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ISSN 2414-3146

Crystal structure of tris[(pyridin-1-ium-2-yl)-methyl]amine trichloride–methanol–water (1/1.829/0.342)

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Received 24 May 2018
Accepted 4 June 2018

Edited by A. J. Lough, University of Toronto, Canada

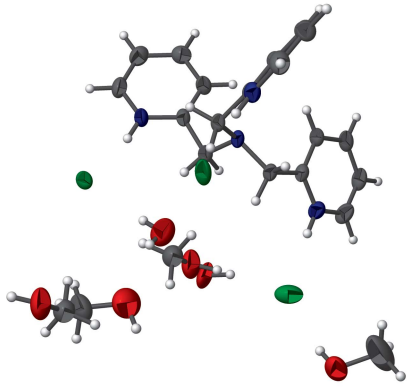
Keywords: crystal structure; protonated ligand; hydrogen bonding.

CCDC reference: 1847161

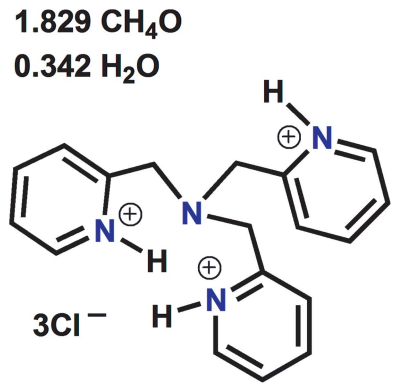
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_{18}H_{21}N_4^{3+}\cdot 3Cl^-.1.829CH_4O.0.342H_2O$, the three pyridyl secondary amine N atoms are protonated with N—H···Cl hydrogen bonds present. The crystal structure contains a region of partially occupied and disordered methanol and water solvent. One of the three chloride anions is involved in hydrogen bonding to three methanol molecules, two of which are disordered.

3D view



Chemical scheme



Structure description

Tris(2-pyridylmethyl)amine (TPMA) is one of the two most studied tetradentate tripodal amine ligands with complexes reported with all first row transition metals (except titanium), most second and third row metals, and majority of the lanthanide ions (Blackman, 2005). Complexes employing the TPMA ligand framework are used in many reactions such as alkane hydroxylation (Costas *et al.*, 2004), ethane polymerization (Robertson *et al.*, 2003), radical polymerization (Schroder *et al.*, 2012), and photocaging (Sharma *et al.*, 2014), to name a few. In addition to the neutral form of TPMA, the triprotonated salt has also been reported with the following counter-ions: $3HClO_4$ (Britton *et al.*, 1991), $(SO_4)(NO_3)$ (Hazell *et al.*, 1999), $(CF_3SO_3)_2(PF_6)$, $(Br)(PF_6)_2$, and $(Cl)(PF_6)_2$ (Sugimoto *et al.*, 2002). There are over 700 reported structures incorporating the *tris*(2-pyridylmethyl)amine ligand derivative and to date only seven have been published of just the ligand with three of its pyridyl amine N atoms protonated (CSD Version 5.38; Groom *et al.*, 2016). The protonated form of TPMA introduces new coordination modes and reaction possibilities for the ligand. Given the diverse application of compounds incorporating the *tris*(2-pyridylmethyl)amine moiety, herein we report on the synthesis and crystal structure obtained for the title compound.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl1	0.88	2.15	3.018 (2)	167
N3—H3A···Cl2	0.88	2.13	3.007 (2)	173
N4—H4A···Cl3	0.88	2.18	3.062 (2)	176
O1—H1···Cl3	0.84	2.32	3.145 (2)	168
O2—H2A···Cl3	0.84	2.34	3.174 (6)	171
O2B—H2B···Cl1^{i}	0.84	2.42	3.241 (19)	167
O2C—H2C···Cl1	0.83	2.53	3.36 (2)	173
O2D—H2E···Cl3	0.84	1.93	2.727 (16)	158

Symmetry code: (i) $-x+2, -y+2, -z+1$.

