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Tetrakis(1,10-phenanthroline)calcium(II) bis(perchlorate) 4-(dimethylamino)benzaldehyde disolvate

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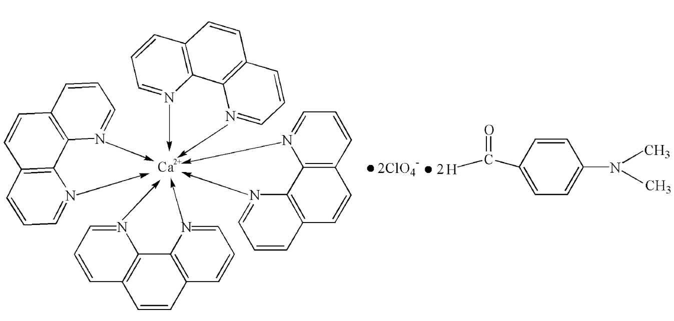
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.017 Å; disorder in solvent or counterion; R factor = 0.079; wR factor = 0.388; data-to-parameter ratio = 12.1.

In the title compound, $[Ca(C_{12}H_8N_2)_4](ClO_4)_2\cdot 2C_9H_{11}NO$, the Ca^{2+} cation (site symmetry 2) is coordinated by four bidentate 1,10-phenanthroline (phen) molecules, resulting in a square-antiprismatic CaN_8 polyhedron for the metal ion. Two disordered perchlorate ions (Cl site symmetry 2 in both cases) and a 4-(dimethylamino)benzaldehyde molecule complete the structure. A large number of π–π stacking interactions involving the phen aromatic rings [centroid separations are in the range 3.667 (6)–3.907 (7) Å] help to stabilize the structure. The O atoms of the perchlorate anions are disordered equally over two sites each.

Related literature

For background, see: Summers (1978); Guo *et al.* (2004); Tai *et al.* (2005).



Experimental

Crystal data

$[Ca(C_{12}H_8N_2)_4](ClO_4)_2\cdot 2C_9H_{11}NO$
M_r = 1258.17
Tetragonal, $I4_1/a$
a = 17.455 (3) Å
c = 38.952 (3) Å
V = 11868 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 298 (2) K
0.45 × 0.42 × 0.40 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.889, T_{max} = 0.900
29937 measured reflections
5234 independent reflections
1808 reflections with $I > 2\sigma(I)$
R_{int} = 0.103

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.388
S = 1.13
5234 reflections
433 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca1—N3	2.593 (7)	Ca1—N2	2.631 (7)
Ca1—N4	2.604 (7)	Ca1—N1	2.641 (7)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2432).

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supplementary materials

Acta Cryst. (2007). E**63**, m1827 [**doi:10.1107/S1600536807027055**]

Tetrakis(1,10-phenanthroline)calcium(II) bis(perchlorate) 4-(dimethylamino)benzaldehyde disolvate

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Comment

Phenanthroline and its derivatives and their complexes with metal ions have received considerable attention over the past three decades (Summers, 1978). This may be attributed to unusual structural features in the resultant metal complexes and their biological activities. The chemical and pharmacological properties of the complexes on phenanthroline have been investigated extensively, owing to their chelating ability with metal ions and to their potentially beneficial activities, such as catalytic, antitumor, antineoplastic and antibacterial (Guo *et al.*, 2004). As part of our onging studies of metal coordination complexes (Tai *et al.*, 2005), the synthesis and structure of the title compound, (I), is reported.

Four N,*N*-bidentate ligands are attached to the calcium ion (site symmetry 2) resulting in a CaN_8 unit (Table 1).

Various π-π stacking interactions of the 1,10-phenanthroline rings help to consolidate the crystal packing.

Experimental

5 mmol of calcium perchlorate was added to a solution of 1,10-phenanthroline (10 mmol) and 4-(dimethylamino)benzaldehyde (5 mmol) in in 10 ml of methanol. The mixture was continuously stirred for 3 h at refluxing temperature, then filtered, Brown blocks of (I) were obtained by evaporation the filtrate after two weeks.

Refinement

The H atoms were geometrically placed (C—H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Figures

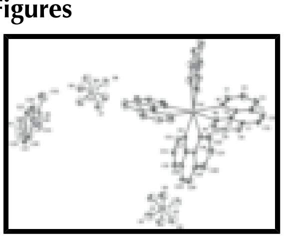


Fig. 1. The molecular structure of (I) showing 30% displacement ellipsoids. H atoms omitted for clarity. The unlabelled atoms in the cation, the Cl1 and Cl2 perchlorate ions are generated by the symmetry operations (−*x*, 3/2 − *y*, *z*), (1 − *x*, 3/2 − *y*, *z*) and (−*x*, 1/2 − *y*, *z*), respectively.

Tetrakis(1,10-phenanthroline)calcium(II) bis(perchlorate) 4-(dimethylamino)benzaldehyde disolvate

Crystal data

$[Ca(C_{12}H_8N_2)_4](ClO_4)_2·2C_9H_{11}NO$	$Z = 8$

M_r = 1258.17	F_{000} = 5232
Tetragonal, $I4_1/a$	D_x = 1.408 Mg m^{-3}
Hall symbol: -I 4ad	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 17.455 (3) Å	Cell parameters from 2661 reflections
b = 17.455 (3) Å	θ = 2.7–20.5º
c = 38.952 (3) Å	μ = 0.27 mm^{-1}
α = 90º	T = 298 (2) K
β = 90º	Block, brown
γ = 90º	0.45 × 0.42 × 0.40 mm
V = 11868 (3) Å^3	

