

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

m-Xylylenediaminium dinitrateSofian Gatfaoui,^a Hassouna Dhaouadi,^{b*} Thierry Roisnel,^c Mohamed Rzaigui^a and Houda Marouani^a^aLaboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna Bizerte, Tunisia, ^bLaboratoire des Matériaux Utiles, Institut National de Recherche et d'Analyse Physico-chimique, Pole Technologique de Sidi-Thabet, 2020 Tunis, Tunisia, and ^cCentre de Diffractométrie X, UMR 6226 CNRS, Unité Sciences Chimiques de Rennes, Université de Rennes I, 263 Avenue du Général Leclerc, 35042 Rennes, France

Correspondence e-mail: dhaouadihassouna@yahoo.fr

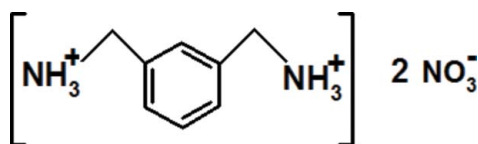
Received 13 February 2014; accepted 28 February 2014

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.047; wR factor = 0.129; data-to-parameter ratio = 16.6.

The asymmetric unit of the title salt, $\text{C}_8\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$, contains two independent dications and four independent nitrate anions. The crystal structure consists of discrete nitrate ions, three of which stack in layers parallel to (001) at $z = 0$ and 0.5. These layers are connected *via* *m*-xylylenediaminium dications. The fourth anion is sandwiched by the two independent organic cations in the asymmetric unit. In the crystal, the ions are connected by a large number of bifurcated and non-bifurcated $\text{N}-\text{H} \cdots \text{O}(\text{O})$ hydrogen bonds, forming sheets parallel to (100). These sheets are connected by $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional network.

Related literature

For related nitrate salts, see: Gatfaoui *et al.* (2013, 2014); Marouani *et al.* (2012); Kefi *et al.* (2013). For the dichloride salt of the title cation, see: Cheng & Li (2008). For background to hydrogen bonding and aromatic $\pi-\pi$ stacking interactions, see: Brown (1976); Blessing (1986); Janiak (2000).



Experimental

Crystal data

$\text{C}_8\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{NO}_3^-$
 $M_r = 262.23$
 Monoclinic, $P2_1/c$
 $a = 21.4308$ (7) Å
 $b = 5.7255$ (2) Å
 $c = 20.4476$ (5) Å
 $\beta = 108.502$ (1)°

$V = 2379.28$ (13) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 150$ K
 $0.47 \times 0.24 \times 0.17$ mm

Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2006)
 $T_{\min} = 0.889$, $T_{\max} = 0.979$

19108 measured reflections
 5457 independent reflections
 4429 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.129$
 $S = 1.04$
 5457 reflections

329 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O3}$	0.91	2.06	2.9545 (16)	168
$\text{N1}-\text{H1B} \cdots \text{O6}$	0.91	2.34	2.9872 (18)	128
$\text{N1}-\text{H1B} \cdots \text{O9}^{\text{i}}$	0.91	2.23	2.9554 (17)	137
$\text{N1}-\text{H1C} \cdots \text{O2}^{\text{i}}$	0.91	2.29	3.197 (2)	173
$\text{N1}-\text{H1C} \cdots \text{O3}^{\text{i}}$	0.91	2.42	3.0837 (16)	130
$\text{N2}-\text{H2B} \cdots \text{O10}^{\text{ii}}$	0.91	2.48	3.032 (2)	119
$\text{N2}-\text{H2B} \cdots \text{O12}^{\text{ii}}$	0.91	1.96	2.8391 (19)	162
$\text{N2}-\text{H2C} \cdots \text{O10}^{\text{iii}}$	0.91	1.92	2.829 (2)	173
$\text{N2}-\text{H2C} \cdots \text{O11}^{\text{iii}}$	0.91	2.51	3.074 (2)	120
$\text{N3}-\text{H3A} \cdots \text{O5}$	0.91	2.42	3.0008 (17)	122
$\text{N3}-\text{H3A} \cdots \text{O6}$	0.91	1.91	2.8155 (16)	175
$\text{N3}-\text{H3B} \cdots \text{O4}^{\text{iv}}$	0.91	1.93	2.7974 (17)	159
$\text{N3}-\text{H3B} \cdots \text{O6}^{\text{iv}}$	0.91	2.50	2.9910 (16)	114
$\text{N3}-\text{H3C} \cdots \text{O3}$	0.91	2.03	2.8897 (19)	157
$\text{N4}-\text{H4A} \cdots \text{O1}$	0.91	2.35	3.079 (2)	137
$\text{N4}-\text{H4A} \cdots \text{O2}$	0.91	2.15	2.9967 (19)	155
$\text{N4}-\text{H4B} \cdots \text{O8}^{\text{v}}$	0.91	2.42	3.0673 (16)	128
$\text{N4}-\text{H4B} \cdots \text{O9}^{\text{v}}$	0.91	2.12	2.9368 (17)	150
$\text{N4}-\text{H4C} \cdots \text{O7}^{\text{iii}}$	0.91	2.52	3.2192 (18)	134
$\text{N4}-\text{H4C} \cdots \text{O8}^{\text{iii}}$	0.91	1.99	2.8810 (16)	165
$\text{C7}-\text{H7} \cdots \text{O2}^{\text{i}}$	0.95	2.53	3.309 (2)	140
$\text{C8}-\text{H8A} \cdots \text{O12}^{\text{vi}}$	0.99	2.46	3.373 (2)	153
$\text{C9}-\text{H9B} \cdots \text{O4}^{\text{vii}}$	0.99	2.31	3.267 (2)	163
$\text{C16}-\text{H16A} \cdots \text{O4}^{\text{iii}}$	0.99	2.33	3.267 (2)	157

