−0.0726	1.1590	0.045*
H323	0.8448	0.0322	1.0592	0.045*
C4	0.5233 (4)	0.2303 (3)	1.0504 (3)	0.0245 (6)
H4	0.5982	0.1670	0.9908	0.031*
S5	0.40954 (11)	0.35433 (7)	0.86311 (7)	0.0265 (2)
C6	0.2292 (4)	0.5433 (3)	0.7434 (3)	0.0241 (6)
H6	0.2934	0.4895	0.6741	0.030*
C7	0.1059 (4)	0.6632 (3)	0.7289 (3)	0.0239 (6)
N7	0.0768 (4)	0.6987 (3)	0.6188 (2)	0.0278 (6)
C71	0.1732 (6)	0.6157 (3)	0.5125 (3)	0.0372 (8)
H711	0.3070	0.6078	0.4951	0.046*
H712	0.1244	0.6520	0.4422	0.046*
H713	0.1531	0.5315	0.5287	0.046*
C72	−0.0522 (5)	0.8200 (3)	0.5977 (3)	0.0343 (8)
H721	−0.1634	0.8390	0.6653	0.043*
H722	−0.0887	0.8143	0.5215	0.043*
H723	0.0091	0.8879	0.5923	0.043*
C8	0.0147 (4)	0.7430 (3)	0.8354 (3)	0.0258 (7)
H8	−0.0662	0.8250	0.8282	0.032*
C9	0.0430 (5)	0.7022 (3)	0.9465 (3)	0.0263 (7)
H9	−0.0202	0.7566	1.0155	0.033*
N10	0.1816 (4)	0.5488 (2)	1.0768 (2)	0.0232 (5)
C11	0.2953 (4)	0.4392 (3)	1.1023 (3)	0.0226 (6)
C12	0.4104 (4)	0.3402 (3)	1.0157 (3)	0.0231 (6)
C13	0.2576 (4)	0.5031 (3)	0.8561 (3)	0.0216 (6)
C14	0.1637 (4)	0.5808 (3)	0.9632 (3)	0.0223 (6)
N1	0.7431 (4)	0.0916 (3)	0.7386 (3)	0.0341 (7)
O1	0.7351 (4)	0.1430 (3)	0.6394 (3)	0.0543 (8)
O2	0.8749 (4)	0.0886 (3)	0.7856 (3)	0.0531 (8)
O3	0.6206 (5)	0.0440 (3)	0.7940 (3)	0.0568 (9)
O1W	0.0499 (4)	0.2807 (3)	0.7190 (2)	0.0354 (6)
H11W	−0.012 (6)	0.223 (5)	0.738 (4)	0.043 (12)*
H12W	−0.022 (7)	0.334 (5)	0.772 (5)	0.049 (13)*