The asymmetric unit is shown in Fig. 1. The three pyridyl secondary amine nitrogen atoms are protonated with N—H···Cl hydrogen bonds present (Table 1). The crystal structure contains a region of partially occupied and disordered methanol and water solvent. One of the three chloride anions is involved in hydrogen bonding to three methanol molecules, two of which are disordered.

Synthesis and crystallization

Synthesis of *tris*(2-pyridylmethyl)amine (TPMA): TPMA was synthesized according to modified literature procedures (Britovsek *et al.*, 2005). A 500 ml round-bottom flask was charged with 100 ml of dichloromethane solvent. While mixing, 2-(aminomethyl)pyridine (1.62 ml, 15.0 mmol) and sodium triacetoxyborohydride (9.63 g, 44.2 mmol) were added, generating a clear solution. 2-Pyridinecarboxaldehyde (3.38 g, 31.54 mmol) was slowly added to the mixture, producing a yellow-colored solution. The reaction was allowed to mix for 24 h and interrupted with the addition of sodium

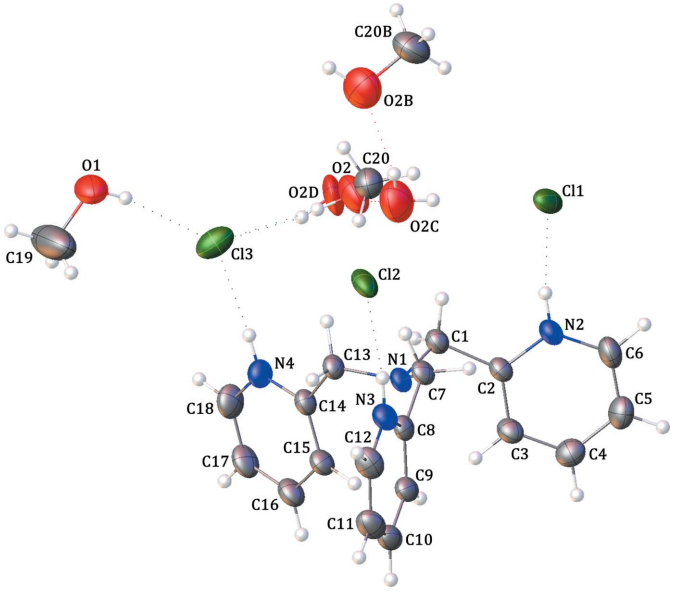


Figure 1
The asymmetric unit of the title compound showing displacement ellipsoids at the 50% probability level. Hydrogen bonds are shown as dotted lines.

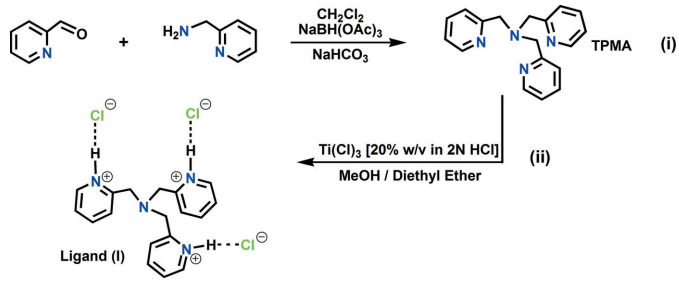


Figure 2
Synthetic scheme for the title compound, $[C_{18}H_{21}N_4^{3+}\cdot Cl^-]$ (**1**).

hydrogen carbonate until a pH of 10 was achieved. Extractions were performed on the resulting solution with ethyl acetate and the organic layers collected and combined. The organic layer was subsequently dried using magnesium sulfate ($MgSO_4$) and solvent removed using a rotary evaporator to generate a yellow residue. This residue was dried under vacuum for three h to produce the desired ligand as a yellow solid (4.43 g, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ3.86 (*s*, 2H), δ7.51 (d, 1H), δ7.63 (*t*, 1H), δ 8.52 (*d*, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 60.60, 122.35, 123.32, 136.59, 149.35, 159.81. FT–IR (solid) ν (cm^{-1}): 3048 (*s*), 3009 (*s*), 2920 (*s*), 2803 (*s*), 1585 (*s*), 1566 (*s*), 970 (*s*), 745 (*s*).