Data collection

Bruker SMART CCD diffractometer	5234 independent reflections
Radiation source: fine-focus sealed tube	1808 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.103
T = 298(2) K	θ_{max} = 25.0º
ω scans	θ_{min} = 1.3º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -20 \rightarrow 20$
T_{min} = 0.889, T_{max} = 0.900	$k = -20 \rightarrow 20$
29937 measured reflections	$l = -46 \rightarrow 30$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.1079P)^2 + 113.9196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.079	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.388	$\Delta\rho_{max}$ = 0.41 e Å^{-3}
S = 1.13	$\Delta\rho_{min}$ = −0.56 e Å^{-3}
5234 reflections	Extinction correction: none
433 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ca1	0.0000	0.7500	0.12539 (6)	0.0351 (6)	
Cl1	0.5000	0.7500	0.02830 (9)	0.0715 (11)	
Cl2	0.0000	0.2500	0.02789 (8)	0.0603 (10)	
N1	−0.0545 (4)	0.8700 (4)	0.15864 (19)	0.0474 (19)	
N2	0.0017 (4)	0.8820 (4)	0.09279 (19)	0.0452 (19)	
N3	0.1283 (4)	0.7490 (4)	0.09188 (19)	0.0452 (19)	
N4	0.1188 (4)	0.8022 (4)	0.15835 (19)	0.0462 (19)	
N5	0.2086 (6)	0.0408 (6)	0.1909 (3)	0.086 (3)	
O1	0.2703 (8)	−0.0671 (6)	0.0342 (3)	0.153 (5)	
O2	0.5000	0.7500	0.0637 (3)	0.114 (4)	
O3	0.5413 (15)	0.8168 (15)	0.0180 (6)	0.107 (7)	0.50
O4	0.4339 (13)	0.741 (2)	0.0105 (5)	0.103 (7)	0.50
O5	0.5532 (14)	0.6898 (15)	0.0198 (5)	0.110 (7)	0.50
O6	0.0000	0.2500	0.0636 (3)	0.094 (4)	
O7	0.0611 (13)	0.2976 (13)	0.0161 (5)	0.092 (6)	0.50
O8	−0.0639 (12)	0.3007 (11)	0.0189 (4)	0.091 (5)	0.50
O9	−0.0071 (17)	0.1840 (12)	0.0108 (5)	0.089 (6)	0.50
C1	−0.0806 (6)	0.8672 (6)	0.1906 (3)	0.060 (3)	
H1	−0.0858	0.8191	0.2006	0.072*	
C2	−0.1006 (6)	0.9302 (7)	0.2101 (3)	0.068 (3)	
H2	−0.1174	0.9248	0.2326	0.082*	
C3	−0.0950 (6)	1.0007 (7)	0.1951 (3)	0.071 (3)	
H3	−0.1092	1.0441	0.2074	0.085*	
C4	−0.0685 (6)	1.0082 (6)	0.1618 (3)	0.055 (3)	
C5	−0.0482 (5)	0.9408 (5)	0.1440 (3)	0.044 (2)	
C6	−0.0206 (5)	0.9465 (5)	0.1093 (3)	0.044 (2)	
C7	−0.0164 (5)	1.0191 (6)	0.0936 (3)	0.055 (3)	
C8	0.0096 (6)	1.0232 (7)	0.0594 (3)	0.067 (3)	
H8	0.0132	1.0702	0.0483	0.080*	
C9	0.0293 (6)	0.9581 (7)	0.0431 (3)	0.065 (3)	
H9	0.0455	0.9595	0.0203	0.078*	
C10	0.0251 (5)	0.8889 (6)	0.0604 (2)	0.052 (2)	
H10	0.0394	0.8447	0.0488	0.062*	
C11	−0.0615 (6)	1.0812 (6)	0.1450 (4)	0.069 (3)	
H11	−0.0741	1.1257	0.1569	0.083*	
C12	−0.0371 (6)	1.0860 (6)	0.1124 (3)	0.068 (3)	
H12	−0.0335	1.1337	0.1019	0.082*	
C13	0.1337 (6)	0.7300 (6)	0.0587 (2)	0.055 (3)	
H13	0.0893	0.7150	0.0473	0.066*	
C14	0.2021 (7)	0.7315 (6)	0.0403 (3)	0.065 (3)	

H14	0.2027	0.7218	0.0168	0.078*
C15	0.2674 (7)	0.7476 (6)	0.0573 (3)	0.067 (3)
H15	0.3139	0.7458	0.0458	0.080*
C16	0.2660 (6)	0.7666 (6)	0.0918 (3)	0.060 (3)
C17	0.1935 (5)	0.7696 (5)	0.1083 (3)	0.044 (2)
C18	0.1890 (5)	0.7927 (5)	0.1433 (3)	0.048 (2)
C19	0.2581 (6)	0.8087 (6)	0.1616 (3)	0.062 (3)
C20	0.2527 (7)	0.8315 (7)	0.1959 (3)	0.080 (4)
H20	0.2968	0.8404	0.2087	0.096*
C21	0.1828 (7)	0.8407 (6)	0.2104 (3)	0.072 (3)
H21	0.1783	0.8566	0.2331	0.087*
C22	0.1170 (6)	0.8257 (6)	0.1907 (3)	0.060 (3)
H22	0.0694	0.8326	0.2010	0.072*
C23	0.3336 (6)	0.7822 (6)	0.1108 (4)	0.070 (3)
H23	0.3811	0.7797	0.1000	0.084*
C24	0.3295 (6)	0.8005 (7)	0.1442 (4)	0.076 (3)
H24	0.3746	0.8081	0.1564	0.091*
C25	0.3071 (10)	−0.0484 (7)	0.0583 (4)	0.112 (6)
H25	0.3600	−0.0476	0.0555	0.135*
C26	0.2777 (10)	−0.0262 (7)	0.0920 (4)	0.093 (5)
C27	0.2001 (9)	−0.0254 (7)	0.1016 (5)	0.104 (6)
H27	0.1632	−0.0407	0.0858	0.124*
C28	0.1778 (8)	−0.0032 (8)	0.1332 (4)	0.092 (5)
H28	0.1258	−0.0030	0.1383	0.110*
C29	0.2297 (7)	0.0196 (6)	0.1587 (4)	0.069 (3)
C30	0.3079 (7)	0.0191 (6)	0.1488 (3)	0.073 (3)
H30	0.3448	0.0349	0.1645	0.087*
C31	0.3309 (7)	−0.0042 (7)	0.1166 (3)	0.081 (4)
H31	0.3828	−0.0052	0.1112	0.097*
C32	0.1287 (8)	0.0439 (9)	0.2004 (4)	0.130 (6)
H32A	0.1014	0.0753	0.1843	0.196*
H32B	0.1239	0.0653	0.2230	0.196*
H32C	0.1076	−0.0069	0.2002	0.196*
C33	0.2644 (8)	0.0570 (8)	0.2170 (4)	0.103 (4)
H33A	0.2985	0.0141	0.2193	0.154*
H33B	0.2388	0.0659	0.2384	0.154*
H33C	0.2931	0.1017	0.2107	0.154*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0386 (13)	0.0338 (13)	0.0330 (12)	0.0015 (10)	0.000	0.000
Cl1	0.061 (3)	0.107 (4)	0.046 (2)	−0.007 (3)	0.000	0.000
Cl2	0.083 (3)	0.060 (3)	0.0385 (19)	−0.006 (3)	0.000	0.000
N1	0.051 (5)	0.048 (5)	0.043 (5)	0.004 (4)	−0.002 (4)	−0.002 (4)
N2	0.049 (5)	0.039 (5)	0.048 (5)	0.000 (4)	−0.007 (4)	0.007 (4)
N3	0.045 (5)	0.041 (4)	0.050 (5)	−0.001 (3)	0.005 (4)	0.002 (4)
N4	0.047 (5)	0.044 (5)	0.047 (5)	0.000 (4)	−0.005 (4)	0.001 (4)