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *CRYSCAL* (T. Roisnel, local program).

This work was supported by the Tunisian Ministry of High Education Scientific Research.

Supporting information for this paper is available from the IUCr electronic archives (Reference: BH2495).

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
 Blessing, R. H. (1986). *Acta Cryst.* **B42**, 613–621.
 Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal impact GbR, Bonn, Germany.

- Brown, I. D. (1976). *Acta Cryst.* **A32**, 24–31.
- Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheng, H. & Li, H. (2008). *Acta Cryst.* **E64**, o2060.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gatfaoui, S., Marouani, H. & Rzaigui, M. (2013). *Acta Cryst.* **E69**, o1453.
- Gatfaoui, S., Rzaigui, M. & Marouani, H. (2014). *Acta Cryst.* **E70**, o198.
- Janiak, J. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Kefi, C., Marouani, H. & Rzaigui, M. (2013). *Acta Cryst.* **E69**, o1475.
- Marouani, H., Raouafi, N., Toumi Akriche, S., Al-Deyab, S. S. & Rzaigui, M. (2012). *Eur. J. Chem.* **9**, 772–779.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2014). E70, o398–o399 [doi:10.1107/S1600536814004620]

m-Xylylenediaminium dinitrate

Sofian Gatfaoui, Hassouna Dhaouadi, Thierry Roisnel, Mohamed Rzaigui and Houda Marouani

S1. Experimental

S1.1. Synthesis and crystallization

An aqueous solution containing 4 mmol of HNO₃ in 10 ml of water was added to 2 mmol of *m*-xylylenediamine in 10 ml of water. The obtained solution was stirred for 1 h and then left to stand at room temperature. Colorless single crystals of the title compound were obtained after one week.

S1.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms bonded to C and N atoms were treated as riding with C—H = 0.99 Å (methylene) or 0.95 Å (aromatic CH), N—H = 0.91 Å (NH₃), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$.

S2. Results and discussion

As a part of our study of crystal packing containing the nitrate anion (Marouani *et al.*, 2012; Gatfaoui *et al.*, 2013, 2014; Kefi *et al.*, 2013), we report here the preparation and the structural investigation of a new organic nitrate, (C₈H₁₄N₂)(NO₃)₂ (I). The asymmetric unit of (I) is composed of two *m*-xylylenediaminium dications and four nitrate anions (Fig. 1). The structure of the compound consists of discrete nitrate ions stacked in layers parallel to the (001) plane at $z = 0$ and $1/2$, for N6/O4/O5/O6, N7/O7/O8/O9, N8/O10/O11/O12 and at $z = 0.25$ and 0.75 for N5/O1/O2/O3, separated by organic cations. Each organic entity is connected to different nitrate layers at $z = 0$ and $1/2$. At the same time, the N5O₃ nitrate groups ensure the cohesion between the organic groups (Fig. 2). The structural cohesion is established by a three-dimensional network of N—H⋯O and weak C—H⋯O hydrogen bonds.

Interatomic bond lengths and angles of the nitrate anions spread respectively within the ranges 1.2314 (19)–1.2719 (17) Å and 118.69 (15)–121.48 (13)°. These geometrical features have also been noticed in other related crystal structures (Gatfaoui *et al.*, 2013, 2014).

