



# Crystal structure of 1,4,8,11-tetramethyl-1,4,8,11-tetraazoniacyclotetradecane bis(perchlorate) dichloride from synchrotron X-ray data

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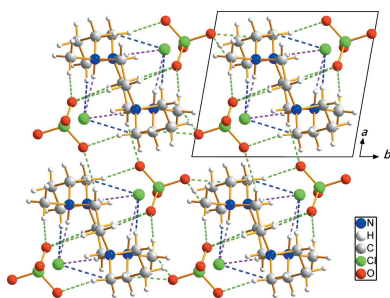
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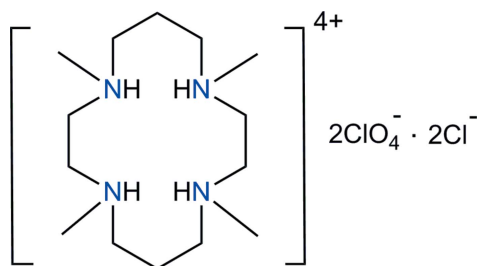
The crystal structure of title salt,  $C_{14}H_{36}N_4^{4+} \cdot 2ClO_4^- \cdot 2Cl^-$ , has been determined using synchrotron radiation at 220 K. The structure determination reveals that protonation has occurred at all four amine N atoms. The asymmetric unit contains one half-cation (completed by crystallographic inversion symmetry), one perchlorate anion and one chloride anion. A distortion of the perchlorate anion is due to its involvement in hydrogen-bonding interactions with the cations. The crystal structure is consolidated by intermolecular hydrogen bonds involving the 1,4,8,11-tetramethyl-1,4,8,11-tetraazoniacyclotetradecane N—H and C—H groups as donor groups, and the O atoms of the perchlorate and chloride anion as acceptor groups, giving rise to a three-dimensional network.

## 1. Chemical context

Tetraazamacrocycle 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC,  $C_{14}H_{32}N_4$ ) is one of the most useful azamacrocycles because of its ability to act as an effective metal-ion binding site and its basic properties. N-Substituted TMC is a basic amine that may form a dication,  $C_{14}H_{34}N_4^{2+}$ , or a tetracation,  $C_{14}H_{36}N_4^{4+}$ , in which the N—H bonds are generally active in hydrogen-bond formation. These di- or tetraammonium cations may be suitable for the removal of toxic heavy-metal ions. Because of a difference in the chirality of the secondary NH centers, the macrocyclic compounds can exhibit five conformations, *viz.* *trans*-I (*RSRS*), *trans*-II (*RSRR*), *trans*-III (*RRSS*), *trans*-IV (*SRRS*) and *trans*-V (*RRRR*) (Choi, 2009). Previously, the crystal structures for *trans*-[Ni(TMC)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O, [Ni(TMC)](O<sub>3</sub>SCF<sub>3</sub>) (Barefield *et al.*, 1986), [Cu(TMC)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (Lee *et al.*, 1986), [Cu(TMC)](ClO<sub>4</sub>)<sub>2</sub> (Maimon *et al.*, 2001), [Ag(TMC)](ClO<sub>4</sub>)<sub>2</sub> (Po *et al.*, 1991), [Cu(NCS)(TMC)]ClO<sub>4</sub> (Lu *et al.*, 1998) and [Cu(TMC)](BF<sub>4</sub>)<sub>2</sub> (Bucher *et al.*, 2001b) have been characterized crystallographically. In addition, first-row transition-metal complexes of the form  $[M^II Cl(TMC)]^+$  [*M* = Zn (Alcock *et al.*, 1978), Mn (Bucher *et al.*, 2001a), Ni (Nishigaki *et al.*, 2010), Fe (Bedford *et al.*, 2016) and Co (Van Heuvelen *et al.*, 2017)] have been determined. Two independent ring conformations, *trans*-III and *trans*-IV, in the crystal structure of free TMC were also found (Willey *et al.*, 1994), but there is no report of a structure with any combination of the 1,4,8,11-tetramethyl-1,4,8,11-tetraazoniacyclotetradecane cation and ClO<sub>4</sub><sup>−</sup> and Cl<sup>−</sup> anions. We report here the preparation of a new compound [H<sub>4</sub>TMC](ClO<sub>4</sub>)<sub>2</sub>Cl<sub>2</sub>, (I), and



its structural characterization by synchrotron single-crystal X-ray diffraction.



