Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,4,8,11-Tetraazoniacyclotetradecane diaquatetrachloridomanganese(II) dichloride dihydrate

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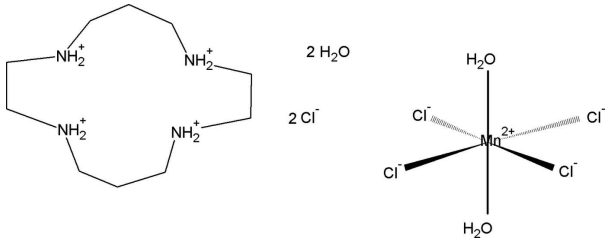
Received 30 July 2010; accepted 9 August 2010

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.002 Å; R factor = 0.018; wR factor = 0.059; data-to-parameter ratio = 18.3.

The title compound, $(C_{10}H_{28}N_4)[MnCl_4(H_2O)_2]Cl_2\cdot 2H_2O$, consists of isolated octahedral $[MnCl_4(H_2O)_2]^{2-}$ anions, tetraprotonated 1,4,8,11-tetraazoniacyclotetradecane cations, chloride anions and water molecules connected by a network of hydrogen bonds. The Mn^{II} atom is situated on an inversion centre, and the 1,4,8,11-tetraazoniacyclotetradecane cation is located on a mirror plane.

Related literature

For bond distances and angles in the cyclam molecule, see: Melson (1979).



Experimental

Crystal data

$(C_{10}H_{28}N_4)[MnCl_4(H_2O)_2]Cl_2\cdot 2H_2O$
M_r = 544.1
Orthorhombic, *Pnma*
a = 14.8492 (2) Å
b = 19.3511 (3) Å
c = 7.8772 (1) Å
V = 2263.50 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.31 mm^{-1}
T = 292 K
0.36 × 0.22 × 0.16 mm

Data collection

Oxford Diffraction CCD diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)
T_{min} = 0.721, T_{max} = 0.840
26200 measured reflections
2429 independent reflections
1999 reflections with $I > 3\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.059
S = 1.09
2429 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1M···O2	0.87	2.01	2.8367 (16)	159
N1—H1N···Cl2^{i}	0.87	2.51	3.2465 (11)	143
N1—H1N···Cl1^{ii}	0.87	2.77	3.2317 (11)	115
O1—H1O···O2	0.82 (1)	1.94 (1)	2.7474 (15)	172 (2)
O1—H1P···Cl3	0.82 (1)	2.35 (1)	3.1382 (10)	162 (1)
N2—H2M···O1^{iii}	0.87	2.08	2.8926 (15)	155
N2—H2N···Cl1	0.87	2.48	3.2383 (11)	146
O2—H2O···Cl4^{iv}	0.83 (1)	2.19 (1)	3.0205 (12)	173 (1)
O2—H2P···Cl2^{v}	0.81 (2)	2.52 (2)	3.2832 (11)	157 (1)
C1—H1A···Cl2	0.96	2.71	3.6100 (14)	156
C3—H3N···Cl3	0.96	2.81	3.7016 (14)	155
C5—H5B···Cl4	0.96	2.72	3.6178 (14)	156

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006* and *publCIF* (Westrip, 2010).

The authors acknowledge the institutional research plan No. AVOZ10100521 of the Institute of Physics, the project Praemium Academiae of the Academy of Sciences of the Czech Republic and Unité associée au CNRST (URAC 19).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5316).