Synthesis of *tris*(2-pyridiniummethyl)amine trichloride salt: TPMA (0.100 g, 0.344 mmol) was dissolved in 10 ml methanol in a 100 ml round-bottom flask. Titanium(III) chloride, 20% *w*/*v* solution in 2 *M* HCl (0.266 g, 0.344 mmol) was added to the flask to give a dark-brown-colored solution. This reaction was allowed to mix for 1 h then 30 ml of diethyl ether was transferred into the flask, facilitating the precipitation of product as a light-brown powder. The mixture was filtered and the precipitate washed with excess diethyl ether solvent. The precipitate was dried under vacuum for 30 minutes to yield a light brown colored solid (0.130 g, 85%). Colorless single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in methanol. The reaction scheme is shown in Fig. 2.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. A solvent-occupied site around an inversion center features alternatively two methanol molecules, or one methanol and two water molecules. The latter methanol and water molecules are disordered around the inversion center and hydrogen bonded to each other and neighboring chloride anions. The former methanol molecules are hydrogen-bonded solely to the chloride anions. The disordered methanol molecules were restrained to have similar C—O bond distances. U^{ij} components of all disordered atoms were restrained to be similar for atoms closer to each other than 1.7 Å. Water H-atom positions were initially restrained based on hydrogen-bonding considerations. In the final refinement cycles they were set to ride on their carrier oxygen atoms. Subject to these conditions, the occupancy rates

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{21}N_4^{3+}\cdot 3Cl^-\cdot 1.829CH_4O\cdot 0.342H_2O$
M_r	464.50
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	11.0118 (10), 11.7295 (11), 11.7453 (11)
α, β, γ (°)	66.009 (4), 67.120 (4), 66.057 (4)
V (Å^3)	1220.4 (2)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.59
Crystal size (mm)	0.21 × 0.17 × 0.03
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Krause et al., 2015)
T_{min}, T_{max}	0.343, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31160, 5201, 4537
R_{int}	0.106
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.186, 1.09
No. of reflections	5201
No. of parameters	305
No. of restraints	25
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, −0.50

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015), *SHELXLE* (Hübschle *et al.*, 2011) and *OLEX2* (Dolomanov *et al.*, 2009).

refined to 0.658 (12) for the methanol sites and to two times 0.171 (6) for the disordered water/methanol site.

Acknowledgements

The authors would like to thank Creighton University and Cambridge Isotope Laboratories Inc. for funding support. X-ray crystallography support provided by Dr Matthias Zeller is gratefully acknowledged.

Funding information

This material was supported by the National Science Foundation through the Major Research Instrumentation Program under Grant No. CHE 1625543.

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full crystallographic data

IUCrData (2018). **3**, x180826 [https://doi.org/10.1107/S241431461800826X]

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Crystal data

$C_{18}H_{21}N_4^{3+}\cdot 3Cl^-\cdot 1.829CH_4O\cdot 0.342H_2O$
M_r = 464.50
Triclinic, $P\overline{1}$
a = 11.0118 (10) Å
b = 11.7295 (11) Å
c = 11.7453 (11) Å
α = 66.009 (4)°
β = 67.120 (4)°
γ = 66.057 (4)°
V = 1220.4 (2) Å^3
Z = 2
$F(000)$ = 489
D_x = 1.264 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9629 reflections
θ = 4.3–79.1°
μ = 3.59 mm^{-1}
T = 100 K
Plate, colourless
0.21 × 0.17 × 0.03 mm

Data collection

Bruker D8 Quest CMOS diffractometer
Radiation source: I-mu-S microsource X-ray tube
Laterally graded multilayer (Goebel) mirror monochromator
ω and phi scans
Absorption correction: multi-scan (SADABS; Krause et al., 2015)
T_{min} = 0.343, T_{max} = 0.754
31160 measured reflections
5201 independent reflections
4537 reflections with $I > 2\sigma(I)$
R_{int} = 0.106
θ_{max} = 80.3°, θ_{min} = 4.3°
h = −14→13
k = −14→13
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.186
S = 1.09
5201 reflections
305 parameters
25 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1049P)^2 + 0.6234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

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.