O2W	0.3966 (5)	0.2779 (3)	0.5684 (2)	0.0390 (6)
H21W	0.471 (8)	0.225 (5)	0.597 (5)	0.058 (16)*
H22W	0.306 (7)	0.271 (5)	0.606 (5)	0.044 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0292 (16)	0.0240 (15)	0.0211 (14)	−0.0060 (13)	−0.0038 (12)	−0.0036 (11)
C2	0.0275 (16)	0.0290 (16)	0.0206 (14)	−0.0081 (13)	−0.0058 (12)	0.0002 (12)
C3	0.0210 (15)	0.0255 (15)	0.0258 (15)	−0.0064 (12)	−0.0042 (12)	0.0019 (12)
N3	0.0273 (14)	0.0271 (14)	0.0242 (13)	−0.0021 (11)	−0.0071 (11)	0.0013 (10)
C31	0.0397 (19)	0.0335 (18)	0.0248 (16)	−0.0006 (15)	−0.0098 (14)	0.0040 (13)
C32	0.0344 (19)	0.0325 (18)	0.0309 (17)	0.0059 (14)	−0.0084 (14)	−0.0015 (14)
C4	0.0225 (15)	0.0238 (15)	0.0235 (15)	−0.0022 (12)	−0.0028 (12)	−0.0022 (11)
S5	0.0305 (4)	0.0231 (4)	0.0199 (4)	0.0013 (3)	−0.0048 (3)	−0.0022 (3)
C6	0.0260 (15)	0.0231 (15)	0.0222 (14)	−0.0063 (12)	−0.0041 (12)	−0.0016 (11)
C7	0.0243 (15)	0.0243 (15)	0.0246 (15)	−0.0089 (12)	−0.0064 (12)	0.0022 (12)
N7	0.0320 (15)	0.0231 (13)	0.0250 (13)	−0.0012 (11)	−0.0080 (11)	0.0003 (10)
C71	0.054 (2)	0.0296 (17)	0.0205 (15)	0.0014 (16)	−0.0101 (15)	−0.0008 (13)
C72	0.0382 (19)	0.0294 (17)	0.0303 (17)	−0.0006 (14)	−0.0100 (14)	0.0032 (13)
C8	0.0260 (16)	0.0210 (15)	0.0286 (16)	−0.0036 (12)	−0.0065 (12)	0.0001 (12)
C9	0.0283 (16)	0.0228 (15)	0.0255 (15)	−0.0047 (12)	−0.0040 (12)	−0.0049 (12)
N10	0.0253 (13)	0.0215 (12)	0.0224 (12)	−0.0059 (10)	−0.0052 (10)	−0.0023 (10)
C11	0.0229 (15)	0.0217 (14)	0.0234 (14)	−0.0072 (12)	−0.0040 (11)	−0.0015 (11)
C12	0.0233 (15)	0.0249 (15)	0.0212 (14)	−0.0088 (12)	−0.0028 (11)	−0.0013 (11)
C13	0.0221 (14)	0.0200 (14)	0.0223 (14)	−0.0054 (11)	−0.0049 (11)	−0.0010 (11)
C14	0.0231 (15)	0.0211 (14)	0.0228 (14)	−0.0062 (12)	−0.0053 (11)	−0.0006 (11)
N1	0.0309 (15)	0.0285 (15)	0.0371 (16)	−0.0040 (12)	−0.0014 (13)	−0.0032 (12)
O1	0.0538 (18)	0.0563 (19)	0.0371 (15)	0.0022 (15)	−0.0042 (13)	0.0103 (13)
O2	0.0501 (18)	0.0491 (18)	0.064 (2)	−0.0109 (14)	−0.0253 (15)	0.0024 (15)
O3	0.0553 (19)	0.0553 (19)	0.0579 (19)	−0.0301 (16)	0.0095 (15)	−0.0096 (15)
O1W	0.0364 (14)	0.0331 (14)	0.0320 (13)	−0.0022 (12)	−0.0066 (11)	−0.0059 (11)
O2W	0.0415 (17)	0.0415 (16)	0.0281 (13)	−0.0048 (13)	−0.0054 (13)	0.0017 (11)

Geometric parameters (Å, º)

C1—C2	1.359 (4)	N7—C71	1.458 (4)
C1—C11	1.430 (4)	N7—C72	1.464 (4)
C1—H1	0.95	C71—H711	0.98
C2—C3	1.439 (4)	C71—H712	0.98
C2—H2	0.95	C71—H713	0.98
C3—N3	1.335 (4)	C72—H721	0.98
C3—C4	1.416 (4)	C72—H722	0.98
N3—C32	1.461 (4)	C72—H723	0.98
N3—C31	1.469 (4)	C8—C9	1.361 (4)
C31—H311	0.98	C8—H8	0.95
C31—H312	0.98	C9—C14	1.424 (4)
C31—H313	0.98	C9—H9	0.95

C32—H321	0.98	N10—C11	1.335 (4)
C32—H322	0.98	N10—C14	1.344 (4)
C32—H323	0.98	C11—C12	1.438 (4)
C4—C12	1.373 (4)	C13—C14	1.432 (4)
C4—H4	0.95	N1—O3	1.231 (4)
S5—C13	1.728 (3)	N1—O1	1.238 (4)
S5—C12	1.728 (3)	N1—O2	1.246 (4)
C6—C13	1.376 (4)	O1W—H11W	0.88 (5)
C6—C7	1.415 (4)	O1W—H12W	0.84 (5)
C6—H6	0.95	O2W—H21W	0.81 (6)
C7—N7	1.340 (4)	O2W—H22W	0.75 (5)
C7—C8	1.436 (4)		

