Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

[μ-Cucurbit[6]uril(2−)]bis[pentaaquacalcium(II)] bis[tetrachloridozincate(II)] heptahydrate

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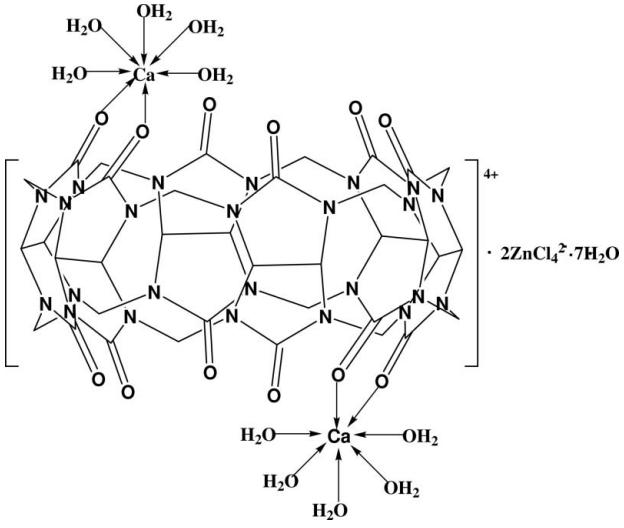
Received 16 April 2007; accepted 19 April 2007

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.007 Å; disorder in solvent or counterion; R factor = 0.061; wR factor = 0.131; data-to-parameter ratio = 14.9.

In the title compound, $[Ca_2(C_{36}H_{36}N_{24}O_{12})(H_2O)_{10}][ZnCl_4]_2\cdot 7H_2O$, each cucurbit[6]uril molecule is coordinated to two calcium cations as a tetradentate ligand. Each calcium cation is coordinated by two neighboring carbonyl O atoms at a portal of the same cage. Heptacoordination of the calcium cation is completed with five water molecules. The transition-metal salt anion $[ZnCl_4]^{2-}$ acts as a counter-ion. The cation is centrosymmetric. The crystal structure involves O—H···O and O—H···Cl hydrogen bonds. One of the water molecules is disordered, with an occupancy of 0.5.

Related literature

For related literature, see: Freeman *et al.* (1981); Gerasko *et al.* (2002); Jansen *et al.* (2001); Samsonenko *et al.* (2001); Whang *et al.* (1998); Burrow *et al.* (1997).



Experimental

Crystal data

$[Ca_2(C_{36}H_{36}N_{24}O_{12})(H_2O)_{10}][ZnCl_4]_2\cdot 7H_2O$
M_r = 1797.66
Monoclinic, $P2_1/n$
a = 14.428 (3) Å
b = 16.397 (4) Å
c = 15.798 (3) Å
β = 108.987 (3)°
V = 3534.0 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.22 mm^{-1}
T = 291 (2) K
0.28 × 0.24 × 0.22 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.72, T_{max} = 0.76
17975 measured reflections
6860 independent reflections
4939 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.131
S = 1.02
6860 reflections
460 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8C···O9	0.97	2.14	2.950 (5)	141
O8—H8D···Cl2^{i}	0.97	2.36	3.137 (4)	136
O9—H9B···O11^{ii}	0.85	2.41	2.840 (5)	112
O11—H11B···O1W^{ii}	0.97	1.97	2.742 (4)	135
O12—H12D···O3W^{ii}	0.97	2.05	2.940 (5)	152
O2W—H2WA···O6^{ii}	0.85	2.23	2.961 (5)	145
O3W—H3WA···Cl1^{ii}	0.96	2.64	3.271 (4)	124
O9—H9C···Cl4	0.85	2.72	3.173 (4)	115
O10—H10C···O1W	0.85	2.41	2.833 (4)	112
O11—H11C···O12	0.97	2.22	3.107 (4)	151
O11—H11C···O9	0.97	2.33	3.004 (5)	126
O1W—H1WA···O3W	0.85	1.91	2.750 (5)	173
O12—H12C···O3^{iii}	0.97	2.09	2.710 (4)	120
O1W—H1WB···O1^{iv}	0.85	2.15	2.737 (4)	126
O3W—H3WB···O2^{iv}	0.96	1.79	2.704 (5)	158
O2W—H2WC···Cl3^{v}	0.85	2.76	3.248 (4)	118

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

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

This work was supported by the National Natural Science Foundation of China (research grant No. 20372032).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2226).