N5	0.077 (8)	0.077 (7)	0.103 (9)	0.000 (6)	0.011 (7)	0.009 (6)
O1	0.234 (14)	0.111 (9)	0.114 (9)	0.002 (9)	−0.064 (9)	−0.002 (7)
O2	0.120 (11)	0.152 (13)	0.069 (8)	−0.018 (9)	0.000	0.000
O3	0.106 (19)	0.128 (19)	0.088 (15)	−0.017 (16)	0.004 (12)	0.004 (15)
O4	0.092 (16)	0.13 (2)	0.083 (15)	−0.012 (16)	−0.017 (12)	−0.007 (16)
O5	0.106 (18)	0.131 (19)	0.094 (15)	0.004 (16)	−0.002 (12)	−0.012 (15)
O6	0.126 (11)	0.099 (9)	0.058 (7)	0.005 (8)	0.000	0.000
O7	0.100 (16)	0.100 (17)	0.074 (13)	−0.009 (14)	0.004 (13)	0.005 (11)
O8	0.101 (15)	0.101 (15)	0.070 (12)	0.007 (12)	−0.007 (11)	−0.001 (10)
O9	0.11 (2)	0.086 (15)	0.068 (13)	0.001 (14)	0.003 (14)	−0.010 (10)
C1	0.070 (7)	0.054 (7)	0.055 (7)	0.001 (5)	0.006 (6)	−0.003 (5)
C2	0.075 (8)	0.078 (8)	0.051 (7)	0.011 (6)	−0.002 (6)	−0.014 (6)
C3	0.073 (8)	0.064 (8)	0.075 (8)	0.019 (6)	−0.015 (6)	−0.028 (6)
C4	0.052 (6)	0.052 (6)	0.060 (7)	0.006 (5)	−0.008 (5)	−0.006 (5)
C5	0.040 (5)	0.040 (6)	0.053 (6)	0.006 (4)	−0.015 (5)	−0.006 (5)
C6	0.040 (5)	0.042 (6)	0.049 (6)	−0.005 (4)	−0.013 (4)	0.008 (5)
C7	0.042 (6)	0.044 (6)	0.077 (8)	−0.003 (4)	−0.020 (5)	0.010 (5)
C8	0.063 (7)	0.061 (7)	0.076 (8)	−0.006 (6)	−0.013 (6)	0.032 (6)
C9	0.061 (7)	0.074 (8)	0.058 (7)	0.004 (6)	−0.002 (5)	0.028 (6)
C10	0.055 (6)	0.053 (6)	0.048 (6)	0.004 (5)	−0.001 (5)	0.007 (5)
C11	0.068 (8)	0.035 (6)	0.105 (10)	0.007 (5)	−0.013 (7)	−0.013 (6)
C12	0.070 (8)	0.040 (7)	0.095 (9)	−0.003 (5)	−0.010 (7)	0.008 (6)
C13	0.059 (7)	0.064 (7)	0.042 (6)	0.007 (5)	0.002 (5)	0.001 (5)
C14	0.079 (8)	0.060 (7)	0.057 (7)	0.008 (6)	0.024 (6)	0.002 (5)
C15	0.060 (7)	0.058 (7)	0.082 (9)	0.000 (5)	0.028 (7)	0.005 (6)
C16	0.049 (7)	0.050 (6)	0.079 (8)	0.003 (5)	0.009 (6)	0.012 (6)
C17	0.038 (6)	0.039 (5)	0.057 (6)	0.001 (4)	0.006 (5)	0.005 (5)
C18	0.041 (6)	0.039 (6)	0.063 (7)	−0.002 (4)	−0.007 (5)	0.002 (5)
C19	0.054 (7)	0.052 (6)	0.080 (8)	−0.004 (5)	−0.014 (6)	−0.001 (6)
C20	0.075 (9)	0.081 (9)	0.083 (9)	−0.009 (7)	−0.029 (7)	−0.009 (7)
C21	0.085 (9)	0.075 (8)	0.057 (7)	−0.010 (7)	−0.024 (7)	−0.012 (6)
C22	0.065 (7)	0.058 (7)	0.056 (7)	0.000 (5)	−0.010 (5)	−0.009 (5)
C23	0.040 (7)	0.068 (8)	0.102 (10)	0.001 (5)	0.007 (6)	0.001 (7)
C24	0.040 (7)	0.081 (9)	0.106 (10)	−0.006 (6)	−0.017 (7)	0.009 (8)
C25	0.171 (16)	0.071 (9)	0.094 (11)	−0.008 (9)	−0.063 (11)	0.004 (8)
C26	0.147 (15)	0.053 (8)	0.078 (10)	−0.014 (8)	−0.055 (10)	0.008 (7)
C27	0.086 (11)	0.064 (9)	0.161 (17)	−0.023 (8)	−0.074 (12)	0.022 (10)
C28	0.072 (9)	0.078 (9)	0.125 (13)	−0.020 (7)	−0.039 (9)	0.026 (9)
C29	0.059 (8)	0.046 (6)	0.103 (10)	−0.006 (5)	−0.019 (7)	0.018 (6)
C30	0.063 (8)	0.060 (7)	0.096 (10)	−0.007 (6)	−0.019 (7)	−0.002 (7)
C31	0.073 (8)	0.067 (8)	0.103 (11)	−0.004 (6)	−0.015 (7)	0.002 (7)
C32	0.094 (12)	0.124 (13)	0.174 (17)	0.009 (10)	0.039 (11)	0.033 (12)
C33	0.115 (12)	0.100 (11)	0.094 (10)	−0.016 (9)	−0.009 (9)	−0.002 (9)