C2—C1—C11	122.5 (3)	C71—H711—109.5	
C2—C1—H1	118.7	C71—H712—109.5	
C11—C1—H1	118.7	C71—H712—109.5	
C1—C2—C3	120.3 (3)	C71—H713—109.5	
C1—C2—H2	119.8	C71—H713—109.5	
C3—C2—H2	119.8	C71—H713—109.5	
N3—C3—C4	120.3 (3)	C72—H721—109.5	
N3—C3—C2	121.4 (3)	C72—H722—109.5	
C4—C3—C2	118.3 (3)	C72—H722—109.5	
C3—N3—C32	120.9 (3)	C72—H723—109.5	
C3—N3—C31	122.9 (3)	C72—H723—109.5	
C32—N3—C31	115.9 (3)	C72—H723—109.5	
N3—C31—H311	109.5	C8—C7—120.6 (3)	
N3—C31—H312	109.5	C8—H8—119.7	
H311—C31—H312	109.5	C8—H8—119.7	
N3—C31—H313	109.5	C9—C14—122.4 (3)	
H311—C31—H313	109.5	C9—H9—118.8	
H312—C31—H313	109.5	C9—H9—118.8	
N3—C32—H321	109.5	N10—C14—123.0 (3)	
N3—C32—H322	109.5	C11—C1—117.9 (3)	
H321—C32—H322	109.5	C11—C12—125.8 (3)	
N3—C32—H323	109.5	C11—C12—116.3 (3)	
H321—C32—H323	109.5	C12—C11—121.7 (3)	
H322—C32—H323	109.5	C12—S5—117.2 (2)	
C12—C4—C3	120.8 (3)	C12—S5—121.0 (2)	
C12—C4—H4	119.6	C13—C14—121.4 (3)	
C3—C4—H4	119.6	C13—S5—117.1 (2)	
C13—S5—C12	103.28 (15)	C13—S5—121.4 (2)	
C13—C6—C7	121.2 (3)	C14—C9—118.0 (3)	
C13—C6—H6	119.4	C14—C13—125.4 (3)	
C7—C6—H6	119.4	C14—C13—116.6 (3)	
N7—C7—C6	120.0 (3)	N1—O1—121.1 (4)	
N7—C7—C8	122.2 (3)	N1—O2—118.4 (3)	
C6—C7—C8	117.8 (3)	N1—O2—120.5 (3)	
C7—N7—C71	120.7 (3)	O1W—H12W—95 (4)	

C7—N7—C72	122.9 (3)	O2W—H22W—102 (5)	
N7—C72—116.4 (3)			
C11—C1—C2—C3	−0.3 (5)	C2—C1—C11—C12	0.4 (5)
C1—C2—C3—N3	−180.0 (3)	C3—C4—C12—C11	0.4 (5)
C1—C2—C3—C4	0.2 (5)	C3—C4—C12—S5	−178.8 (2)
C4—C3—N3—C32	−2.6 (5)	N10—C11—C12—C4	−180.0 (3)
C2—C3—N3—C32	177.6 (3)	C1—C11—C12—C4	−0.5 (4)
C4—C3—N3—C31	−176.6 (3)	N10—C11—C12—S5	−0.8 (4)
C2—C3—N3—C31	3.5 (5)	C1—C11—C12—S5	178.7 (2)
N3—C3—C4—C12	179.9 (3)	C13—S5—C12—C4	−178.9 (2)
C2—C3—C4—C12	−0.2 (5)	C13—S5—C12—C11	1.9 (3)
C13—C6—C7—N7	−178.2 (3)	C7—C6—C13—C14	0.1 (5)
C13—C6—C7—C8	1.4 (5)	C7—C6—C13—S5	179.4 (2)
C6—C7—N7—C71	−1.0 (5)	C12—S5—C13—C6	179.2 (2)
C8—C7—N7—C71	179.4 (3)	C12—S5—C13—C14	−1.5 (3)
C6—C7—N7—C72	178.5 (3)	C11—N10—C14—C9	−177.9 (3)
C8—C7—N7—C72	−1.2 (5)	C11—N10—C14—C13	1.6 (5)
N7—C7—C8—C9	177.9 (3)	C8—C9—C14—N10	−179.6 (3)
C6—C7—C8—C9	−1.8 (5)	C8—C9—C14—C13	0.9 (5)
C7—C8—C9—C14	0.6 (5)	C6—C13—C14—N10	179.3 (3)
C14—N10—C11—C1	179.3 (3)	S5—C13—C14—N10	0.0 (4)
C14—N10—C11—C12	−1.2 (5)	C6—C13—C14—C9	−1.2 (4)
C2—C1—C11—N10	180.0 (3)	S5—C13—C14—C9	179.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O2^{i}	0.88 (5)	1.91 (5)	2.789 (4)	174 (4)
O1*W*—H12*W*···N10^{ii}	0.84 (5)	2.10 (5)	2.929 (4)	172 (4)
O2*W*—H21*W*···O1	0.81 (6)	2.14 (6)	2.886 (5)	154 (5)
O2*W*—H22*W*···O1*W*	0.75 (5)	2.05 (5)	2.792 (4)	171 (5)

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