References

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
Melson, G. A. (1979). Editor. *Coordination Chemistry of Macrocyclic Compounds*. New York: Plenum.
Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Praha, Czech Republic.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2010). E**66**, m1103 [https://doi.org/10.1107/S1600536810031958]

1,4,8,11-Tetraazoniacyclotetradecane diaquatetrachloridomanganese(II) dichloride dihydrate

Michaela Pojarová, Karla Fejfarová and Brahim El Bali

S1. Comment

The structure contains isolated $[MnCl_4(H_2O)_2]^{2-}$ octahedron and centrosymmetric tetraprotonated 1,4,8,11-tetraazacyclodecane (cyclamH4^{4+}) moieties connected by a network of N—H···*X* (*X*= O, Cl) hydrogen bonds (Fig. 1). The positive charge of the cyclamH4^{4+} is out-balanced beside the octahedral anion with two chloride ions. Two molecules of water participate in the manganese coordination, whereas the third water molecule forms bridge between chloride anion (Cl4), nitrogen atom (N1) in 1,4,8,11-tetraazacyclodecane (cyclam) and water (O1) molecule in $[MnCl_4(H_2O)_2]$. The cyclam molecules and [MnCl4(H_2O)2] octahedral are arranged into alternating layers parallel with *ab*. In direction of *c* axis the cyclam molecules form infinite channels (Fig. 2). The molecules of cyclam are in a distance of 7.877 Å with chloride anion between the middle CH_2 groups in propyl chains (C6···Cl4 3.952 Å, Cl4···C6 3.923Å on one side and C4···Cl3 3.855 Å, Cl3···C4 4.022Å on the other side of channels). The tetra-protonated cyclam $(C_{10}H_{28}N_4)^{4+}$ exhibits C—C, C—N bond distances and angles in the range usually found for the cyclam molecule (Melson, 1979). The tetra-protonated macrocycle adopts an endodentate quadrangular (3,4,3,4)-A conformation which is the most stable among the four possible conformations, the *exo* orientation of the four nitrogen atoms gives rise to the maximal charge separation. The free water molecule participates also in a cyclic system of hydrogen bonds between water (O1) molecule coordinated to manganese and chloride anions (Cl3 and Cl4). The six-membered cycle is formed by hydrogen bonds between O1—H1o···O2—H2o···Cl4···H2o—O2···H1o—O1—H1p···Cl3···H1p—O1 (Fig. 4).

S2. Experimental

To an acidic solution of cyclam (1 mmol) was added $MnCl_2.4H_2O$ (1 mmol) in 10 ml of distilled water. The mixture was then stirred at room temperature for 3 h after which it was left to evaporate in air. After three weeks, crystals appeared, which were filtered off and washed with 90% ethanol solution.

S3. Refinement

All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. Despite of it the hydrogen atoms bonded to carbon and nitrogen atoms were constrained to ideal positions. The O—H distances were restrained to 0.82 Å with sigma 0.01. The isotropic temperature parameters of hydrogen atoms were calculated as 1.2*U_{eq} of the parent atom.)