Geometric parameters (Å, °)

Ca1—N3^{i}	2.593 (7)	C4—C5	1.410 (12)
Ca1—N3	2.593 (7)	C4—C11	1.437 (14)
Ca1—N4	2.604 (7)	C5—C6	1.438 (13)

Ca1—N4^{i}	2.604 (7)	C6—C7	1.409 (12)
Ca1—N2^{i}	2.631 (7)	C7—C8	1.407 (14)
Ca1—N2	2.631 (7)	C7—C12	1.426 (14)
Ca1—N1	2.641 (7)	C8—C9	1.348 (14)
Ca1—N1^{i}	2.641 (7)	C8—H8	0.9300
Cl1—O4	1.36 (2)	C9—C10	1.385 (13)
Cl1—O4^{ii}	1.36 (2)	C9—H9	0.9300
Cl1—O2	1.377 (13)	C10—H10	0.9300
Cl1—O3^{ii}	1.43 (2)	C11—C12	1.341 (15)
Cl1—O3	1.43 (2)	C11—H11	0.9300
Cl1—O5	1.44 (2)	C12—H12	0.9300
Cl1—O5^{ii}	1.44 (2)	C13—C14	1.393 (13)
Cl2—O9	1.34 (2)	C13—H13	0.9300
Cl2—O9^{iii}	1.34 (2)	C14—C15	1.349 (15)
Cl2—O6	1.389 (11)	C14—H14	0.9300
Cl2—O7^{iii}	1.43 (2)	C15—C16	1.382 (14)
Cl2—O7	1.43 (2)	C15—H15	0.9300
Cl2—O8^{iii}	1.466 (19)	C16—C23	1.418 (15)
Cl2—O8	1.466 (19)	C16—C17	1.422 (13)
N1—C1	1.325 (11)	C17—C18	1.421 (13)
N1—C5	1.366 (11)	C18—C19	1.432 (13)
N2—C10	1.331 (11)	C19—C20	1.396 (15)
N2—C6	1.353 (11)	C19—C24	1.425 (15)
N3—C13	1.338 (11)	C20—C21	1.354 (15)
N3—C17	1.354 (11)	C20—H20	0.9300
N4—C22	1.326 (11)	C21—C22	1.405 (14)
N4—C18	1.368 (11)	C21—H21	0.9300
N5—C29	1.356 (16)	C22—H22	0.9300
N5—C33	1.436 (15)	C23—C24	1.343 (16)
N5—C32	1.445 (15)	C23—H23	0.9300
O1—C25	1.183 (15)	C24—H24	0.9300
O3—O4^{ii}	1.14 (3)	C25—C26	1.46 (2)
O3—O5^{ii}	1.66 (3)	C25—H25	0.9300
O4—O3^{ii}	1.14 (3)	C26—C31	1.386 (16)
O4—O5^{ii}	1.28 (3)	C26—C27	1.41 (2)
O5—O4^{ii}	1.28 (3)	C27—C28	1.35 (2)
O5—O3^{ii}	1.66 (3)	C27—H27	0.9300
O7—O9^{iii}	1.02 (2)	C28—C29	1.403 (16)
O7—O8^{iii}	1.72 (3)	C28—H28	0.9300
O8—O9^{iii}	1.31 (3)	C29—C30	1.419 (15)
O8—O7^{iii}	1.72 (3)	C30—C31	1.380 (16)
O9—O7^{iii}	1.02 (2)	C30—H30	0.9300
O9—O8^{iii}	1.31 (3)	C31—H31	0.9300
C1—C2	1.382 (13)	C32—H32A	0.9600
C1—H1	0.9300	C32—H32B	0.9600

C2—C3	1.365 (15)	C32—H32C	0.9600
C2—H2	0.9300	C33—H33A	0.9600
C3—C4	1.385 (14)	C33—H33B	0.9600
C3—H3	0.9300	C33—H33C	0.9600