In this crystal arrangement two independent *m*-xylylenediaminium cations are present. Both ammonium groups in each cation adopt a *cis* conformation with respect to the benzene ring. The *trans* conformation has been observed in C₈H₁₄N₂²⁺·2Cl⁻ (Cheng & Li, 2008). Thus, the cation conformation is modified when substituting nitrate anions by chlorides. Examination of the organic cations shows that the bond distances and angles show no significant differences from those obtained in other compounds involving the same organic groups (Cheng & Li, 2008). The aromatic rings are planar with an average deviation of 0.0022 Å and form a dihedral angle of 3.85° in the asymmetric unit. The inter-planar distance between nearby benzene rings in the crystal structure is in the vicinity of 4.59 Å, which is much longer than 3.80 Å, value required for the formation of π – π interactions (Janiak, 2000).

The established weak H-bonds (Brown, 1976; Blessing, 1986) of types N—H⋯O and C—H⋯O involve oxygen atoms of the nitrate anions as acceptors, and the protonated nitrogen atoms and carbon atoms of *m*-xylylenediaminium as

donors.

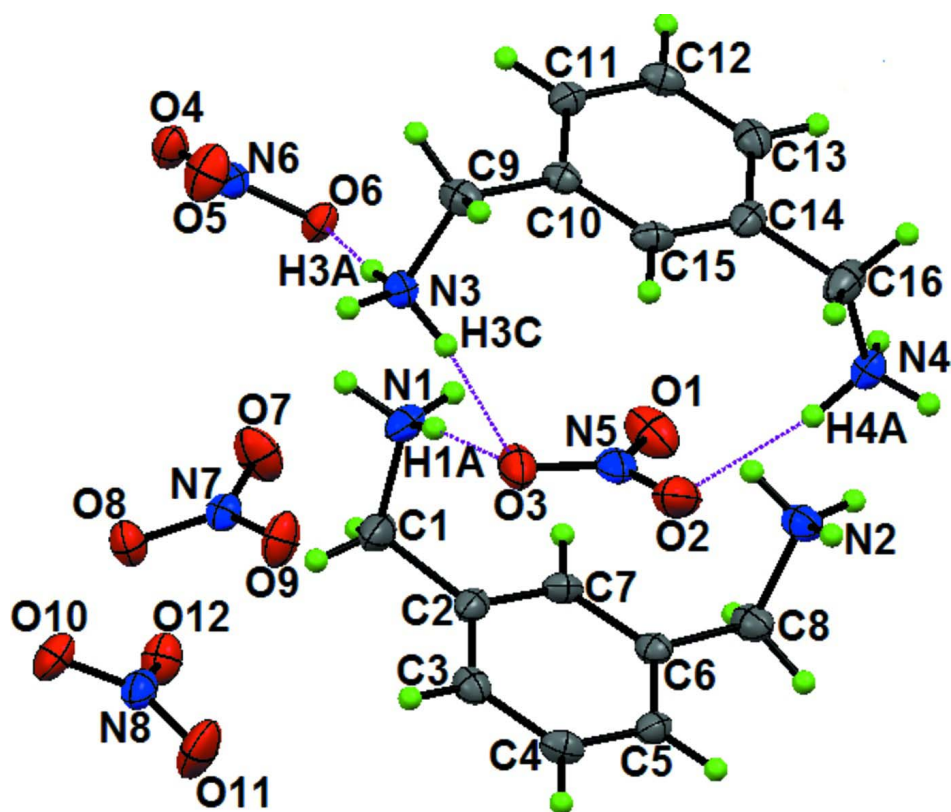


Figure 1

An *ORTEP* view of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines.