## 2. Structural commentary

An ellipsoid plot of the molecular components in (I) is shown in Fig. 1 along with the atom-numbering scheme. The asymmetric unit consists of one half of the macrocycle, which lies about a center of inversion, one perchlorate anion and one chloride anion. The tetra-protonated amine of the title compound has a distorted *trans*-IV conformation, which is comparable to the *trans*-I or *trans*-III conformations of the dicationic in  $[\text{H}_2\text{TMC}][\text{As}_4\text{O}_2\text{Cl}_{10}]$  and  $[\text{H}_2\text{TMC}][\text{Sb}_2\text{OCl}_6]$ , respectively (Willey *et al.*, 1993). Within the centrosymmetric tetra-protonated  $\text{C}_{14}\text{H}_{36}\text{N}_4^{4+}$  amine unit, the C–C and N–C bond lengths vary from 1.522 (2) to 1.527 (2) Å and from 1.5033 (19) to 1.5181 (18) Å, respectively. The N–C–C and C–N–C angles range from 113.55 (12) to 116.19 (12)° and 108.49 (12) to 112.37 (11)°, respectively. The bond lengths and angles within the tetraammonium cations are comparable to the corresponding values determined for the TMC moiety in  $[\text{H}_4\text{TMC}]_2[\text{Sb}_4\text{F}_{15}][\text{HF}_2]\text{F}_4$  (Becker & Mattes, 1996),  $[\text{H}_2\text{TMC}][\text{As}_4\text{O}_2\text{Cl}_{10}]$ ,  $[\text{H}_2\text{TMC}][\text{Sb}_2\text{OCl}_6]$  (Willey *et al.*, 1993),  $[\text{H}_4\text{TMC}][\text{H}_2\text{TMC}][\text{W}(\text{CN})_8]_2 \cdot 4\text{H}_2\text{O}$  (Nowicka *et al.*, 2012),

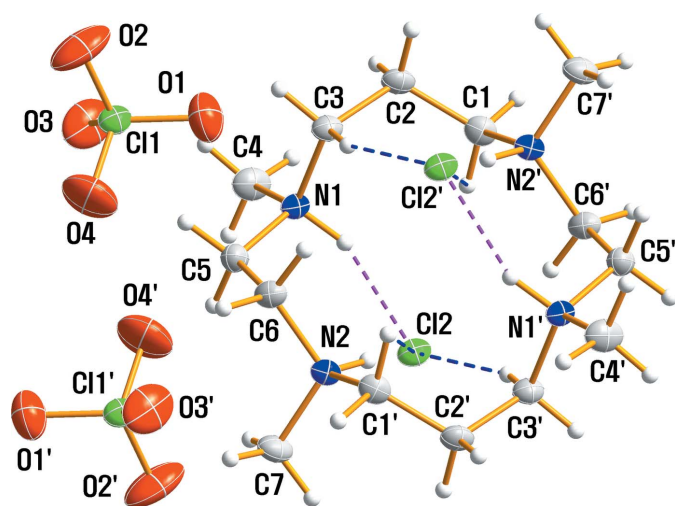


Figure 1

The structures of the molecular components in (I), drawn with displacement ellipsoids at the 50% probability level. Dashed lines represent hydrogen-bonding interactions and primed atoms are related by the symmetry operation  $(-x + 1, -y + 1, -z)$ .