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supplementary materials

Acta Cryst. (2007). E**63**, m1480-m1481 [**doi:10.1107/S1600536807019435**]

[μ-Cucurbit[6]uril(2-)]bis[pentaaquacalcium(II)] bis[tetrachloridozincate(II)] heptahydrate

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Comment

The construction of inorganic-organic hybrid supramolecular compounds of cucurbit[6]uril containing large pores or channels has developed significantly in recent years (Freeman *et al.*, 1981; Gerasko *et al.*, 2002). This paper follows a new structural report on cucurbit[6]uril with both coordinated calcium cation and transition-metal salt anion $ZnCl_4^{2-}$ as contra-ion.

As shown in Fig.1, each cucurbit[6]uril molecule is coordinated to two calcium cations as a tetradentate ligand, which is differs from the works reported by Freeman and Samsonenko in which cucurbit[6]uril molecules serves as bidentate ligands (Freeman *et al.*, 1981; Samsonenko *et al.*, 2001). The inner cavity of the cucurbit[6]uril molecule is filled with a guest water molecule, O7, its occupied probability is 0.5 and disordered over two positions. Each calcium cation is coordinated by two neighboring carbonyl O atoms (O4 and O5) at a portal of the same cage. The bond lengths are 2.383 (3) and 2.479 (3) Å for Ca1—O4 and Ca1—O5, respectively. Hepta-coordination at the Calcium cation is completed with five water molecules O8, O9, O10, O11 and O12. The Ca—O bond lengths vary from 2.366 (3) to 2.389 (3) Å.

Experimental

Cucurbit[6]uril was prepared by modified methods (Whang *et al.*, 1998; Jansen *et al.*, 2001), and the other reagents were commercially available and without further purification. The title adduct suitable for X-ray crystallographic analysis was prepared by slow evaporation of the hydrochloric acid (4*M*) solution of cucurbit[6]uril (50 mg, 0.05 mmol), $CaCl_2$ (35 mg, 0.32 mmol) and $ZnCl_2$ (40 mg, 0.29 mmol).

Refinement

H atoms were positioned geometrically and refined using a riding model with C—H = 0.97–0.98 Å, O—H = 0.85–0.97 Å, and with U_{iso}(H) = 1.2 times U_{eq}(C).

Figures

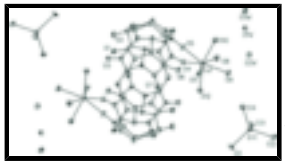


Fig. 1. View of the title adduct, showing the labeling of the non-H atoms and 30% probability ellipsoids. Labels of H atoms have been omitted for clarity. Symmetry codes: (i) 1/2 − *x*, 1/2 + *y*, 3/2 − *z*.

[μ-Cucurbit[6]uril]bis[pentaaquacalcium(II)] bis[tetrachloridozinc(II)] septhydrate

Crystal data

$[Ca_2(C_{36}H_{36}N_{24}O_{12})(H_2O_1)_{10}][ZnCl_4]_2 \cdot 7H_2O$	$F_{000} = 1844$
$M_r = 1797.66$	$D_x = 1.689$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5973 reflections
$a = 14.428$ (3) Å	$\theta = 2.1$–26.4º
$b = 16.397$ (4) Å	$\mu = 1.22$ mm^{-1}
$c = 15.798$ (3) Å	$T = 291$ (2) K
$\beta = 108.987$ (3)º	Block, colourless
$V = 3534.0$ (13) Å^3	0.28 × 0.24 × 0.22 mm
$Z = 2$	