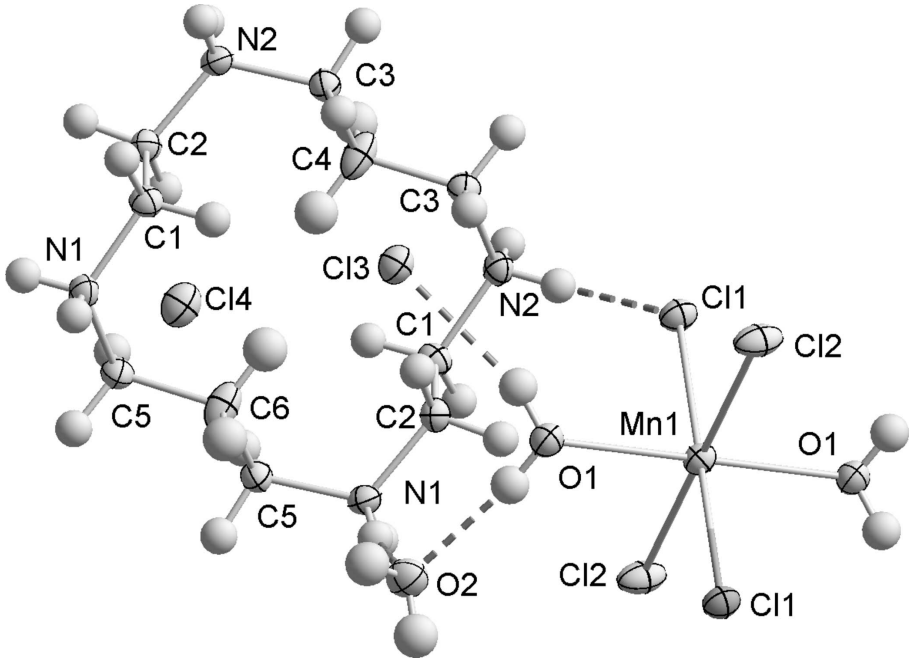


Figure 1

View of the cyclamH4^{4+} cation, the $[MnCl_4(H_2O)_2]^{2-}$ anion, free water molecule and chloride anions, together with atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

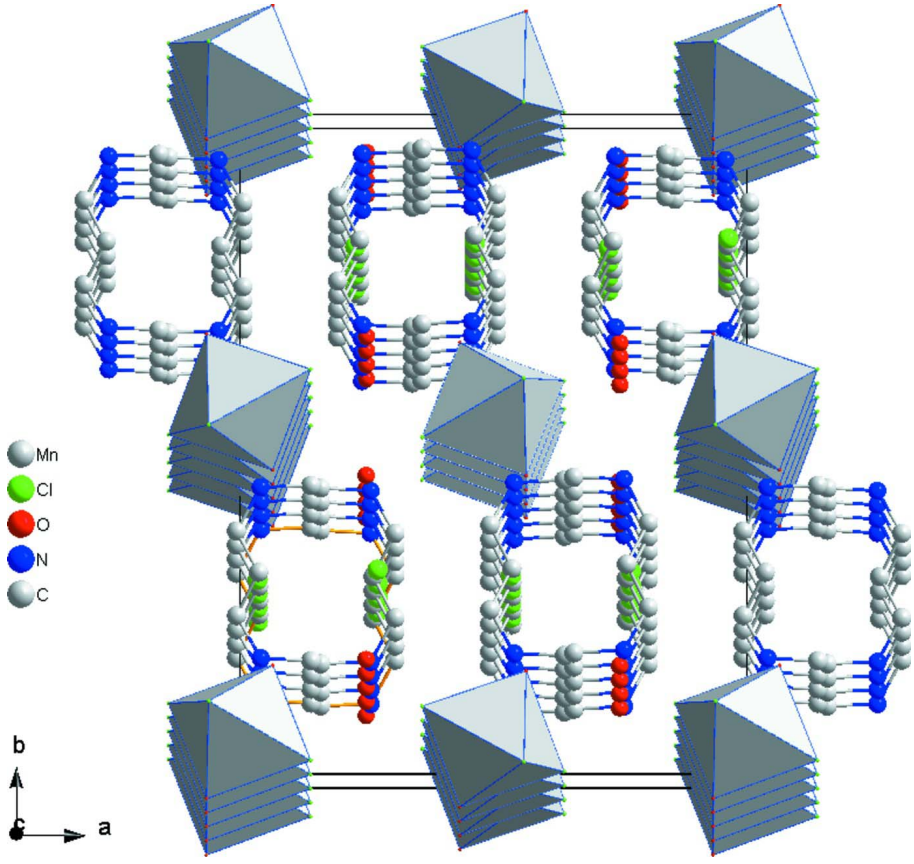


Figure 2

Projection along the *c* axis, showing the channels formed by the cyclam cavity.