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 $\cdots$ Cl2	0.99	2.13	3.0701 (14)	159
N2–H2 $\cdots$ Cl2	0.99	2.17	3.1038 (15)	156
C1–H1A $\cdots$ Cl2	0.98	2.77	3.6868 (17)	157
C5–H5AB $\cdots$ O3	0.98	2.39	3.351 (3)	167
C3–H3A $\cdots$ Cl2 <sup>i</sup>	0.98	2.67	3.6274 (17)	164
C3–H3AB $\cdots$ O2 <sup>ii</sup>	0.98	2.52	3.288 (3)	135
C4–H4A $\cdots$ O4 <sup>iii</sup>	0.97	2.49	3.429 (3)	164
C4–H4C $\cdots$ O2 <sup>ii</sup>	0.97	2.39	3.171 (3)	137
C5–H5A $\cdots$ O3 <sup>iii</sup>	0.98	2.34	3.317 (3)	173
C6–H6AB $\cdots$ O4 <sup>iv</sup>	0.98	2.31	3.231 (3)	156
C6–H6A $\cdots$ Cl2 <sup>i</sup>	0.98	2.80	3.7414 (17)	161
C7–H7B $\cdots$ O3 <sup>iii</sup>	0.97	2.40	3.333 (3)	161

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

$[\text{Ga}_2(\text{C}_3\text{H}_7)_4(\text{OH})_2](\text{TMC})$  (Boag *et al.*, 2000), TMC (Willey *et al.*, 1994), *trans*- $[\text{Ni}(\text{TMC})(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (Barefield *et al.*, 1986), *trans*- $[\text{Os}(\text{TMC})(\text{O})_2](\text{PF}_6)_2$  (Kelly *et al.*, 1996),  $[\text{Cu}(\text{TMC})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (Lee *et al.*, 1986),  $[\text{Cu}(\text{NCS})(\text{TMC})]\text{ClO}_4$  (Lu *et al.*, 1998) and  $[\text{Cu}(\text{TMC})](\text{BF}_4)_2$  (Bucher *et al.*, 2001b). The Cl–O bond distances in the tetrahedral  $\text{ClO}_4^-$  anion range from 1.4180 (17) to 1.4380 (16) Å and the O–Cl–O angles from 106.85 (14)–110.94 (12)°. A distortion of the  $\text{ClO}_4^-$  anion undoubtedly results from its involvement in hydrogen-bonding interactions with the cations.

## 3. Supramolecular features

Extensive N–H $\cdots$ Cl, C–H $\cdots$ Cl and C–H $\cdots$ O hydrogen-bonding interactions occur in the crystal structure (Table 1). A crystal packing diagram of (I) viewed perpendicular to the *ab* plane is shown in Fig. 2.

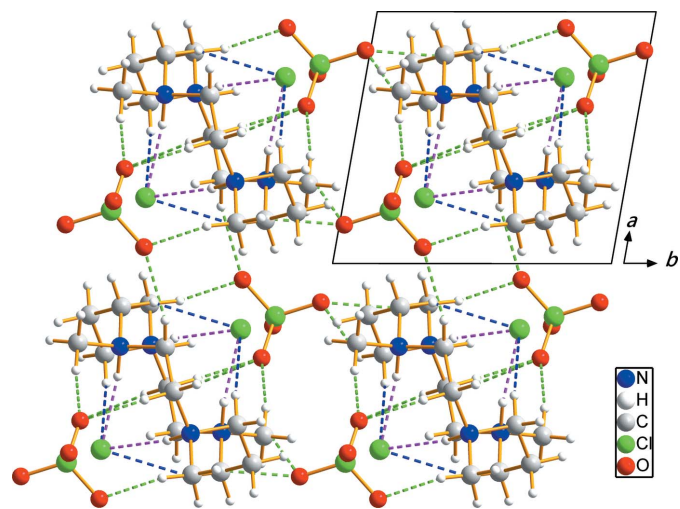


Figure 2

The crystal packing of compound (I), viewed perpendicular to the *ab* plane. Dashed lines represent N–H $\cdots$ Cl (purple), C–H $\cdots$ Cl (blue) and C–H $\cdots$ O (green) hydrogen-bonding interactions, respectively.

The N—H···Cl and C—H···Cl hydrogen bonds link the two Cl<sup>−</sup> anions to the C<sub>14</sub>H<sub>36</sub>N<sub>4</sub><sup>4+</sup> cation while C—H···O hydrogen bonds interconnect neighboring cations with the ClO<sub>4</sub><sup>−</sup> anions. An extensive array of these contacts generates a three-dimensional network of molecules, and these hydrogen-bonding interactions help to consolidate the crystal structure.