Data collection

Bruker SMART APEX CCD diffractometer	6860 independent reflections
Radiation source: sealed tube	4939 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.051$
$T = 291$(2) K	$\theta_{max} = 26.0$º
φ and ω scans	$\theta_{min} = 1.8$º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -17 \rightarrow 17$
$T_{min} = 0.72$, $T_{max} = 0.76$	$k = -20 \rightarrow 13$
17975 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.131$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.99P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
6860 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
460 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	−0.1614 (3)	0.2144 (3)	0.3505 (3)	0.0308 (9)	
C2	−0.1394 (3)	0.0195 (3)	0.2032 (3)	0.0376 (11)	
C3	−0.1206 (3)	−0.2000 (3)	0.3098 (3)	0.0308 (9)	
C4	0.1202 (3)	0.2273 (3)	0.4369 (3)	0.0308 (9)	
C5	0.1425 (3)	0.0420 (3)	0.2987 (3)	0.0323 (10)	
C6	0.1614 (3)	−0.1851 (3)	0.4007 (3)	0.0346 (10)	
C7	−0.1555 (3)	0.2874 (3)	0.4878 (3)	0.0340 (10)	
H5A	−0.2255	0.2769	0.4666	0.041*	
H5B	−0.1463	0.3454	0.4998	0.041*	
C8	−0.1396 (3)	0.1682 (3)	0.2107 (3)	0.0390 (11)	
H3B	−0.1302	0.2045	0.1657	0.047*	
H3C	−0.2094	0.1584	0.1955	0.047*	
C9	−0.1092 (3)	−0.1247 (3)	0.1791 (3)	0.0435 (12)	
H10A	−0.0902	−0.1465	0.1301	0.052*	
H10B	−0.1801	−0.1269	0.1615	0.052*	
C10	0.1016 (3)	0.2972 (3)	0.5671 (3)	0.0355 (10)	
H2B	0.0863	0.3548	0.5680	0.043*	
H2C	0.1724	0.2920	0.5869	0.043*	
C11	0.1138 (3)	0.1896 (3)	0.2852 (3)	0.0390 (11)	
H6A	0.1847	0.1919	0.3104	0.047*	
H6B	0.0944	0.2230	0.2316	0.047*	
C12	0.1465 (3)	−0.1053 (3)	0.2653 (3)	0.0359 (10)	
H8A	0.2161	−0.0973	0.2954	0.043*	
H8B	0.1384	−0.1283	0.2068	0.043*	
C13	−0.0255 (3)	0.2994 (3)	0.4111 (3)	0.0325 (10)	
H9A	−0.0263	0.3591	0.4097	0.039*	
C14	−0.0222 (3)	0.2635 (3)	0.3232 (3)	0.0313 (9)	
H14A	−0.0276	0.3061	0.2784	0.038*	
C15	−0.0014 (3)	0.0829 (3)	0.1866 (3)	0.0387 (11)	
H4A	−0.0042	0.1107	0.1309	0.046*	
C16	0.0098 (3)	−0.0092 (3)	0.1801 (3)	0.0404 (11)	
H7A	0.0155	−0.0252	0.1223	0.048*	
C17	0.0256 (3)	−0.2159 (3)	0.2784 (3)	0.0351 (10)	