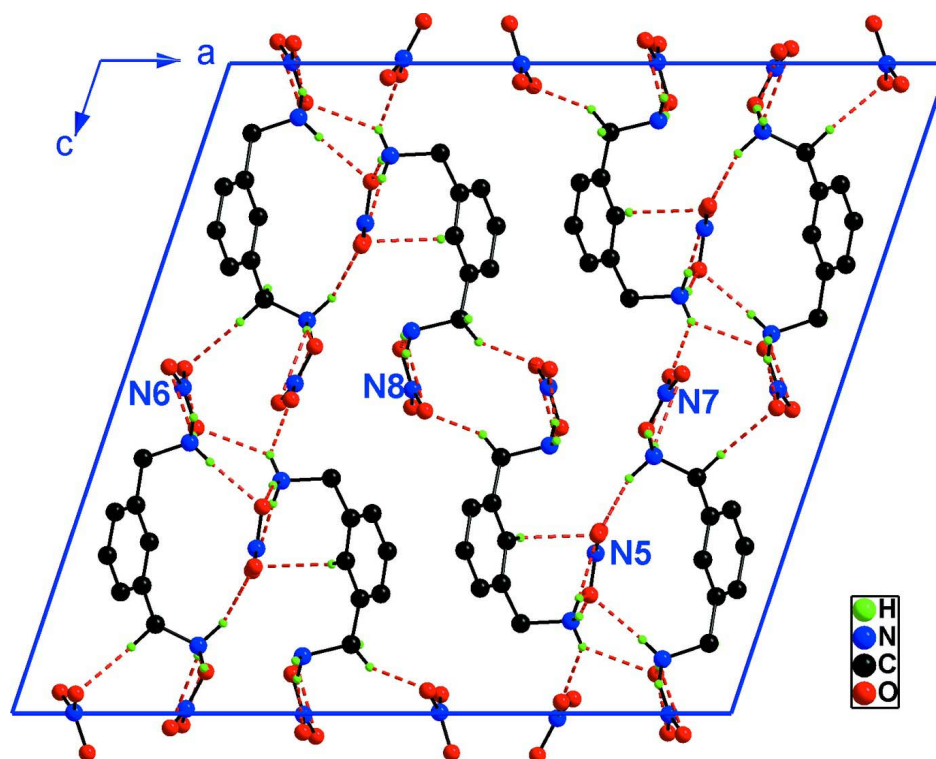


Figure 2

Projection of (I) along the *b* axis. The H-atoms not involved in H-bonding are omitted.

m-Xylylenediaminium dinitrate

Crystal data

$C_8H_{14}N_2^{2+} \cdot 2NO_3^-$

$M_r = 262.23$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 21.4308 (7) \text{ \AA}$

$b = 5.7255 (2) \text{ \AA}$

$c = 20.4476 (5) \text{ \AA}$

$\beta = 108.502 (1)^\circ$

$V = 2379.28 (13) \text{ \AA}^3$

$Z = 8$

$F(000) = 1104$

$D_x = 1.464 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6173 reflections

$\theta = 3.0\text{--}27.3^\circ$

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

$T = 150 \text{ K}$

Prism, colourless

$0.47 \times 0.24 \times 0.17 \text{ mm}$

Data collection

Bruker APEXII
diffractometer

Graphite monochromator

CCD rotation images, thin slices scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2006)

$T_{\min} = 0.889$, $T_{\max} = 0.979$

19108 measured reflections

5457 independent reflections

4429 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -26 \rightarrow 22$

$k = -6 \rightarrow 7$

$l = -27 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.129$

$S = 1.04$

5457 reflections

329 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 1.0374P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.26601 (6)	0.0292 (2)	0.14220 (7)	0.0272 (3)
H1A	0.2554	-0.1199	0.1498	0.041*
H1B	0.2374	0.0818	0.1018	0.041*
H1C	0.2635	0.1223	0.1774	0.041*
C1	0.33450 (8)	0.0351 (3)	0.13828 (9)	0.0329 (4)
H1D	0.3490	0.1991	0.1376	0.040*
H1E	0.3356	-0.0416	0.0953	0.040*
C2	0.38017 (7)	-0.0900 (3)	0.19976 (8)	0.0221 (3)
C3	0.40757 (7)	-0.3050 (3)	0.19264 (8)	0.0236 (3)
H3	0.3998	-0.3709	0.1481	0.028*
C4	0.44632 (7)	-0.4234 (3)	0.25056 (9)	0.0229 (3)
H4	0.4656	-0.5688	0.2453	0.027*
C5	0.45719 (7)	-0.3312 (3)	0.31598 (8)	0.0215 (3)
H5	0.4827	-0.4153	0.3555	0.026*
C6	0.43055 (7)	-0.1149 (3)	0.32352 (8)	0.0198 (3)
C7	0.39272 (7)	0.0044 (3)	0.26535 (8)	0.0208 (3)
H7	0.3751	0.1530	0.2704	0.025*
C8	0.43934 (8)	-0.0113 (3)	0.39380 (9)	0.0278 (4)
H8A	0.4758	-0.0919	0.4288	0.033*
H8B	0.4508	0.1561	0.3938	0.033*
N2	0.37725 (7)	-0.0370 (3)	0.41183 (7)	0.0270 (3)
H2A	0.3426	0.0137	0.3760	0.041*
H2B	0.3802	0.0495	0.4500	0.041*
H2C	0.3713	-0.1899	0.4204	0.041*
N3	0.12089 (6)	-0.4473 (2)	0.08345 (7)	0.0215 (3)
H3A	0.1231	-0.2923	0.0746	0.032*
H3B	0.1162	-0.5304	0.0442	0.032*
H3C	0.1585	-0.4920	0.1166	0.032*
C9	0.06349 (8)	-0.4918 (3)	0.10789 (9)	0.0267 (4)
H9A	0.0552	-0.6620	0.1076	0.032*
H9B	0.0239	-0.4169	0.0759	0.032*
C10	0.07523 (7)	-0.3980 (3)	0.17964 (8)	0.0195 (3)
C11	0.04955 (7)	-0.1832 (3)	0.19040 (8)	0.0205 (3)