#### 4. Database survey

A search of the Cambridge Structural Database (Version 5.41, November 2019; Groom *et al.*, 2016) gave just seven hits for organic compounds containing C<sub>14</sub>H<sub>36</sub>N<sub>4</sub><sup>4+</sup>, C<sub>14</sub>H<sub>34</sub>N<sub>4</sub><sup>2+</sup> or C<sub>14</sub>H<sub>32</sub>N<sub>4</sub> macrocycles: [C<sub>14</sub>H<sub>36</sub>N<sub>4</sub>]<sub>2</sub>[Sb<sub>4</sub>F<sub>15</sub>][HF<sub>2</sub>]<sub>2</sub>F<sub>4</sub> (Becker *et al.*, 1996), [C<sub>14</sub>H<sub>34</sub>N<sub>4</sub>][As<sub>4</sub>O<sub>2</sub>Cl<sub>10</sub>] and [C<sub>14</sub>H<sub>34</sub>N<sub>4</sub>][Sb<sub>2</sub>OCl<sub>6</sub>] (Willey *et al.*, 1993), [C<sub>14</sub>H<sub>36</sub>N<sub>4</sub>][C<sub>14</sub>H<sub>34</sub>N<sub>4</sub>][W(CN)<sub>8</sub>]<sub>2</sub>·4H<sub>2</sub>O (Nowicka *et al.*, 2012), [Ga<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>(OH)<sub>2</sub>](C<sub>14</sub>H<sub>32</sub>N<sub>4</sub>) (Boag *et al.*, 2000) and (C<sub>14</sub>H<sub>32</sub>N<sub>4</sub>) (Willey *et al.*, 1994). However, the crystal structure of the title compound had not been deposited until now. The tetra-protonated amine of the title compound has a *trans*-IV conformation, which is comparable to the *trans*-I or *trans*-III conformation of the dications in [H<sub>2</sub>TMC]-[As<sub>4</sub>O<sub>2</sub>Cl<sub>10</sub>] and [H<sub>2</sub>TMC][Sb<sub>2</sub>OCl<sub>6</sub>], respectively (Willey *et al.*, 1993).

#### 5. Synthesis and crystallization

The free ligand TMC (98%) was purchased from Sigma–Aldrich and used without further purification. All chemicals were reagent grade materials, and were used as received. TMC (0.128 g, 0.5 mmol) was dissolved in 15 mL of 6 M HCl, and 5 mL of a saturated solution of sodium perchlorate including chromium trioxide (0.1 g, 1 mmol) was added to the resulting solution at 298 K. The mixture was stirred for 2 h and the solution was filtered. Block-like pale yellow crystals of (I) suitable for X-ray structural analysis were unexpectedly obtained from the solution at 298 K over a period of a few days.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.97–0.98 Å and N—H = 0.99 Å, and with *U*<sub>iso</sub>(H) values of 1.5 and 1.2 times the *U*<sub>eq</sub> of the parent atoms.

#### Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	C <sub>14</sub> H <sub>36</sub> N <sub>4</sub> <sup>4+</sup> ·2ClO <sub>4</sub> <sup>−</sup> ·2Cl <sup>−</sup>
<i>M</i> <sub>r</sub>	530.27
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	220
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.4990 (15), 8.0790 (16), 9.980 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	81.31 (3), 77.32 (3), 78.39 (3)
<i>V</i> (Å <sup>3</sup> )	574.2 (2)
<i>Z</i>	1
Radiation type	Synchrotron, $\lambda$ = 0.610 Å
$\mu$ (mm <sup>−1</sup> )	0.36
Crystal size (mm)	0.10 × 0.10 × 0.08
Data collection	
Diffractometer	Rayonix MX225HS CCD area detector
Absorption correction	Empirical (using intensity measurements) ( <i>HKL3000sm SCALEPACK</i> ; Otwinowski & Minor, 1997)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.710, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	6573, 3361, 3208
<i>R</i> <sub>int</sub>	0.038
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>−1</sup> )	0.706
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.052, 0.147, 1.05
No. of reflections	3361
No. of parameters	138
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>−3</sup> )	0.97, −0.56

Computer programs: *PAL BL2D-SMDC Program* (Shin *et al.*, 2016), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMONDA* (Putz & Brandenburg, 2014) and *publCIF* (Westrip, 2010).