H11A	0.0315	−0.2473	0.2276	0.042*	
C18	0.0280 (3)	−0.2717 (3)	0.3574 (3)	0.0340 (10)	
H17A	0.0340	−0.3293	0.3434	0.041*	
Ca1	0.34045 (6)	0.11550 (5)	0.48616 (6)	0.0311 (2)	
Cl1	0.60289 (9)	0.00034 (7)	0.96932 (8)	0.0412 (3)	
Cl2	0.85289 (9)	0.06280 (9)	0.97036 (8)	0.0503 (3)	
Cl3	0.73290 (9)	−0.11430 (7)	0.84019 (8)	0.0426 (3)	
Cl4	0.62931 (9)	0.09276 (8)	0.77144 (8)	0.0430 (3)	
N1	−0.1162 (3)	0.2666 (2)	0.4182 (3)	0.0362 (9)	
N2	−0.1056 (2)	0.2085 (2)	0.2959 (2)	0.0339 (8)	
N3	−0.0919 (3)	0.0918 (2)	0.2066 (3)	0.0377 (9)	
N4	−0.0793 (3)	−0.0415 (2)	0.1923 (2)	0.0349 (8)	
N5	−0.0687 (3)	−0.1766 (2)	0.2567 (2)	0.0346 (8)	
N6	−0.0648 (3)	−0.2551 (2)	0.3708 (3)	0.0336 (8)	
N7	0.0629 (2)	0.2681 (2)	0.4773 (2)	0.0312 (8)	
N8	0.0725 (3)	0.2238 (2)	0.3483 (3)	0.0350 (8)	
N9	0.0849 (3)	0.1063 (2)	0.2604 (2)	0.0346 (8)	
N10	0.0985 (3)	−0.0272 (2)	0.2537 (3)	0.0371 (9)	
N11	0.1100 (3)	−0.1633 (2)	0.3164 (2)	0.0349 (8)	
N12	0.1124 (2)	−0.2437 (2)	0.4295 (2)	0.0310 (8)	
O1	−0.2394 (2)	0.1809 (2)	0.3391 (2)	0.0415 (8)	
O2	−0.2196 (2)	0.0094 (2)	0.2103 (3)	0.0495 (9)	
O3	−0.2035 (2)	−0.1792 (2)	0.3023 (2)	0.0415 (8)	
O4	0.2022 (2)	0.19935 (19)	0.4755 (2)	0.0365 (7)	
O5	0.2185 (2)	0.0438 (2)	0.3605 (2)	0.0406 (8)	
O6	0.2422 (2)	−0.15661 (19)	0.4453 (2)	0.0378 (7)	
O7	0.9032 (4)	1.0047 (4)	0.4553 (4)	0.0431 (16)	0.50
H7C	0.9087	1.0217	0.4063	0.052*	0.50
H7D	0.8967	0.9534	0.4474	0.052*	0.50
O8	0.4028 (2)	0.2508 (2)	0.4978 (2)	0.0456 (8)	
H8C	0.4540	0.2197	0.5408	0.055*	
H8D	0.3809	0.3003	0.5191	0.055*	
O9	0.5117 (2)	0.0987 (2)	0.5633 (2)	0.0451 (8)	
H9B	0.5531	0.1230	0.5442	0.054*	
H9C	0.5315	0.0574	0.5968	0.054*	
O10	0.4048 (2)	0.1092 (2)	0.3657 (2)	0.0427 (8)	
H10C	0.4429	0.0694	0.3665	0.051*	
H10D	0.4229	0.1539	0.3487	0.051*	
O11	0.3528 (2)	−0.02801 (19)	0.5115 (2)	0.0388 (7)	
H11B	0.3621	−0.0794	0.5435	0.047*	
H11C	0.3709	0.0216	0.5464	0.047*	
O12	0.3432 (2)	0.1156 (2)	0.6367 (2)	0.0431 (8)	
H12D	0.3778	0.0726	0.6767	0.052*	
H12C	0.3306	0.1662	0.6628	0.052*	
O1W	0.5848 (2)	0.1119 (2)	0.3298 (2)	0.0420 (8)	
H1WA	0.5828	0.0777	0.2888	0.063*	
H1WB	0.6083	0.1567	0.3190	0.063*	
O2W	0.5973 (2)	0.2777 (2)	0.5188 (2)	0.0434 (8)	
H2WA	0.6352	0.2411	0.5497	0.065*	