$N3^{i}$—Ca1—N3	119.5 (3)	N1—C1—H1	117.5
$N3^{i}$—Ca1—N4	159.1 (2)	C2—C1—H1	117.5
N3—Ca1—N4	64.0 (2)	C3—C2—C1	117.7 (11)
$N3^{i}$—Ca1—$N4^{i}$	64.0 (2)	C3—C2—H2	121.2
N3—Ca1—$N4^{i}$	159.1 (2)	C1—C2—H2	121.2
N4—Ca1—$N4^{i}$	120.9 (3)	C2—C3—C4	120.6 (10)
$N3^{i}$—Ca1—$N2^{i}$	75.7 (2)	C2—C3—H3	119.7
N3—Ca1—$N2^{i}$	76.2 (2)	C4—C3—H3	119.7
N4—Ca1—$N2^{i}$	123.6 (2)	C3—C4—C5	117.7 (10)
$N4^{i}$—Ca1—$N2^{i}$	85.5 (2)	C3—C4—C11	122.6 (10)
$N3^{i}$—Ca1—N2	76.2 (2)	C5—C4—C11	119.7 (10)
N3—Ca1—N2	75.7 (2)	N1—C5—C4	122.0 (9)
N4—Ca1—N2	85.5 (2)	N1—C5—C6	118.8 (8)
$N4^{i}$—Ca1—N2	123.6 (2)	C4—C5—C6	119.2 (9)
$N2^{i}$—Ca1—N2	122.3 (3)	N2—C6—C7	121.7 (9)
$N3^{i}$—Ca1—N1	86.0 (2)	N2—C6—C5	119.1 (8)
N3—Ca1—N1	124.3 (2)	C7—C6—C5	119.2 (9)
N4—Ca1—N1	76.6 (2)	C8—C7—C6	118.3 (10)
$N4^{i}$—Ca1—N1	75.5 (2)	C8—C7—C12	121.7 (10)
$N2^{i}$—Ca1—N1	158.0 (2)	C6—C7—C12	120.0 (11)
N2—Ca1—N1	63.0 (2)	C9—C8—C7	119.1 (10)
$N3^{i}$—Ca1—$N1^{i}$	124.3 (2)	C9—C8—H8	120.5
N3—Ca1—$N1^{i}$	86.0 (2)	C7—C8—H8	120.5
N4—Ca1—$N1^{i}$	75.5 (2)	C8—C9—C10	119.4 (10)
$N4^{i}$—Ca1—$N1^{i}$	76.6 (2)	C8—C9—H9	120.3
$N2^{i}$—Ca1—$N1^{i}$	63.0 (2)	C10—C9—H9	120.3
N2—Ca1—$N1^{i}$	158.0 (2)	N2—C10—C9	123.9 (10)
N1—Ca1—$N1^{i}$	121.3 (3)	N2—C10—H10	118.0
O4—Cl1—$O4^{ii}$	118.4 (19)	C9—C10—H10	118.0
O4—Cl1—O2	120.8 (9)	C12—C11—C4	120.8 (10)
$O4^{ii}$—Cl1—O2	120.8 (9)	C12—C11—H11	119.6
O4—Cl1—$O3^{ii}$	48.1 (11)	C4—C11—H11	119.6
$O4^{ii}$—Cl1—$O3^{ii}$	112.3 (13)	C11—C12—C7	121.1 (10)
O2—Cl1—$O3^{ii}$	106.3 (9)	C11—C12—H12	119.4
O4—Cl1—O3	112.3 (13)	C7—C12—H12	119.4
$O4^{ii}$—Cl1—O3	48.1 (11)	N3—C13—C14	123.6 (10)
O2—Cl1—O3	106.3 (9)	N3—C13—H13	118.2
$O3^{ii}$—Cl1—O3	147.3 (18)	C14—C13—H13	118.2
O4—Cl1—O5	110.4 (13)	C15—C14—C13	118.3 (10)

O4^{ii}—Cl1—O5	54.4 (12)	C15—C14—H14	120.8
O2—Cl1—O5	103.2 (9)	C13—C14—H14	120.8
O3^{ii}—Cl1—O5	70.5 (12)	C14—C15—C16	120.9 (10)
O3—Cl1—O5	101.9 (13)	C14—C15—H15	119.5
O4—Cl1—O5^{ii}	54.4 (12)	C16—C15—H15	119.5
O4^{ii}—Cl1—O5^{ii}	110.4 (13)	C15—C16—C23	122.6 (11)
O2—Cl1—O5^{ii}	103.2 (9)	C15—C16—C17	117.7 (10)
O3^{ii}—Cl1—O5^{ii}	101.9 (13)	C23—C16—C17	119.7 (11)
O3—Cl1—O5^{ii}	70.5 (12)	N3—C17—C18	118.8 (8)
O5—Cl1—O5^{ii}	153.6 (17)	N3—C17—C16	121.5 (9)
O9—Cl2—O9^{iii}	120.2 (17)	C18—C17—C16	119.6 (9)
O9—Cl2—O6	119.9 (9)	N4—C18—C17	119.7 (8)
O9^{iii}—Cl2—O6	119.9 (9)	N4—C18—C19	121.1 (10)
O9—Cl2—O7^{iii}	43.0 (10)	C17—C18—C19	119.2 (10)
O9^{iii}—Cl2—O7^{iii}	114.3 (11)	C20—C19—C24	122.9 (11)
O6—Cl2—O7^{iii}	108.7 (8)	C20—C19—C18	118.5 (11)
O9—Cl2—O7	114.3 (11)	C24—C19—C18	118.6 (11)
O9^{iii}—Cl2—O7	43.0 (10)	C21—C20—C19	119.5 (11)
O6—Cl2—O7	108.7 (8)	C21—C20—H20	120.2
O7^{iii}—Cl2—O7	142.6 (17)	C19—C20—H20	120.2
O9—Cl2—O8^{iii}	55.4 (11)	C20—C21—C22	119.2 (11)
O9^{iii}—Cl2—O8^{iii}	109.4 (12)	C20—C21—H21	120.4
O6—Cl2—O8^{iii}	103.8 (7)	C22—C21—H21	120.4
O7^{iii}—Cl2—O8^{iii}	98.1 (11)	N4—C22—C21	123.7 (10)
O7—Cl2—O8^{iii}	73.0 (11)	N4—C22—H22	118.1
O9—Cl2—O8	109.4 (12)	C21—C22—H22	118.1
O9^{iii}—Cl2—O8	55.4 (11)	C24—C23—C16	120.5 (11)
O6—Cl2—O8	103.8 (7)	C24—C23—H23	119.7
O7^{iii}—Cl2—O8	73.0 (11)	C16—C23—H23	119.7
O7—Cl2—O8	98.1 (11)	C23—C24—C19	122.2 (11)
O8^{iii}—Cl2—O8	152.5 (14)	C23—C24—H24	118.9
C1—N1—C5	117.0 (8)	C19—C24—H24	118.9
C1—N1—Ca1	123.7 (6)	O1—C25—C26	126.6 (18)
C5—N1—Ca1	118.9 (6)	O1—C25—H25	116.7
C10—N2—C6	117.6 (8)	C26—C25—H25	116.7
C10—N2—Ca1	122.7 (6)	C31—C26—C27	117.4 (14)
C6—N2—Ca1	119.7 (6)	C31—C26—C25	117.2 (16)
C13—N3—C17	117.7 (8)	C27—C26—C25	125.4 (14)
C13—N3—Ca1	123.3 (6)	C28—C27—C26	121.6 (13)
C17—N3—Ca1	119.0 (6)	C28—C27—H27	119.2
C22—N4—C18	117.9 (8)	C26—C27—H27	119.2
C22—N4—Ca1	123.9 (6)	C27—C28—C29	122.8 (14)
C18—N4—Ca1	117.3 (6)	C27—C28—H28	118.6
C29—N5—C33	121.6 (11)	C29—C28—H28	118.6