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## supporting information

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## Crystal structure of 1,4,8,11-tetramethyl-1,4,8,11-tetraazoniacyclotetradecane bis(perchlorate) dichloride from synchrotron X-ray data

Dohyun Moon and Jong-Ha Choi

### Computing details

Data collection: *PAL BL2D-SMDC Program* (Shin *et al.*, 2016); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND4* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### 1,4,8,11-Tetramethyl-1,4,8,11-tetraazoniacyclotetradecane bis(perchlorate) dichloride

#### Crystal data

$C_{14}H_{36}N_4^{4+} \cdot 2ClO_4^- \cdot 2Cl^-$

$M_r = 530.27$

Triclinic, *P1*

$a = 7.4990$  (15) Å

$b = 8.0790$  (16) Å

$c = 9.980$  (2) Å

$\alpha = 81.31$  (3)°

$\beta = 77.32$  (3)°

$\gamma = 78.39$  (3)°

$V = 574.2$  (2) Å<sup>3</sup>

$Z = 1$

$F(000) = 280$

$D_x = 1.533$  Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda = 0.610$  Å

Cell parameters from 91694 reflections

$\theta = 0.4$ – $33.7$ °

$\mu = 0.36$  mm<sup>-1</sup>

$T = 220$  K

Block, pale yellow

$0.10 \times 0.10 \times 0.08$  mm

#### Data collection

Rayonix MX225HS CCD area detector  
diffractometer

Radiation source: PLSII 2D bending magnet

$\omega$  scan

Absorption correction: empirical (using  
intensity measurements)

(*HKL3000sm Scalepack*; Otwinowski & Minor,  
1997)

$T_{\min} = 0.710$ ,  $T_{\max} = 1.000$

6573 measured reflections

3361 independent reflections

3208 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 25.5$ °,  $\theta_{\min} = 1.8$ °

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 14$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.147$

$S = 1.05$

3361 reflections

138 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1013P)^2 + 0.2815P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.97$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.56$  e Å<sup>-3</sup>

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.67545 (16)	0.40154 (15)	0.21687 (13)	0.0182 (2)
H1	0.702337	0.480395	0.131812	0.022*
N2	0.32976 (16)	0.70943 (15)	0.15397 (13)	0.0187 (2)
H2	0.447969	0.698634	0.085623	0.022*
C1	0.82761 (19)	0.26947 (19)	−0.07624 (16)	0.0213 (3)
H1A	0.844476	0.382168	−0.061678	0.026*
H1AB	0.942570	0.216566	−0.133336	0.026*
C2	0.7951 (2)	0.16181 (18)	0.06343 (16)	0.0222 (3)
H2A	0.911494	0.135809	0.097951	0.027*
H2AB	0.766041	0.053719	0.048851	0.027*
C3	0.6416 (2)	0.24003 (18)	0.17554 (15)	0.0202 (3)
H3A	0.524235	0.264324	0.142544	0.024*
H3AB	0.628253	0.156392	0.257539	0.024*
C4	0.8394 (2)	0.3698 (2)	0.2869 (2)	0.0289 (3)
H4A	0.852000	0.474931	0.316837	0.043*
H4B	0.951096	0.328712	0.222555	0.043*
H4C	0.820747	0.285389	0.366416	0.043*
C5	0.5084 (2)	0.48877 (19)	0.31152 (15)	0.0219 (3)
H5A	0.541977	0.588041	0.339066	0.026*
H5AB	0.480340	0.410569	0.395386	0.026*
C6	0.3326 (2)	0.54741 (19)	0.25240 (16)	0.0220 (3)
H6A	0.315943	0.456530	0.203864	0.026*
H6AB	0.226499	0.564160	0.329274	0.026*
C7	0.3152 (2)	0.8628 (2)	0.22684 (18)	0.0267 (3)
H7A	0.305431	0.964466	0.161379	0.040*
H7B	0.424822	0.852681	0.266082	0.040*
H7C	0.205791	0.870354	0.300087	0.040*
Cl1	0.21029 (5)	0.17202 (5)	0.52791 (4)	0.02439 (13)
O1	0.2471 (3)	0.1745 (2)	0.38061 (17)	0.0494 (4)
O2	0.1539 (3)	0.0175 (3)	0.5935 (3)	0.0669 (6)
O3	0.3753 (3)	0.1946 (3)	0.5690 (2)	0.0560 (5)
O4	0.0647 (3)	0.3129 (3)	0.5618 (3)	0.0662 (6)
Cl2	0.73888 (5)	0.71235 (4)	0.00536 (4)	0.02198 (13)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0174 (5)	0.0170 (5)	0.0224 (5)	−0.0036 (4)	−0.0087 (4)	−0.0011 (4)
N2	0.0150 (5)	0.0180 (5)	0.0242 (5)	−0.0023 (4)	−0.0058 (4)	−0.0042 (4)