H2WC	0.5939	0.3171	0.5527	0.065*
O3W	0.5930 (3)	−0.0055 (2)	0.2081 (2)	0.0460 (8)
H3WA	0.5656	0.0291	0.1571	0.069*
H3WB	0.6620	−0.0120	0.2188	0.069*
Zn1	0.70585 (4)	0.01177 (3)	0.88953 (3)	0.03279 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.022 (2)	0.031 (2)	0.032 (2)	0.0042 (17)	−0.0022 (17)	0.0092 (18)
C2	0.028 (2)	0.050 (3)	0.028 (2)	−0.002 (2)	−0.0007 (18)	−0.001 (2)
C3	0.028 (2)	0.032 (2)	0.028 (2)	−0.0056 (18)	0.0042 (17)	−0.0099 (18)
C4	0.029 (2)	0.028 (2)	0.032 (2)	−0.0014 (17)	0.0068 (18)	0.0094 (18)
C5	0.030 (2)	0.045 (3)	0.022 (2)	−0.0009 (19)	0.0083 (18)	0.0044 (18)
C6	0.023 (2)	0.040 (3)	0.038 (3)	0.0015 (19)	0.0056 (19)	−0.0092 (19)
C7	0.029 (2)	0.026 (2)	0.045 (3)	0.0086 (17)	0.0082 (19)	0.0002 (19)
C8	0.031 (2)	0.056 (3)	0.025 (2)	0.002 (2)	0.0026 (18)	0.013 (2)
C9	0.029 (2)	0.056 (3)	0.036 (3)	−0.008 (2)	−0.0019 (19)	−0.013 (2)
C10	0.029 (2)	0.030 (2)	0.042 (3)	−0.0089 (18)	0.0044 (19)	−0.002 (2)
C11	0.035 (2)	0.047 (3)	0.032 (2)	−0.002 (2)	0.007 (2)	0.009 (2)
C12	0.035 (2)	0.044 (3)	0.031 (2)	0.003 (2)	0.0126 (19)	−0.005 (2)
C13	0.030 (2)	0.025 (2)	0.040 (3)	0.0052 (18)	0.0083 (19)	0.0108 (18)
C14	0.029 (2)	0.028 (2)	0.033 (2)	0.0027 (17)	0.0052 (18)	0.0137 (18)
C15	0.027 (2)	0.049 (3)	0.033 (3)	−0.005 (2)	−0.0002 (18)	0.005 (2)
C16	0.031 (2)	0.049 (3)	0.036 (3)	−0.002 (2)	0.003 (2)	0.000 (2)
C17	0.036 (2)	0.037 (3)	0.030 (2)	0.0040 (19)	0.0077 (19)	−0.0145 (19)
C18	0.031 (2)	0.034 (2)	0.034 (2)	−0.0014 (18)	0.0058 (18)	−0.0099 (19)
Ca1	0.0262 (4)	0.0315 (5)	0.0298 (4)	0.0022 (3)	0.0013 (3)	−0.0012 (4)
Cl1	0.0536 (7)	0.0444 (7)	0.0435 (6)	0.0105 (5)	0.0403 (6)	0.0066 (5)
Cl2	0.0398 (6)	0.0648 (8)	0.0355 (7)	−0.0135 (6)	−0.0027 (5)	−0.0041 (6)
Cl3	0.0498 (7)	0.0398 (6)	0.0434 (7)	0.0038 (5)	0.0223 (5)	−0.0032 (5)
Cl4	0.0395 (6)	0.0496 (7)	0.0385 (6)	0.0177 (5)	0.0106 (5)	0.0175 (5)
N1	0.037 (2)	0.0281 (19)	0.040 (2)	−0.0044 (16)	0.0069 (17)	−0.0003 (16)
N2	0.0246 (18)	0.040 (2)	0.033 (2)	−0.0034 (16)	0.0050 (15)	0.0055 (16)
N3	0.0265 (19)	0.046 (2)	0.036 (2)	0.0023 (17)	0.0043 (16)	−0.0043 (17)
N4	0.032 (2)	0.040 (2)	0.030 (2)	−0.0081 (17)	0.0059 (16)	0.0008 (16)
N5	0.0269 (18)	0.045 (2)	0.028 (2)	−0.0005 (16)	0.0038 (15)	−0.0053 (16)
N6	0.0276 (19)	0.039 (2)	0.033 (2)	0.0031 (16)	0.0090 (15)	−0.0057 (16)
N7	0.0263 (18)	0.0329 (19)	0.030 (2)	0.0020 (15)	0.0028 (15)	−0.0014 (15)
N8	0.0313 (19)	0.041 (2)	0.031 (2)	0.0040 (16)	0.0079 (16)	0.0139 (16)
N9	0.0280 (19)	0.039 (2)	0.031 (2)	−0.0042 (16)	0.0006 (15)	0.0021 (16)
N10	0.034 (2)	0.039 (2)	0.034 (2)	−0.0012 (17)	0.0055 (16)	0.0014 (17)
N11	0.0234 (18)	0.044 (2)	0.032 (2)	−0.0035 (16)	0.0011 (15)	−0.0023 (17)
N12	0.0258 (18)	0.0274 (19)	0.035 (2)	−0.0035 (15)	0.0033 (15)	−0.0003 (15)
O1	0.0319 (17)	0.049 (2)	0.041 (2)	−0.0062 (15)	0.0093 (15)	0.0006 (15)
O2	0.0330 (18)	0.058 (2)	0.057 (2)	−0.0008 (16)	0.0135 (16)	−0.0056 (18)
O3	0.0305 (17)	0.051 (2)	0.0401 (19)	−0.0005 (15)	0.0078 (14)	−0.0087 (15)
O4	0.0277 (16)	0.0439 (18)	0.0342 (17)	0.0034 (14)	0.0051 (13)	0.0023 (14)