Refinement. A solvate occupied site around an inversion center features alternatively two methanol molecules, or one methanol and two water molecules. The latter methanol and water molecules are disordered around the inversion center and hydrogen bonded with each other and neighboring chloride anions. The former methanol molecules are H-bonded solely to the chloride anions. The disordered methanol molecules were restrained to have similar C-O bond distances. Uij components of all disordered atoms were restrained to be similar for atoms closer to each other than 1.7 Angstrom. Water H atom positions were initially restrained based on H-bonding considerations. In the final refinement cycles they were set to ride on their carrier oxygen atoms. Subject to these conditions the occupancy rates refined to 0.658 (12) for the methanol sites and to two times 0.171 (12) for the disordered water/methanol site.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.7392 (2)	0.7069 (2)	0.4204 (2)	0.0305 (5)	
H1A	0.761811	0.756260	0.456684	0.037*	
H1B	0.792022	0.613793	0.448384	0.037*	
C2	0.5876 (2)	0.7207 (2)	0.4709 (2)	0.0295 (4)	
C3	0.5218 (3)	0.6746 (2)	0.4280 (2)	0.0348 (5)	
H3	0.572215	0.633215	0.361721	0.042*	
C4	0.3821 (3)	0.6886 (3)	0.4815 (3)	0.0412 (6)	
H4	0.336434	0.656489	0.452391	0.049*	
C5	0.3088 (3)	0.7499 (3)	0.5781 (3)	0.0448 (6)	
H5	0.212920	0.760207	0.615750	0.054*	
C6	0.3774 (3)	0.7947 (3)	0.6176 (3)	0.0425 (6)	
H6	0.328958	0.837108	0.683264	0.051*	
C7	0.7324 (2)	0.8986 (2)	0.2344 (2)	0.0290 (4)	
H7A	0.797823	0.933560	0.239289	0.035*	
H7B	0.640732	0.931171	0.291206	0.035*	
C8	0.7236 (2)	0.9456 (2)	0.0975 (2)	0.0287 (4)	
C9	0.6717 (2)	0.8883 (2)	0.0512 (2)	0.0319 (5)	
H9	0.641573	0.813655	0.106105	0.038*	
C10	0.6643 (2)	0.9409 (3)	−0.0761 (3)	0.0380 (5)	
H10	0.629787	0.901558	−0.108752	0.046*	
C11	0.7067 (3)	1.0498 (3)	−0.1552 (3)	0.0438 (6)	
H11	0.701645	1.086207	−0.242381	0.053*	
C12	0.7566 (3)	1.1056 (3)	−0.1060 (3)	0.0428 (6)	
H12	0.784745	1.181719	−0.158549	0.051*	
C13	0.9275 (2)	0.7057 (2)	0.2246 (2)	0.0286 (4)	
H13A	0.977926	0.703263	0.279685	0.034*	
H13B	0.956330	0.764555	0.137102	0.034*	
C14	0.9630 (2)	0.5706 (2)	0.2164 (2)	0.0301 (5)	
C15	0.8830 (2)	0.5325 (2)	0.1812 (2)	0.0339 (5)	
H15	0.797596	0.591364	0.165025	0.041*	
C16	0.9277 (3)	0.4074 (3)	0.1696 (3)	0.0394 (5)	
H16	0.874242	0.381700	0.142761	0.047*	