C1	0.0144 (6)	0.0238 (6)	0.0281 (7)	-0.0034 (5)	-0.0074 (5)	-0.0056 (5)
C2	0.0200 (6)	0.0181 (6)	0.0301 (7)	0.0004 (5)	-0.0105 (5)	-0.0041 (5)
C3	0.0201 (6)	0.0175 (6)	0.0263 (6)	-0.0051 (5)	-0.0095 (5)	-0.0026 (5)
C4	0.0247 (7)	0.0285 (8)	0.0402 (8)	-0.0049 (6)	-0.0196 (6)	-0.0047 (6)
C5	0.0237 (6)	0.0216 (6)	0.0213 (6)	-0.0028 (5)	-0.0066 (5)	-0.0032 (5)
C6	0.0183 (6)	0.0193 (6)	0.0278 (7)	-0.0035 (5)	-0.0043 (5)	-0.0012 (5)
C7	0.0304 (8)	0.0198 (7)	0.0346 (8)	-0.0038 (5)	-0.0133 (6)	-0.0085 (6)
C11	0.0237 (2)	0.0222 (2)	0.0294 (2)	-0.00633 (14)	-0.00871 (15)	-0.00105 (14)
O1	0.0545 (10)	0.0648 (11)	0.0346 (7)	-0.0209 (8)	-0.0060 (7)	-0.0131 (7)
O2	0.0720 (13)	0.0481 (10)	0.0887 (15)	-0.0350 (9)	-0.0404 (12)	0.0356 (10)
O3	0.0533 (10)	0.0629 (11)	0.0691 (12)	-0.0267 (9)	-0.0400 (9)	0.0023 (9)
O4	0.0504 (10)	0.0561 (11)	0.0837 (15)	0.0128 (9)	-0.0007 (10)	-0.0290 (10)
C12	0.01828 (19)	0.0202 (2)	0.0293 (2)	-0.00692 (13)	-0.00735 (14)	0.00056 (13)