C29—N5—C32	120.6 (12)	N5—C29—C28	123.8 (12)
C33—N5—C32	117.8 (13)	N5—C29—C30	121.0 (11)
O4^{ii}—O3—Cl1	62.5 (17)	C28—C29—C30	115.2 (13)
O4^{ii}—O3—O5^{ii}	109 (2)	C31—C30—C29	122.0 (12)
Cl1—O3—O5^{ii}	55.1 (11)	C31—C30—H30	119.0
O3^{ii}—O4—O5^{ii}	134 (3)	C29—C30—H30	119.0
O3^{ii}—O4—Cl1	69.3 (18)	C30—C31—C26	120.9 (13)
O5^{ii}—O4—Cl1	66.2 (15)	C30—C31—H31	119.5
O4^{ii}—O5—Cl1	59.4 (14)	C26—C31—H31	119.5
O4^{ii}—O5—O3^{ii}	103 (2)	N5—C32—H32A	109.5
Cl1—O5—O3^{ii}	54.4 (11)	N5—C32—H32B	109.5
O9^{iii}—O7—Cl2	63.7 (19)	H32A—C32—H32B	109.5
O9^{iii}—O7—O8^{iii}	111 (3)	N5—C32—H32C	109.5
Cl2—O7—O8^{iii}	54.5 (10)	H32A—C32—H32C	109.5
O9^{iii}—O8—Cl2	57.3 (12)	H32B—C32—H32C	109.5
O9^{iii}—O8—O7^{iii}	99.3 (15)	N5—C33—H33A	109.5
Cl2—O8—O7^{iii}	52.5 (9)	N5—C33—H33B	109.5
O7^{iii}—O9—O8^{iii}	140 (3)	H33A—C33—H33B	109.5
O7^{iii}—O9—Cl2	73 (2)	N5—C33—H33C	109.5
O8^{iii}—O9—Cl2	67.4 (14)	H33A—C33—H33C	109.5
N1—C1—C2	125.0 (10)	H33B—C33—H33C	109.5

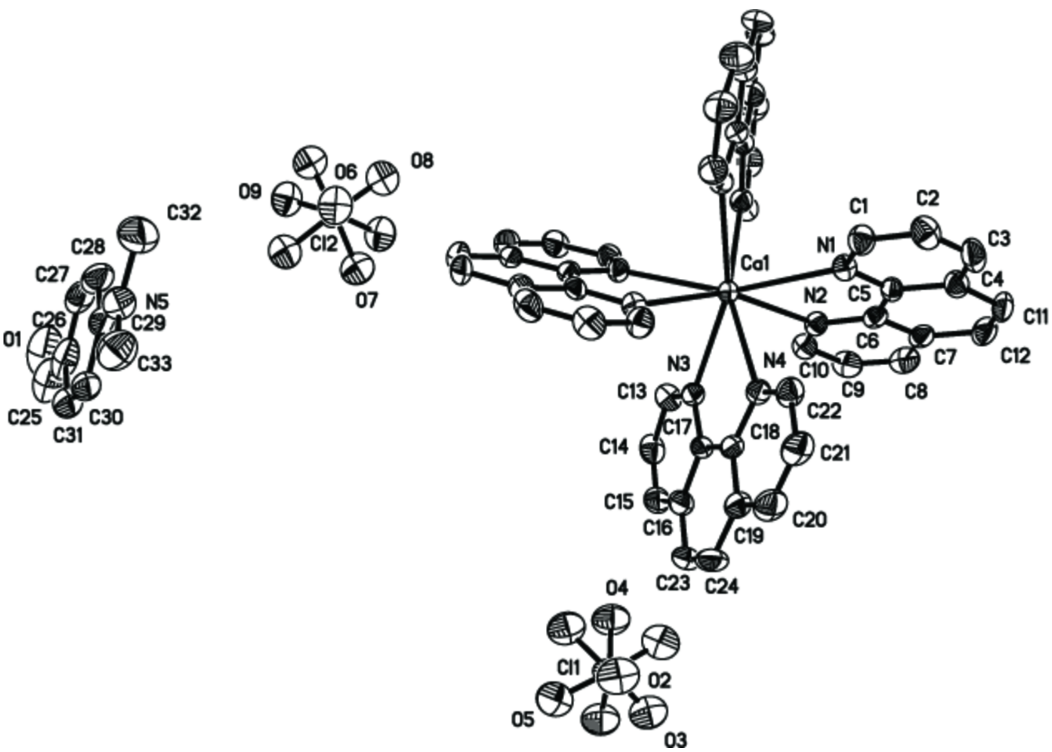
N3^{i}—Ca1—N1—C1	105.0 (8)	O6—Cl2—O8—O7^{iii}	−105.7 (9)
N3—Ca1—N1—C1	−131.6 (7)	O7—Cl2—O8—O7^{iii}	142.7 (17)
N4—Ca1—N1—C1	−86.6 (8)	O8^{iii}—Cl2—O8—O7^{iii}	74.3 (9)
N4^{i}—Ca1—N1—C1	40.8 (7)	O9^{iii}—Cl2—O9—O7^{iii}	−94.2 (19)
N2^{i}—Ca1—N1—C1	71.7 (10)	O6—Cl2—O9—O7^{iii}	85.8 (19)
N2—Ca1—N1—C1	−178.5 (8)	O7—Cl2—O9—O7^{iii}	−142.5 (19)
N1^{i}—Ca1—N1—C1	−23.2 (7)	O8^{iii}—Cl2—O9—O7^{iii}	172 (2)
N3^{i}—Ca1—N1—C5	−82.6 (6)	O8—Cl2—O9—O7^{iii}	−34 (2)
N3—Ca1—N1—C5	40.8 (7)	O9^{iii}—Cl2—O9—O8^{iii}	93.7 (12)
N4—Ca1—N1—C5	85.8 (6)	O6—Cl2—O9—O8^{iii}	−86.3 (12)
N4^{i}—Ca1—N1—C5	−146.8 (7)	O7^{iii}—Cl2—O9—O8^{iii}	−172 (2)
N2^{i}—Ca1—N1—C5	−115.9 (8)	O7—Cl2—O9—O8^{iii}	45.4 (14)
N2—Ca1—N1—C5	−6.1 (6)	O8—Cl2—O9—O8^{iii}	154.1 (13)
N1^{i}—Ca1—N1—C5	149.2 (7)	C5—N1—C1—C2	−0.9 (15)
N3^{i}—Ca1—N2—C10	−84.1 (7)	Ca1—N1—C1—C2	171.6 (8)
N3—Ca1—N2—C10	41.8 (7)	N1—C1—C2—C3	1.7 (17)
N4—Ca1—N2—C10	106.2 (7)	C1—C2—C3—C4	−1.4 (16)
N4^{i}—Ca1—N2—C10	−129.3 (7)	C2—C3—C4—C5	0.4 (15)
N2^{i}—Ca1—N2—C10	−21.3 (6)	C2—C3—C4—C11	−179.9 (10)
N1—Ca1—N2—C10	−176.7 (8)	C1—N1—C5—C4	−0.2 (13)