C17	1.0499 (3)	0.3208 (3)	0.1970 (3)	0.0439 (6)	
H17	1.080228	0.234662	0.190965	0.053*	
C18	1.1263 (3)	0.3607 (3)	0.2329 (3)	0.0459 (6)	
H18	1.210376	0.302125	0.252413	0.055*	
N1	0.77877 (18)	0.75601 (17)	0.27902 (17)	0.0268 (4)	
N2	0.5133 (2)	0.7793 (2)	0.56423 (18)	0.0328 (4)	
H2	0.555239	0.808911	0.591621	0.039*	
N3	0.7651 (2)	1.05090 (19)	0.01713 (19)	0.0328 (4)	
H3A	0.799582	1.086001	0.046347	0.039*	
N4	1.0823 (2)	0.4836 (2)	0.2407 (2)	0.0356 (4)	
H4A	1.133956	0.507866	0.262558	0.043*	
Cl1	0.61836 (6)	0.91845 (6)	0.65626 (6)	0.0409 (2)	
Cl2	0.90850 (6)	1.15367 (6)	0.10913 (6)	0.0426 (2)	
Cl3	1.27468 (7)	0.56406 (7)	0.30465 (8)	0.0527 (2)	
O1	1.5645 (3)	0.6130 (3)	0.1571 (3)	0.0642 (7)	
H1	1.489251	0.599521	0.206423	0.096*	
C19	1.5992 (7)	0.5753 (9)	0.0479 (6)	0.127 (3)	
H19A	1.536095	0.636347	−0.005699	0.191*	
H19B	1.591865	0.487127	0.074178	0.191*	
H19C	1.693985	0.575950	−0.001960	0.191*	
O2	1.0260 (6)	0.7171 (6)	0.4915 (4)	0.0664 (15)	0.658 (12)
H2A	1.088991	0.683497	0.435259	0.100*	0.658 (12)
C20	0.9976 (7)	0.8532 (7)	0.4447 (6)	0.0545 (15)	0.658 (12)
H20A	0.985163	0.884194	0.357778	0.082*	0.658 (12)
H20B	1.074621	0.877445	0.441206	0.082*	0.658 (12)
H20C	0.913107	0.893280	0.502527	0.082*	0.658 (12)
O2B	1.0765 (19)	1.046 (2)	0.4480 (15)	0.082 (6)	0.171 (6)
H2B	1.159884	1.041305	0.427888	0.123*	0.171 (6)
C20B	1.009 (3)	1.073 (4)	0.564 (2)	0.071 (6)	0.171 (6)
H20D	0.980969	1.167871	0.549005	0.107*	0.171 (6)
H20E	1.071433	1.029612	0.620632	0.107*	0.171 (6)
H20F	0.927584	1.042209	0.606031	0.107*	0.171 (6)
O2C	0.924 (2)	0.902 (2)	0.432 (2)	0.077 (5)	0.171 (6)
H2C	0.852103	0.898903	0.491772	0.116*	0.171 (6)
H2D	0.947702	0.964886	0.426682	0.116*	0.171 (6)
O2D	1.0703 (18)	0.642 (3)	0.506 (2)	0.082 (7)	0.171 (6)
H2E	1.116877	0.630924	0.432940	0.122*	0.171 (6)
H2F	1.006250	0.711260	0.496388	0.122*	0.171 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0308 (10)	0.0306 (11)	0.0301 (10)	−0.0057 (8)	−0.0062 (8)	−0.0141 (8)
C2	0.0326 (11)	0.0278 (10)	0.0286 (10)	−0.0066 (8)	−0.0055 (8)	−0.0137 (8)
C3	0.0391 (12)	0.0345 (12)	0.0360 (11)	−0.0129 (10)	−0.0065 (9)	−0.0167 (9)
C4	0.0413 (13)	0.0413 (14)	0.0446 (13)	−0.0161 (11)	−0.0123 (11)	−0.0114 (11)
C5	0.0345 (12)	0.0495 (15)	0.0436 (14)	−0.0133 (11)	−0.0020 (10)	−0.0143 (12)
C6	0.0371 (12)	0.0469 (14)	0.0366 (12)	−0.0063 (11)	−0.0001 (10)	−0.0211 (11)