H11	0.0256	-0.0906	0.1521	0.025*
C12	0.05893 (7)	-0.1046 (3)	0.25702 (9)	0.0234 (3)
H12	0.0410	0.0413	0.2642	0.028*
C13	0.09441 (8)	-0.2383 (3)	0.31318 (8)	0.0248 (3)
H13	0.1005	-0.1838	0.3587	0.030*
C14	0.12113 (7)	-0.4520 (3)	0.30315 (8)	0.0242 (3)
C15	0.11106 (7)	-0.5290 (3)	0.23635 (8)	0.0216 (3)
H15	0.1291	-0.6747	0.2291	0.026*
C16	0.15782 (8)	-0.6046 (4)	0.36295 (10)	0.0368 (4)
H16A	0.1348	-0.6021	0.3979	0.044*
H16B	0.1575	-0.7675	0.3466	0.044*
N4	0.22723 (6)	-0.5286 (2)	0.39575 (7)	0.0227 (3)
H4A	0.2492	-0.5372	0.3644	0.034*
H4B	0.2470	-0.6234	0.4322	0.034*
H4C	0.2279	-0.3787	0.4108	0.034*
N5	0.26305 (6)	-0.4703 (3)	0.24641 (7)	0.0287 (3)
O1	0.26758 (7)	-0.2898 (3)	0.28036 (7)	0.0436 (4)
O2	0.26855 (6)	-0.6677 (3)	0.27431 (7)	0.0415 (3)
O3	0.25175 (6)	-0.4589 (2)	0.18215 (6)	0.0350 (3)
N6	0.08581 (6)	0.0558 (2)	-0.00143 (7)	0.0236 (3)
O4	0.07924 (6)	0.2525 (2)	-0.03009 (6)	0.0283 (3)
O5	0.05713 (7)	-0.1176 (2)	-0.03262 (6)	0.0391 (3)
O6	0.12308 (5)	0.03715 (19)	0.06066 (6)	0.0246 (3)
N7	0.23961 (6)	-0.4784 (2)	-0.00724 (7)	0.0219 (3)
O7	0.22667 (7)	-0.3051 (2)	0.02227 (7)	0.0402 (3)
O8	0.24994 (6)	-0.4545 (2)	-0.06438 (6)	0.0290 (3)
O9	0.24162 (6)	-0.6782 (2)	0.01751 (6)	0.0346 (3)
N8	0.40614 (7)	0.0407 (3)	0.00192 (7)	0.0279 (3)
O10	0.37062 (6)	0.0189 (2)	-0.06046 (6)	0.0332 (3)
O11	0.43303 (8)	-0.1319 (3)	0.03493 (7)	0.0481 (4)
O12	0.41292 (6)	0.2396 (2)	0.02899 (6)	0.0347 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0203 (6)	0.0296 (8)	0.0274 (7)	0.0020 (5)	0.0012 (5)	0.0040 (6)
C1	0.0228 (8)	0.0458 (11)	0.0301 (9)	0.0040 (7)	0.0082 (7)	0.0153 (8)
C2	0.0159 (7)	0.0263 (8)	0.0237 (8)	-0.0021 (6)	0.0056 (6)	0.0068 (6)
C3	0.0215 (7)	0.0271 (8)	0.0233 (8)	-0.0056 (6)	0.0086 (6)	-0.0042 (7)
C4	0.0222 (7)	0.0159 (7)	0.0332 (9)	-0.0007 (6)	0.0126 (6)	-0.0017 (6)
C5	0.0173 (7)	0.0213 (8)	0.0257 (8)	0.0015 (6)	0.0063 (6)	0.0059 (6)
C6	0.0152 (6)	0.0218 (7)	0.0226 (7)	-0.0026 (6)	0.0062 (5)	-0.0019 (6)
C7	0.0167 (7)	0.0163 (7)	0.0307 (8)	0.0012 (5)	0.0093 (6)	0.0023 (6)
C8	0.0214 (7)	0.0342 (9)	0.0277 (8)	-0.0031 (7)	0.0076 (6)	-0.0080 (7)
N2	0.0245 (7)	0.0318 (8)	0.0266 (7)	0.0001 (6)	0.0106 (6)	-0.0073 (6)
N3	0.0225 (6)	0.0219 (7)	0.0205 (6)	-0.0001 (5)	0.0073 (5)	-0.0005 (5)
C9	0.0220 (7)	0.0303 (9)	0.0290 (9)	-0.0045 (6)	0.0100 (6)	-0.0094 (7)
C10	0.0167 (7)	0.0191 (7)	0.0240 (8)	-0.0035 (5)	0.0083 (6)	-0.0023 (6)