N1^{i}—Ca1—N2—C10	76.3 (10)	Ca1—N1—C5—C4	−173.1 (6)
N3^{i}—Ca1—N2—C6	97.0 (6)	C1—N1—C5—C6	−179.7 (8)
N3—Ca1—N2—C6	−137.0 (6)	Ca1—N1—C5—C6	7.4 (10)
N4—Ca1—N2—C6	−72.7 (6)	C3—C4—C5—N1	0.4 (14)
N4^{i}—Ca1—N2—C6	51.9 (7)	C11—C4—C5—N1	−179.3 (9)
N2^{i}—Ca1—N2—C6	159.9 (7)	C3—C4—C5—C6	179.9 (9)
N1—Ca1—N2—C6	4.5 (6)	C11—C4—C5—C6	0.2 (13)
N1^{i}—Ca1—N2—C6	−102.6 (8)	C10—N2—C6—C7	−2.7 (12)
N3^{i}—Ca1—N3—C13	−17.2 (6)	Ca1—N2—C6—C7	176.2 (6)
N4—Ca1—N3—C13	−173.8 (8)	C10—N2—C6—C5	178.3 (8)
N4^{i}—Ca1—N3—C13	77.0 (10)	Ca1—N2—C6—C5	−2.8 (10)
N2^{i}—Ca1—N3—C13	47.2 (7)	N1—C5—C6—N2	−3.1 (12)
N2—Ca1—N3—C13	−81.9 (7)	C4—C5—C6—N2	177.4 (8)
N1—Ca1—N3—C13	−124.0 (7)	N1—C5—C6—C7	177.8 (8)
N1^{i}—Ca1—N3—C13	110.4 (7)	C4—C5—C6—C7	−1.7 (12)
N3^{i}—Ca1—N3—C17	161.9 (7)	N2—C6—C7—C8	2.0 (13)
N4—Ca1—N3—C17	5.2 (6)	C5—C6—C7—C8	−179.0 (8)
N4^{i}—Ca1—N3—C17	−103.9 (9)	N2—C6—C7—C12	−177.0 (8)
N2^{i}—Ca1—N3—C17	−133.7 (6)	C5—C6—C7—C12	2.0 (13)
N2—Ca1—N3—C17	97.2 (6)	C6—C7—C8—C9	0.1 (14)
N1—Ca1—N3—C17	55.0 (7)	C12—C7—C8—C9	179.2 (10)
N1^{i}—Ca1—N3—C17	−70.6 (6)	C7—C8—C9—C10	−1.4 (15)
N3^{i}—Ca1—N4—C22	77.3 (10)	C6—N2—C10—C9	1.4 (14)
N3—Ca1—N4—C22	−177.5 (8)	Ca1—N2—C10—C9	−177.5 (7)
N4^{i}—Ca1—N4—C22	−20.6 (7)	C8—C9—C10—N2	0.7 (16)
N2^{i}—Ca1—N4—C22	−127.4 (7)	C3—C4—C11—C12	−178.6 (11)
N2—Ca1—N4—C22	106.3 (7)	C5—C4—C11—C12	1.1 (16)
N1—Ca1—N4—C22	43.0 (7)	C4—C11—C12—C7	−0.8 (17)
N1^{i}—Ca1—N4—C22	−84.8 (7)	C8—C7—C12—C11	−179.8 (10)
N3^{i}—Ca1—N4—C18	−114.1 (8)	C6—C7—C12—C11	−0.8 (15)
N3—Ca1—N4—C18	−8.9 (6)	C17—N3—C13—C14	−1.0 (14)
N4^{i}—Ca1—N4—C18	148.0 (7)	Ca1—N3—C13—C14	178.0 (7)
N2^{i}—Ca1—N4—C18	41.1 (7)	N3—C13—C14—C15	5.0 (15)
N2—Ca1—N4—C18	−85.1 (6)	C13—C14—C15—C16	−3.9 (16)
N1—Ca1—N4—C18	−148.4 (6)	C14—C15—C16—C23	178.6 (10)
N1^{i}—Ca1—N4—C18	83.8 (6)	C14—C15—C16—C17	−0.9 (15)
O4—Cl1—O3—O4^{ii}	−109 (3)	C13—N3—C17—C18	177.8 (8)
O2—Cl1—O3—O4^{ii}	117.0 (16)	Ca1—N3—C17—C18	−1.3 (10)
O3^{ii}—Cl1—O3—O4^{ii}	−63.0 (16)	C13—N3—C17—C16	−4.0 (13)
O5—Cl1—O3—O4^{ii}	9(2)	Ca1—N3—C17—C16	176.9 (6)
O5^{ii}—Cl1—O3—O4^{ii}	−144 (2)	C15—C16—C17—N3	5.0 (14)
O4—Cl1—O3—O5^{ii}	35.6 (13)	C23—C16—C17—N3	−174.5 (9)
O4^{ii}—Cl1—O3—O5^{ii}	144 (2)	C15—C16—C17—C18	−176.8 (9)