C7	0.0313 (10)	0.0227 (10)	0.0334 (11)	−0.0022 (8)	−0.0075 (8)	−0.0155 (8)
C8	0.0246 (9)	0.0248 (10)	0.0345 (11)	−0.0001 (8)	−0.0052 (8)	−0.0165 (8)
C9	0.0297 (10)	0.0296 (11)	0.0386 (12)	−0.0015 (9)	−0.0094 (9)	−0.0190 (9)
C10	0.0329 (11)	0.0408 (13)	0.0418 (13)	0.0029 (10)	−0.0144 (10)	−0.0232 (10)
C11	0.0472 (14)	0.0430 (14)	0.0362 (12)	−0.0005 (11)	−0.0170 (11)	−0.0142 (11)
C12	0.0486 (14)	0.0353 (13)	0.0365 (12)	−0.0070 (11)	−0.0101 (11)	−0.0097 (10)
C13	0.0263 (10)	0.0255 (10)	0.0347 (11)	−0.0041 (8)	−0.0047 (8)	−0.0162 (8)
C14	0.0289 (10)	0.0276 (10)	0.0316 (10)	−0.0041 (8)	−0.0038 (8)	−0.0148 (8)
C15	0.0348 (11)	0.0304 (11)	0.0390 (12)	−0.0041 (9)	−0.0079 (9)	−0.0200 (9)
C16	0.0437 (13)	0.0366 (13)	0.0416 (13)	−0.0108 (10)	−0.0037 (10)	−0.0232 (10)
C17	0.0463 (14)	0.0297 (12)	0.0521 (15)	−0.0040 (10)	−0.0043 (11)	−0.0242 (11)
C18	0.0377 (13)	0.0317 (13)	0.0596 (16)	0.0031 (10)	−0.0118 (12)	−0.0197 (12)
N1	0.0276 (8)	0.0232 (8)	0.0287 (9)	−0.0033 (7)	−0.0041 (7)	−0.0142 (7)
N2	0.0343 (10)	0.0342 (10)	0.0304 (9)	−0.0071 (8)	−0.0045 (8)	−0.0169 (8)
N3	0.0356 (10)	0.0274 (9)	0.0353 (10)	−0.0059 (8)	−0.0072 (8)	−0.0148 (8)
N4	0.0310 (9)	0.0298 (10)	0.0438 (11)	−0.0021 (8)	−0.0097 (8)	−0.0160 (8)
Cl1	0.0433 (3)	0.0357 (3)	0.0502 (4)	0.0041 (2)	−0.0214 (3)	−0.0262 (3)
Cl2	0.0456 (3)	0.0473 (4)	0.0439 (3)	−0.0208 (3)	0.0041 (3)	−0.0301 (3)
Cl3	0.0524 (4)	0.0438 (4)	0.0657 (5)	−0.0210 (3)	−0.0312 (3)	0.0017 (3)
O1	0.0560 (13)	0.0882 (18)	0.0741 (15)	−0.0317 (13)	−0.0074 (11)	−0.0474 (14)
C19	0.116 (4)	0.234 (9)	0.091 (4)	−0.102 (5)	0.015 (3)	−0.095 (5)
O2	0.066 (3)	0.078 (3)	0.050 (2)	−0.023 (3)	0.008 (2)	−0.035 (2)
C20	0.043 (3)	0.068 (4)	0.059 (3)	−0.012 (3)	−0.009 (2)	−0.033 (3)
O2B	0.078 (10)	0.102 (13)	0.059 (8)	−0.029 (9)	−0.010 (7)	−0.022 (8)
C20B	0.078 (14)	0.082 (16)	0.069 (12)	−0.015 (12)	−0.020 (10)	−0.045 (11)
O2C	0.064 (9)	0.075 (9)	0.080 (9)	0.000 (8)	−0.015 (8)	−0.036 (7)
O2D	0.041 (8)	0.12 (2)	0.064 (10)	0.002 (10)	0.009 (7)	−0.062 (13)

Geometric parameters (Å, º)