C11	0.0177 (7)	0.0185 (7)	0.0247 (8)	-0.0015 (5)	0.0061 (6)	0.0030 (6)
C12	0.0213 (7)	0.0187 (7)	0.0328 (9)	-0.0016 (6)	0.0121 (6)	-0.0045 (7)
C13	0.0224 (7)	0.0298 (8)	0.0232 (8)	-0.0072 (6)	0.0089 (6)	-0.0041 (7)
C14	0.0167 (7)	0.0282 (8)	0.0266 (8)	-0.0044 (6)	0.0053 (6)	0.0089 (7)
C15	0.0169 (7)	0.0161 (7)	0.0329 (9)	0.0000 (5)	0.0095 (6)	0.0016 (6)
C16	0.0233 (8)	0.0447 (11)	0.0379 (10)	-0.0055 (8)	0.0032 (7)	0.0207 (9)
N4	0.0243 (6)	0.0205 (6)	0.0205 (7)	0.0010 (5)	0.0033 (5)	0.0015 (5)
N5	0.0175 (6)	0.0420 (9)	0.0270 (7)	-0.0025 (6)	0.0077 (5)	-0.0016 (7)
O1	0.0410 (8)	0.0502 (9)	0.0449 (8)	-0.0155 (6)	0.0210 (6)	-0.0169 (7)
O2	0.0359 (7)	0.0463 (8)	0.0471 (8)	0.0113 (6)	0.0200 (6)	0.0128 (7)
O3	0.0266 (6)	0.0554 (8)	0.0228 (6)	-0.0075 (6)	0.0077 (5)	-0.0010 (6)
N6	0.0241 (7)	0.0254 (7)	0.0209 (7)	0.0023 (5)	0.0067 (5)	-0.0019 (6)
O4	0.0364 (6)	0.0253 (6)	0.0220 (6)	0.0069 (5)	0.0073 (5)	0.0029 (5)
O5	0.0484 (8)	0.0304 (7)	0.0296 (7)	-0.0083 (6)	-0.0002 (6)	-0.0073 (6)
O6	0.0269 (6)	0.0243 (6)	0.0186 (5)	0.0021 (4)	0.0013 (4)	-0.0001 (5)
N7	0.0217 (6)	0.0213 (7)	0.0212 (7)	-0.0024 (5)	0.0046 (5)	-0.0005 (5)
O7	0.0586 (9)	0.0290 (7)	0.0412 (7)	-0.0008 (6)	0.0275 (7)	-0.0099 (6)
O8	0.0389 (7)	0.0267 (6)	0.0250 (6)	-0.0006 (5)	0.0152 (5)	0.0014 (5)
O9	0.0478 (8)	0.0246 (6)	0.0266 (6)	-0.0043 (5)	0.0051 (5)	0.0072 (5)
N8	0.0237 (7)	0.0338 (8)	0.0251 (7)	-0.0016 (6)	0.0063 (6)	0.0087 (6)
O10	0.0302 (6)	0.0347 (7)	0.0261 (6)	-0.0003 (5)	-0.0034 (5)	0.0037 (5)
O11	0.0600 (9)	0.0416 (8)	0.0322 (7)	0.0123 (7)	-0.0005 (6)	0.0127 (6)
O12	0.0406 (7)	0.0324 (7)	0.0282 (6)	-0.0058 (5)	0.0070 (5)	0.0025 (5)

Geometric parameters (Å, °)