1,4,8,11-Tetraazoniacyclotetradecane diaquatetrachloridomanganese(II) dichloride dihydrate

Crystal data

$(C_{10}H_{28}N_4)[MnCl_4(H_2O)_2]Cl_2·2H_2O$
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Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
a = 14.8492 (2) Å
b = 19.3511 (3) Å
c = 7.8772 (1) Å
V = 2263.50 (5) Å^3
Z = 4

F(000) = 1132
D_x = 1.596 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71069 Å
Cell parameters from 16479 reflections
θ = 2.5–26.5°
μ = 1.31 mm^{-1}
T = 292 K
Prism, colourless
0.36 × 0.22 × 0.16 mm

Data collection

Oxford Diffraction CCD diffractometer
Radiation source: X-ray tube
Graphite monochromator
Detector resolution: 8.3438 pixels mm^{-1}
Rotation method data acquisition using *ω* scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2005)
T_{min} = 0.721, T_{max} = 0.840

26200 measured reflections
2429 independent reflections
1999 reflections with $I > 3\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.5°, θ_{min} = 2.7°
h = −18→18
k = −24→24
l = −9→9

Refinement

Refinement on F^2
$R[F > 3\sigma(F)] = 0.018$
$wR(F) = 0.059$
$S = 1.09$
2429 reflections
133 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + 0.0016I^2]$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.10$ e Å^{-3}

Special details

Experimental. CrysAlis RED, Oxford Diffraction Ltd., Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.

Refinement. The refinement was carried out against all reflections. The conventional *R*-factor is always based on *F*. The goodness of fit as well as the weighted *R*-factor are based on *F* and F^2 for refinement carried out on *F* and F^2, respectively. The threshold expression is used only for calculating *R*-factors *etc*. and it is not relevant to the choice of reflections for refinement.
All the H atoms were discrenible in difference Fourier maps and could be refined to reasonable geometry. Despite of it the H atoms bonded to catbon and nitrogen atoms were constrained to ideal positions. The O—H distances were restrained to 0.82 Å with σ 0.01. The isotropic temperature parameters of hydrogen atoms were calculated as 1.2*U_{eq} of the parent atom.
The program used for refinement, Jana2006, uses the weighting scheme based on the experimental expectations, see _refine_ls_weighting_details,

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0	0	0	0.01920 (9)
Cl1	−0.06104 (2)	0.040619 (17)	0.28548 (4)	0.02344 (10)
Cl3	0.03588 (3)	0.25	0.10590 (6)	0.02742 (14)
Cl2	0.14001 (2)	−0.046308 (19)	0.14869 (4)	0.03195 (11)
Cl4	0.27203 (4)	0.25	0.80690 (7)	0.03300 (16)
O1	0.06526 (7)	0.10208 (5)	−0.04773 (13)	0.0246 (3)
O2	0.24961 (7)	0.11049 (6)	−0.02640 (14)	0.0323 (3)
N1	0.25833 (7)	0.12044 (5)	0.33251 (14)	0.0211 (3)
N2	0.04152 (7)	0.12050 (5)	0.59062 (14)	0.0203 (3)
C1	0.15939 (9)	0.11683 (7)	0.36796 (16)	0.0212 (4)
C2	0.14089 (8)	0.11699 (7)	0.55731 (17)	0.0206 (4)
C3	−0.00618 (8)	0.18592 (7)	0.54150 (17)	0.0217 (4)
C4	0.03729 (16)	0.25	0.6165 (3)	0.0314 (6)
C5	0.30646 (9)	0.18591 (6)	0.38037 (17)	0.0228 (4)
C6	0.26338 (16)	0.25	0.3046 (3)	0.0329 (7)
H1m	0.268045	0.111373	0.225895	0.0253*
H1n	0.285152	0.085355	0.379572	0.0253*
H2m	0.031159	0.111526	0.697062	0.0244*
H2n	0.015046	0.085424	0.542836	0.0244*
H1a	0.134992	0.075561	0.318388	0.0254*
H1b	0.129816	0.155584	0.31619	0.0254*
H2a	0.165029	0.07569	0.607205	0.0247*