C1—N1	1.464 (3)	C14—N4	1.347 (3)
C1—C2	1.500 (3)	C14—C15	1.379 (3)
C1—H1A	0.9900	C15—C16	1.392 (3)
C1—H1B	0.9900	C15—H15	0.9500
C2—N2	1.343 (3)	C16—C17	1.381 (4)
C2—C3	1.377 (3)	C16—H16	0.9500
C3—C4	1.384 (4)	C17—C18	1.364 (4)
C3—H3	0.9500	C17—H17	0.9500
C4—C5	1.391 (4)	C18—N4	1.352 (3)
C4—H4	0.9500	C18—H18	0.9500
C5—C6	1.363 (4)	N2—H2	0.8800
C5—H5	0.9500	N3—H3A	0.8800
C6—N2	1.344 (3)	N4—H4A	0.8800
C6—H6	0.9500	O1—C19	1.389 (5)
C7—N1	1.462 (3)	O1—H1	0.8400
C7—C8	1.503 (3)	C19—H19A	0.9800
C7—H7A	0.9900	C19—H19B	0.9800
C7—H7B	0.9900	C19—H19C	0.9800

C8—N3	1.342 (3)	O2—C20	1.402 (10)
C8—C9	1.387 (3)	O2—H2A	0.8400
C9—C10	1.388 (3)	C20—H20A	0.9800
C9—H9	0.9500	C20—H20B	0.9800
C10—C11	1.377 (4)	C20—H20C	0.9800
C10—H10	0.9500	O2B—C20B	1.378 (18)
C11—C12	1.382 (4)	O2B—H2B	0.8400
C11—H11	0.9500	C20B—H20D	0.9800
C12—N3	1.347 (3)	C20B—H20E	0.9800
C12—H12	0.9500	C20B—H20F	0.9800
C13—N1	1.466 (3)	O2C—H2C	0.8344
C13—C14	1.504 (3)	O2C—H2D	0.8490
C13—H13A	0.9900	O2D—H2E	0.8422
C13—H13B	0.9900	O2D—H2F	0.8339

N1—C1—C2	110.62 (18)	N4—C14—C13	117.9 (2)
N1—C1—H1A	109.5	C15—C14—C13	123.8 (2)
C2—C1—H1A	109.5	C14—C15—C16	119.8 (2)
N1—C1—H1B	109.5	C14—C15—H15	120.1
C2—C1—H1B	109.5	C16—C15—H15	120.1
H1A—C1—H1B	108.1	C17—C16—C15	120.0 (2)
N2—C2—C3	118.5 (2)	C17—C16—H16	120.0
N2—C2—C1	118.0 (2)	C15—C16—H16	120.0
C3—C2—C1	123.4 (2)	C18—C17—C16	119.0 (2)
C2—C3—C4	120.0 (2)	C18—C17—H17	120.5
C2—C3—H3	120.0	C16—C17—H17	120.5
C4—C3—H3	120.0	N4—C18—C17	120.0 (2)
C3—C4—C5	119.6 (2)	N4—C18—H18	120.0
C3—C4—H4	120.2	C17—C18—H18	120.0
C5—C4—H4	120.2	C7—N1—C1	111.28 (17)
C6—C5—C4	118.7 (2)	C7—N1—C13	111.07 (17)
C6—C5—H5	120.6	C1—N1—C13	111.83 (17)
C4—C5—H5	120.6	C2—N2—C6	122.8 (2)
N2—C6—C5	120.3 (2)	C2—N2—H2	118.6
N2—C6—H6	119.8	C6—N2—H2	118.6
C5—C6—H6	119.8	C8—N3—C12	123.2 (2)
N1—C7—C8	110.26 (17)	C8—N3—H3A	118.4
N1—C7—H7A	109.6	C12—N3—H3A	118.4
C8—C7—H7A	109.6	C14—N4—C18	122.9 (2)
N1—C7—H7B	109.6	C14—N4—H4A	118.5
C8—C7—H7B	109.6	C18—N4—H4A	118.5
H7A—C7—H7B	108.1	C19—O1—H1	109.5
N3—C8—C9	118.6 (2)	O1—C19—H19A	109.5
N3—C8—C7	117.7 (2)	O1—C19—H19B	109.5
C9—C8—C7	123.6 (2)	H19A—C19—H19B	109.5
C8—C9—C10	119.4 (2)	O1—C19—H19C	109.5
C8—C9—H9	120.3	H19A—C19—H19C	109.5
C10—C9—H9	120.3	H19B—C19—H19C	109.5