N1—C1	1.495 (2)	C9—H9B	0.9900
N1—H1A	0.9100	C10—C15	1.390 (2)
N1—H1B	0.9100	C10—C11	1.393 (2)
N1—H1C	0.9100	C11—C12	1.388 (2)
C1—C2	1.507 (2)	C11—H11	0.9500
C1—H1D	0.9900	C12—C13	1.389 (2)
C1—H1E	0.9900	C12—H12	0.9500
C2—C7	1.391 (2)	C13—C14	1.393 (2)
C2—C3	1.392 (2)	C13—H13	0.9500
C3—C4	1.388 (2)	C14—C15	1.386 (2)
C3—H3	0.9500	C14—C16	1.506 (2)
C4—C5	1.387 (2)	C15—H15	0.9500
C4—H4	0.9500	C16—N4	1.489 (2)
C5—C6	1.393 (2)	C16—H16A	0.9900
C5—H5	0.9500	C16—H16B	0.9900
C6—C7	1.388 (2)	N4—H4A	0.9100
C6—C8	1.510 (2)	N4—H4B	0.9100
C7—H7	0.9500	N4—H4C	0.9100
C8—N2	1.496 (2)	N5—O1	1.2314 (19)
C8—H8A	0.9900	N5—O2	1.255 (2)
C8—H8B	0.9900	N5—O3	1.2599 (18)
N2—H2A	0.9100	N6—O4	1.2566 (17)

N2—H2B	0.9100	N6—O5	1.2334 (18)
N2—H2C	0.9100	N6—O6	1.2719 (17)
N3—C9	1.489 (2)	N7—O7	1.2379 (18)
N3—H3A	0.9100	N7—O8	1.2637 (17)
N3—H3B	0.9100	N7—O9	1.2459 (17)
N3—H3C	0.9100	N8—O10	1.2671 (18)
C9—C10	1.507 (2)	N8—O11	1.2321 (19)
C9—H9A	0.9900	N8—O12	1.2542 (19)
C1—N1—H1A	109.5	N3—C9—C10	111.42 (12)
C1—N1—H1B	109.5	N3—C9—H9A	109.3
H1A—N1—H1B	109.5	C10—C9—H9A	109.3
C1—N1—H1C	109.5	N3—C9—H9B	109.3
H1A—N1—H1C	109.5	C10—C9—H9B	109.3
H1B—N1—H1C	109.5	H9A—C9—H9B	108.0
N1—C1—C2	109.48 (13)	C15—C10—C11	119.09 (14)
N1—C1—H1D	109.8	C15—C10—C9	119.82 (14)
C2—C1—H1D	109.8	C11—C10—C9	121.08 (14)
N1—C1—H1E	109.8	C12—C11—C10	120.02 (14)
C2—C1—H1E	109.8	C12—C11—H11	120.0
H1D—C1—H1E	108.2	C10—C11—H11	120.0
C7—C2—C3	119.06 (14)	C11—C12—C13	120.23 (15)
C7—C2—C1	119.72 (15)	C11—C12—H12	119.9
C3—C2—C1	121.14 (15)	C13—C12—H12	119.9
C4—C3—C2	120.05 (14)	C12—C13—C14	120.34 (15)
C4—C3—H3	120.0	C12—C13—H13	119.8
C2—C3—H3	120.0	C14—C13—H13	119.8
C5—C4—C3	120.59 (15)	C15—C14—C13	118.81 (14)
C5—C4—H4	119.7	C15—C14—C16	119.58 (16)
C3—C4—H4	119.7	C13—C14—C16	121.55 (16)
C4—C5—C6	119.72 (14)	C14—C15—C10	121.51 (14)
C4—C5—H5	120.1	C14—C15—H15	119.2
C6—C5—H5	120.1	C10—C15—H15	119.2
C7—C6—C5	119.42 (14)	N4—C16—C14	112.69 (13)
C7—C6—C8	119.01 (14)	N4—C16—H16A	109.1
C5—C6—C8	121.52 (14)	C14—C16—H16A	109.1
C6—C7—C2	121.13 (14)	N4—C16—H16B	109.1
C6—C7—H7	119.4	C14—C16—H16B	109.1
C2—C7—H7	119.4	H16A—C16—H16B	107.8
N2—C8—C6	110.10 (12)	C16—N4—H4A	109.5
N2—C8—H8A	109.6	C16—N4—H4B	109.5
C6—C8—H8A	109.6	H4A—N4—H4B	109.5
N2—C8—H8B	109.6	C16—N4—H4C	109.5
C6—C8—H8B	109.6	H4A—N4—H4C	109.5
H8A—C8—H8B	108.2	H4B—N4—H4C	109.5
C8—N2—H2A	109.5	O1—N5—O2	121.35 (15)
C8—N2—H2B	109.5	O1—N5—O3	119.95 (15)
H2A—N2—H2B	109.5	O2—N5—O3	118.69 (15)