H2b	0.169981	0.156082	0.608522	0.0247*
H3a	−0.067928	0.183451	0.577083	0.026*
H3n	−0.007609	0.18981	0.420039	0.026*
H4a	0.100476	0.25	0.590704	0.0377*
H4b	0.029252	0.25	0.737419	0.0377*
H5a	0.368181	0.18312	0.344749	0.0273*
H5b	0.308095	0.190111	0.50176	0.0273*
H6a	0.200057	0.25	0.329167	0.0394*
H6b	0.272047	0.25	0.183783	0.0394*
H2o	0.2545 (12)	0.1474 (6)	−0.080 (2)	0.0387*
H2p	0.2810 (10)	0.0859 (8)	−0.085 (2)	0.0387*
H1o	0.1201 (6)	0.1002 (8)	−0.042 (2)	0.0296*
H1p	0.0475 (11)	0.1365 (6)	0.0039 (18)	0.0296*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02119 (16)	0.01807 (15)	0.01834 (15)	0.00097 (11)	−0.00088 (10)	0.00132 (11)
Cl1	0.0257 (2)	0.02367 (17)	0.02098 (17)	0.00260 (12)	−0.00054 (12)	−0.00266 (13)
Cl3	0.0298 (3)	0.0235 (2)	0.0290 (3)	0	−0.0005 (2)	0
Cl2	0.0316 (2)	0.0361 (2)	0.02823 (19)	0.01481 (15)	−0.00806 (14)	−0.00686 (15)
Cl4	0.0394 (3)	0.0291 (3)	0.0305 (3)	0	−0.0040 (2)	0
O1	0.0262 (5)	0.0217 (5)	0.0260 (5)	−0.0011 (4)	0.0017 (4)	−0.0027 (4)
O2	0.0351 (6)	0.0327 (6)	0.0290 (6)	0.0005 (5)	0.0060 (4)	0.0008 (5)
N1	0.0225 (6)	0.0184 (5)	0.0224 (6)	0.0031 (4)	0.0018 (4)	−0.0012 (5)
N2	0.0223 (6)	0.0179 (5)	0.0207 (6)	−0.0024 (4)	0.0023 (4)	0.0014 (4)
C1	0.0198 (6)	0.0208 (6)	0.0230 (7)	−0.0017 (5)	−0.0010 (5)	−0.0022 (5)
C2	0.0186 (6)	0.0221 (6)	0.0210 (6)	0.0009 (5)	−0.0010 (5)	0.0026 (5)
C3	0.0191 (7)	0.0200 (7)	0.0259 (7)	0.0011 (5)	−0.0014 (5)	0.0002 (6)
C4	0.0448 (13)	0.0191 (9)	0.0304 (11)	0	−0.0135 (10)	0
C5	0.0185 (7)	0.0214 (7)	0.0285 (7)	−0.0010 (5)	−0.0013 (5)	0.0002 (6)
C6	0.0451 (13)	0.0208 (10)	0.0327 (12)	0	−0.0135 (9)	0

Geometric parameters (Å, º)

Mn1—Cl1	2.5488 (3)	N2—H2n	0.8700
Mn1—Cl1^{i}	2.5488 (3)	C1—C2	1.5166 (18)
Mn1—Cl2	2.5490 (4)	C1—H1a	0.9600
Mn1—Cl2^{i}	2.5490 (4)	C1—H1b	0.9600
Mn1—O1	2.2322 (10)	C2—H2a	0.9600
Mn1—O1^{i}	2.2322 (10)	C2—H2b	0.9600
O1—H1o	0.817 (9)	C3—C4	1.5176 (18)
O1—H1p	0.824 (13)	C3—H3a	0.9600
O2—H2o	0.833 (13)	C3—H3n	0.9600
O2—H2p	0.812 (15)	C4—H4a	0.960
N1—C1	1.4971 (17)	C4—H4b	0.960
N1—C5	1.5026 (16)	C5—C6	1.5179 (18)
N1—H1m	0.8700	C5—H5a	0.9600