O2—Cl1—O3—O5^{ii}	−98.6 (10)	C23—C16—C17—C18	3.7 (14)
O3^{ii}—Cl1—O3—O5^{ii}	81.4 (10)	C22—N4—C18—C17	−178.3 (8)
O5—Cl1—O3—O5^{ii}	153.7 (17)	Ca1—N4—C18—C17	12.4 (10)
O4^{ii}—Cl1—O4—O3^{ii}	95.4 (19)	C22—N4—C18—C19	−1.0 (13)
O2—Cl1—O4—O3^{ii}	−84.6 (19)	Ca1—N4—C18—C19	−170.3 (7)
O3—Cl1—O4—O3^{ii}	148.7 (19)	N3—C17—C18—N4	−7.5 (13)
O5—Cl1—O4—O3^{ii}	36 (2)	C16—C17—C18—N4	174.2 (8)
O5^{ii}—Cl1—O4—O3^{ii}	−169 (2)	N3—C17—C18—C19	175.0 (8)
O4^{ii}—Cl1—O4—O5^{ii}	−95.7 (16)	C16—C17—C18—C19	−3.2 (13)
O2—Cl1—O4—O5^{ii}	84.3 (16)	N4—C18—C19—C20	2.4 (14)
O3^{ii}—Cl1—O4—O5^{ii}	169 (2)	C17—C18—C19—C20	179.8 (9)
O3—Cl1—O4—O5^{ii}	−42.4 (17)	N4—C18—C19—C24	−177.7 (9)
O5—Cl1—O4—O5^{ii}	−155.4 (17)	C17—C18—C19—C24	−0.3 (14)
O4—Cl1—O5—O4^{ii}	111 (2)	C24—C19—C20—C21	177.7 (11)
O2—Cl1—O5—O4^{ii}	−118.6 (13)	C18—C19—C20—C21	−2.4 (17)
O3^{ii}—Cl1—O5—O4^{ii}	138.5 (18)	C19—C20—C21—C22	1.0 (18)
O3—Cl1—O5—O4^{ii}	−8.4 (18)	C18—N4—C22—C21	−0.5 (14)
O5^{ii}—Cl1—O5—O4^{ii}	61.4 (13)	Ca1—N4—C22—C21	168.0 (8)
O4—Cl1—O5—O3^{ii}	−27.5 (14)	C20—C21—C22—N4	0.5 (17)
O4^{ii}—Cl1—O5—O3^{ii}	−138.5 (18)	C15—C16—C23—C24	179.9 (11)
O2—Cl1—O5—O3^{ii}	102.9 (10)	C17—C16—C23—C24	−0.7 (16)
O3—Cl1—O5—O3^{ii}	−146.9 (19)	C16—C23—C24—C19	−3.0 (18)
O5^{ii}—Cl1—O5—O3^{ii}	−77.1 (10)	C20—C19—C24—C23	−176.6 (12)
O9—Cl2—O7—O9^{iii}	109 (3)	C18—C19—C24—C23	3.5 (17)
O6—Cl2—O7—O9^{iii}	−114.1 (17)	O1—C25—C26—C31	−178.4 (13)
O7^{iii}—Cl2—O7—O9^{iii}	65.9 (17)	O1—C25—C26—C27	2(2)
O8^{iii}—Cl2—O7—O9^{iii}	147 (2)	C31—C26—C27—C28	1.0 (19)
O8—Cl2—O7—O9^{iii}	−7(2)	C25—C26—C27—C28	−179.1 (13)
O9—Cl2—O7—O8^{iii}	−37.8 (11)	C26—C27—C28—C29	−1(2)
O9^{iii}—Cl2—O7—O8^{iii}	−147 (2)	C33—N5—C29—C28	174.2 (11)
O6—Cl2—O7—O8^{iii}	99.1 (8)	C32—N5—C29—C28	−2.5 (18)
O7^{iii}—Cl2—O7—O8^{iii}	−80.9 (8)	C33—N5—C29—C30	−5.5 (17)
O8—Cl2—O7—O8^{iii}	−153.3 (14)	C32—N5—C29—C30	177.7 (11)
O9—Cl2—O8—O9^{iii}	−114 (2)	C27—C28—C29—N5	−178.7 (12)
O6—Cl2—O8—O9^{iii}	117.0 (11)	C27—C28—C29—C30	1.1 (18)
O7^{iii}—Cl2—O8—O9^{iii}	−137.3 (14)	N5—C29—C30—C31	178.2 (11)
O7—Cl2—O8—O9^{iii}	5.4 (16)	C28—C29—C30—C31	−1.6 (16)
O8^{iii}—Cl2—O8—O9^{iii}	−63.0 (11)	C29—C30—C31—C26	1.8 (18)
O9—Cl2—O8—O7^{iii}	23.3 (13)	C27—C26—C31—C30	−1.4 (17)
O9^{iii}—Cl2—O8—O7^{iii}	137.3 (14)	C25—C26—C31—C30	178.7 (11)

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

Fig. 1


O9
O6
O8
C32
C28
Cl2
Ca1
N1
C1
C2
C3
C4
C5
C11
N2
C6
C7
C12
C27
N5
C26
C29
O1
C33
O7
N3
N4
C10
C9
C8
C13
C17
C18
C22
C25
C31
C30
C14
C21
C15
C16
C19
C20
C23
C24
O4
Cl1
O2
O5
O3