*Geometric parameters (Å, °)*

N1—C4	1.5037 (19)	C4—H4A	0.9700
N1—C3	1.5095 (18)	C4—H4B	0.9700
N1—C5	1.5116 (19)	C4—H4C	0.9700
N1—H1	0.9900	C5—C6	1.522 (2)
N2—C7	1.5033 (19)	C5—H5A	0.9800
N2—C6	1.513 (2)	C5—H5AB	0.9800
N2—C1 <sup>i</sup>	1.5181 (18)	C6—H6A	0.9800
N2—H2	0.9900	C6—H6AB	0.9800
C1—C2	1.526 (2)	C7—H7A	0.9700
C1—H1A	0.9800	C7—H7B	0.9700
C1—H1AB	0.9800	C7—H7C	0.9700
C2—C3	1.527 (2)	C11—O2	1.4180 (17)
C2—H2A	0.9800	C11—O1	1.4328 (16)
C2—H2AB	0.9800	C11—O4	1.4342 (19)
C3—H3A	0.9800	C11—O3	1.4380 (16)
C3—H3AB	0.9800		
C4—N1—C3	111.91 (12)	N1—C4—H4A	109.5
C4—N1—C5	108.49 (12)	N1—C4—H4B	109.5
C3—N1—C5	112.37 (11)	H4A—C4—H4B	109.5
C4—N1—H1	108.0	N1—C4—H4C	109.5
C3—N1—H1	108.0	H4A—C4—H4C	109.5
C5—N1—H1	108.0	H4B—C4—H4C	109.5
C7—N2—C6	112.12 (12)	N1—C5—C6	116.19 (12)
C7—N2—C1 <sup>i</sup>	111.00 (11)	N1—C5—H5A	108.2
C6—N2—C1 <sup>i</sup>	109.81 (11)	C6—C5—H5A	108.2
C7—N2—H2	107.9	N1—C5—H5AB	108.2
C6—N2—H2	107.9	C6—C5—H5AB	108.2
C1 <sup>i</sup> —N2—H2	107.9	H5A—C5—H5AB	107.4
N2 <sup>i</sup> —C1—C2	113.55 (12)	N2—C6—C5	115.16 (12)
N2 <sup>i</sup> —C1—H1A	108.9	N2—C6—H6A	108.5
C2—C1—H1A	108.9	C5—C6—H6A	108.5

N2 <sup>i</sup> —C1—H1AB	108.9	N2—C6—H6AB	108.5
C2—C1—H1AB	108.9	C5—C6—H6AB	108.5
H1A—C1—H1AB	107.7	H6A—C6—H6AB	107.5
C1—C2—C3	116.36 (12)	N2—C7—H7A	109.5
C1—C2—H2A	108.2	N2—C7—H7B	109.5
C3—C2—H2A	108.2	H7A—C7—H7B	109.5
C1—C2—H2AB	108.2	N2—C7—H7C	109.5
C3—C2—H2AB	108.2	H7A—C7—H7C	109.5
H2A—C2—H2AB	107.4	H7B—C7—H7C	109.5
N1—C3—C2	114.13 (12)	O2—C11—O1	110.75 (13)
N1—C3—H3A	108.7	O2—C11—O4	110.14 (15)
C2—C3—H3A	108.7	O1—C11—O4	106.85 (14)
N1—C3—H3AB	108.7	O2—C11—O3	110.94 (12)
C2—C3—H3AB	108.7	O1—C11—O3	108.56 (12)
H3A—C3—H3AB	107.6	O4—C11—O3	109.50 (14)
N2 <sup>i</sup> —C1—C2—C3	-69.05 (16)	C3—N1—C5—C6	-61.62 (16)
C4—N1—C3—C2	-66.31 (16)	C7—N2—C6—C5	-69.95 (16)
C5—N1—C3—C2	171.33 (11)	C1 <sup>i</sup> —N2—C6—C5	166.15 (12)
C1—C2—C3—N1	-62.42 (16)	N1—C5—C6—N2	-77.80 (16)
C4—N1—C5—C6	174.11 (13)		

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ C12	0.99	2.13	3.0701 (14)	159
N2—H2 $\cdots$ C12	0.99	2.17	3.1038 (15)	156
C1—H1A $\cdots$ C12	0.98	2.77	3.6868 (17)	157
C5—H5AB $\cdots$ O3	0.98	2.39	3.351 (3)	167
C3—H3A $\cdots$ C12 <sup>i</sup>	0.98	2.67	3.6274 (17)	164
C3—H3AB $\cdots$ O2 <sup>ii</sup>	0.98	2.52	3.288 (3)	135
C4—H4A $\cdots$ O4 <sup>iii</sup>	0.97	2.49	3.429 (3)	164
C4—H4C $\cdots$ O2 <sup>ii</sup>	0.97	2.39	3.171 (3)	137
C5—H5A $\cdots$ O3 <sup>iii</sup>	0.98	2.34	3.317 (3)	173
C6—H6AB $\cdots$ O4 <sup>iv</sup>	0.98	2.31	3.231 (3)	156
C6—H6A $\cdots$ C12 <sup>i</sup>	0.98	2.80	3.7414 (17)	161
C7—H7B $\cdots$ O3 <sup>iii</sup>	0.97	2.40	3.333 (3)	161

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