C8—N2—H2C	109.5	O4—N6—O6	118.86 (13)
H2A—N2—H2C	109.5	O5—N6—O4	121.10 (13)
H2B—N2—H2C	109.5	O5—N6—O6	120.04 (13)
C9—N3—H3A	109.5	O7—N7—O9	121.48 (13)
C9—N3—H3B	109.5	O7—N7—O8	119.70 (13)
H3A—N3—H3B	109.5	O9—N7—O8	118.80 (13)
C9—N3—H3C	109.5	O11—N8—O12	121.20 (14)
H3A—N3—H3C	109.5	O11—N8—O10	119.97 (15)
H3B—N3—H3C	109.5	O12—N8—O10	118.83 (14)
N1—C1—C2—C7	-67.34 (19)	N3—C9—C10—C15	-82.48 (18)
N1—C1—C2—C3	109.35 (17)	N3—C9—C10—C11	98.88 (16)
C7—C2—C3—C4	0.6 (2)	C15—C10—C11—C12	-1.1 (2)
C1—C2—C3—C4	-176.12 (14)	C9—C10—C11—C12	177.56 (14)
C2—C3—C4—C5	1.2 (2)	C10—C11—C12—C13	0.6 (2)
C3—C4—C5—C6	-1.8 (2)	C11—C12—C13—C14	0.3 (2)
C4—C5—C6—C7	0.8 (2)	C12—C13—C14—C15	-0.7 (2)
C4—C5—C6—C8	178.08 (14)	C12—C13—C14—C16	-177.88 (14)
C5—C6—C7—C2	1.0 (2)	C13—C14—C15—C10	0.1 (2)
C8—C6—C7—C2	-176.39 (13)	C16—C14—C15—C10	177.42 (14)
C3—C2—C7—C6	-1.7 (2)	C11—C10—C15—C14	0.7 (2)
C1—C2—C7—C6	175.10 (14)	C9—C10—C15—C14	-177.94 (13)
C7—C6—C8—N2	73.72 (19)	C15—C14—C16—N4	102.05 (19)
C5—C6—C8—N2	-103.59 (16)	C13—C14—C16—N4	-80.8 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>A</i> ...O3	0.91	2.06	2.9545 (16)	168
N1—H1 <i>B</i> ...O6	0.91	2.34	2.9872 (18)	128
N1—H1 <i>B</i> ...O9 ⁱ	0.91	2.23	2.9554 (17)	137
N1—H1 <i>C</i> ...O2 ⁱ	0.91	2.29	3.197 (2)	173
N1—H1 <i>C</i> ...O3 ⁱ	0.91	2.42	3.0837 (16)	130
N2—H2 <i>B</i> ...O10 ⁱⁱ	0.91	2.48	3.032 (2)	119
N2—H2 <i>B</i> ...O12 ⁱⁱ	0.91	1.96	2.8391 (19)	162
N2—H2 <i>C</i> ...O10 ⁱⁱⁱ	0.91	1.92	2.829 (2)	173
N2—H2 <i>C</i> ...O11 ⁱⁱⁱ	0.91	2.51	3.074 (2)	120
N3—H3 <i>A</i> ...O5	0.91	2.42	3.0008 (17)	122
N3—H3 <i>A</i> ...O6	0.91	1.91	2.8155 (16)	175
N3—H3 <i>B</i> ...O4 ^{iv}	0.91	1.93	2.7974 (17)	159
N3—H3 <i>B</i> ...O6 ^{iv}	0.91	2.50	2.9910 (16)	114
N3—H3 <i>C</i> ...O3	0.91	2.03	2.8897 (19)	157
N4—H4 <i>A</i> ...O1	0.91	2.35	3.079 (2)	137
N4—H4 <i>A</i> ...O2	0.91	2.15	2.9967 (19)	155
N4—H4 <i>B</i> ...O8 ^v	0.91	2.42	3.0673 (16)	128
N4—H4 <i>B</i> ...O9 ^v	0.91	2.12	2.9368 (17)	150
N4—H4 <i>C</i> ...O7 ⁱⁱⁱ	0.91	2.52	3.2192 (18)	134
N4—H4 <i>C</i> ...O8 ⁱⁱⁱ	0.91	1.99	2.8810 (16)	165

C7—H7…O2 ⁱ	0.95	2.53	3.309 (2)	140
C8—H8A…O12 ^{vi}	0.99	2.46	3.373 (2)	153
C9—H9B…O4 ^{vii}	0.99	2.31	3.267 (2)	163
C16—H16A…O4 ⁱⁱⁱ	0.99	2.33	3.267 (2)	157

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