N1—H1n	0.8700	C5—H5b	0.9600
N2—C2	1.5004 (16)	C6—H6a	0.960
N2—C3	1.5013 (17)	C6—H6b	0.960
N2—H2m	0.8700		

Cl1—Mn1—Cl1^{i}	180	C2—C1—H1b	109.47
Cl1—Mn1—Cl2	89.601 (11)	H1a—C1—H1b	107.72
Cl1—Mn1—Cl2^{i}	90.399 (11)	N2—C2—C1	110.50 (10)
Cl1—Mn1—O1	91.72 (3)	N2—C2—H2a	109.47
Cl1—Mn1—O1^{i}	88.28 (3)	N2—C2—H2b	109.47
Cl1^{i}—Mn1—Cl2	90.399 (11)	C1—C2—H2a	109.47
Cl1^{i}—Mn1—Cl2^{i}	89.601 (11)	C1—C2—H2b	109.47
Cl1^{i}—Mn1—O1	88.28 (3)	H2a—C2—H2b	108.42
Cl1^{i}—Mn1—O1^{i}	91.72 (3)	N2—C3—C4	112.83 (11)
Cl2—Mn1—Cl2^{i}	180	N2—C3—H3a	109.47
Cl2—Mn1—O1	91.97 (3)	N2—C3—H3n	109.47
Cl2—Mn1—O1^{i}	88.03 (3)	C4—C3—H3a	109.47
Cl2^{i}—Mn1—O1	88.03 (3)	C4—C3—H3n	109.47
Cl2^{i}—Mn1—O1^{i}	91.97 (3)	H3a—C3—H3n	105.89
O1—Mn1—O1^{i}	180	C3—C4—C3^{ii}	109.58 (15)
H1o—O1—H1p	109.3 (16)	C3—C4—H4a	109.47
H2o—O2—H2p	99.4 (15)	C3—C4—H4b	109.47
C1—N1—C5	117.34 (10)	C3^{ii}—C4—H4a	109.47
C1—N1—H1m	109.47	C3^{ii}—C4—H4b	109.47
C1—N1—H1n	109.47	H4a—C4—H4b	109.4
C5—N1—H1m	109.47	N1—C5—C6	112.94 (12)
C5—N1—H1n	109.47	N1—C5—H5a	109.47
H1m—N1—H1n	100.26	N1—C5—H5b	109.47
C2—N2—C3	117.20 (10)	C6—C5—H5a	109.47
C2—N2—H2m	109.47	C6—C5—H5b	109.47
C2—N2—H2n	109.47	H5a—C5—H5b	105.77
C3—N2—H2m	109.47	C5—C6—C5^{ii}	109.58 (16)
C3—N2—H2n	109.47	C5—C6—H6a	109.47
H2m—N2—H2n	100.45	C5—C6—H6b	109.47
N1—C1—C2	111.17 (10)	C5^{ii}—C6—H6a	109.47
N1—C1—H1a	109.47	C5^{ii}—C6—H6b	109.47
N1—C1—H1b	109.47	H6a—C6—H6b	109.4
C2—C1—H1a	109.47		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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O1—H1P···Cl3	0.82 (1)	2.35 (1)	3.1382 (10)	162 (1)
N2—H2M···O1^{v}	0.87	2.08	2.8926 (15)	155
N2—H2N···Cl1	0.87	2.48	3.2383 (11)	146
O2—H2O···Cl4^{vi}	0.83 (1)	2.19 (1)	3.0205 (12)	173 (1)
O2—H2P···Cl2^{vii}	0.81 (2)	2.52 (2)	3.2832 (11)	157 (1)
C1—H1A···Cl2	0.96	2.71	3.6100 (14)	156
C3—H3N···Cl3	0.96	2.81	3.7016 (14)	155
C5—H5B···Cl4	0.96	2.72	3.6178 (14)	156

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