C11—C10—C9	120.2 (2)	C20—O2—H2A	109.5
C11—C10—H10	119.9	O2—C20—H20A	109.5
C9—C10—H10	119.9	O2—C20—H20B	109.5
C10—C11—C12	119.0 (2)	H20A—C20—H20B	109.5
C10—C11—H11	120.5	O2—C20—H20C	109.5
C12—C11—H11	120.5	H20A—C20—H20C	109.5
N3—C12—C11	119.4 (2)	H20B—C20—H20C	109.5
N3—C12—H12	120.3	C20B—O2B—H2B	109.5
C11—C12—H12	120.3	O2B—C20B—H20D	109.5
N1—C13—C14	110.35 (17)	O2B—C20B—H20E	109.5
N1—C13—H13A	109.6	H20D—C20B—H20E	109.5
C14—C13—H13A	109.6	O2B—C20B—H20F	109.5
N1—C13—H13B	109.6	H20D—C20B—H20F	109.5
C14—C13—H13B	109.6	H20E—C20B—H20F	109.5
H13A—C13—H13B	108.1	H2C—O2C—H2D	107.6
N4—C14—C15	118.3 (2)	H2E—O2D—H2F	108.9

N1—C1—C2—N2	−128.9 (2)	C14—C15—C16—C17	1.9 (4)
N1—C1—C2—C3	52.2 (3)	C15—C16—C17—C18	−1.3 (4)
N2—C2—C3—C4	−0.3 (4)	C16—C17—C18—N4	−0.3 (4)
C1—C2—C3—C4	178.6 (2)	C8—C7—N1—C1	−158.24 (18)
C2—C3—C4—C5	0.3 (4)	C8—C7—N1—C13	76.5 (2)
C3—C4—C5—C6	0.0 (4)	C2—C1—N1—C7	74.3 (2)
C4—C5—C6—N2	−0.2 (4)	C2—C1—N1—C13	−160.82 (18)
N1—C7—C8—N3	−140.4 (2)	C14—C13—N1—C7	−153.39 (18)
N1—C7—C8—C9	41.4 (3)	C14—C13—N1—C1	81.6 (2)
N3—C8—C9—C10	0.1 (3)	C3—C2—N2—C6	0.1 (4)
C7—C8—C9—C10	178.2 (2)	C1—C2—N2—C6	−178.9 (2)
C8—C9—C10—C11	−0.7 (3)	C5—C6—N2—C2	0.2 (4)
C9—C10—C11—C12	0.1 (4)	C9—C8—N3—C12	1.3 (3)
C10—C11—C12—N3	1.2 (4)	C7—C8—N3—C12	−177.0 (2)
N1—C13—C14—N4	−143.1 (2)	C11—C12—N3—C8	−1.9 (4)
N1—C13—C14—C15	39.2 (3)	C15—C14—N4—C18	−0.5 (4)
N4—C14—C15—C16	−1.1 (3)	C13—C14—N4—C18	−178.2 (2)
C13—C14—C15—C16	176.5 (2)	C17—C18—N4—C14	1.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.88	2.15	3.018 (2)	167
N3—H3*A*···Cl2	0.88	2.13	3.007 (2)	173
N4—H4*A*···Cl3	0.88	2.18	3.062 (2)	176
O1—H1···Cl3	0.84	2.32	3.145 (2)	168
O2—H2*A*···Cl3	0.84	2.34	3.174 (6)	171
O2*B*—H2*B*···Cl1^{i}	0.84	2.42	3.241 (19)	167

O2*C*—H2*C*···Cl1	0.83	2.53	3.36 (2)	173
O2*D*—H2*E*···Cl3	0.84	1.93	2.727 (16)	158

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+1.