O5	0.0260 (16)	0.049 (2)	0.0353 (18)	−0.0048 (14)	−0.0056 (13)	0.0007 (15)
O6	0.0287 (16)	0.0379 (18)	0.0395 (18)	−0.0066 (14)	0.0010 (13)	0.0032 (14)
O7	0.032 (3)	0.051 (4)	0.040 (4)	0.011 (3)	0.002 (3)	0.008 (3)
O8	0.0425 (19)	0.0368 (18)	0.057 (2)	0.0019 (15)	0.0160 (17)	−0.0069 (16)
O9	0.0315 (17)	0.051 (2)	0.0425 (19)	0.0078 (15)	−0.0020 (14)	−0.0039 (16)
O10	0.0338 (17)	0.054 (2)	0.0378 (18)	−0.0160 (15)	0.0079 (14)	−0.0038 (16)
O11	0.0356 (17)	0.0289 (16)	0.0409 (18)	−0.0001 (13)	−0.0026 (14)	−0.0028 (13)
O12	0.0485 (19)	0.0417 (19)	0.0385 (19)	0.0203 (15)	0.0130 (15)	−0.0049 (15)
O1W	0.0357 (17)	0.0478 (19)	0.0422 (19)	−0.0104 (15)	0.0125 (14)	0.0183 (15)
O2W	0.0388 (18)	0.0439 (19)	0.047 (2)	−0.0014 (15)	0.0131 (15)	−0.0033 (16)
O3W	0.0438 (19)	0.048 (2)	0.0361 (18)	−0.0156 (16)	−0.0008 (15)	−0.0049 (15)
Zn1	0.0340 (3)	0.0351 (3)	0.0277 (3)	−0.0006 (2)	0.0079 (2)	−0.0002 (2)

Geometric parameters (Å, °)

C1—O1	1.212 (5)	C14—N2	1.453 (5)
C1—N1	1.359 (6)	C14—H14A	0.9800
C1—N2	1.361 (6)	C15—N3	1.447 (6)
C2—O2	1.209 (5)	C15—N9	1.453 (5)
C2—N3	1.362 (6)	C15—C16	1.526 (7)
C2—N4	1.370 (6)	C15—H4A	0.9800
C3—O3	1.212 (5)	C16—N10	1.452 (6)
C3—N5	1.350 (6)	C16—N4	1.460 (6)
C3—N6	1.373 (6)	C16—H7A	0.9800
C4—O4	1.230 (5)	C17—N5	1.442 (6)
C4—N8	1.345 (6)	C17—N11	1.453 (6)
C4—N7	1.372 (5)	C17—C18	1.540 (6)
C5—O5	1.208 (5)	C17—H11A	0.9800
C5—N9	1.357 (6)	C18—N12	1.445 (5)
C5—N10	1.380 (6)	C18—N6	1.447 (5)
C6—O6	1.241 (5)	C18—H17A	0.9800
C6—N11	1.345 (6)	Ca1—O12	2.366 (3)
C6—N12	1.357 (6)	Ca1—O10	2.376 (3)
C7—N1	1.432 (6)	Ca1—O8	2.379 (3)
C7—N12^{i}	1.441 (6)	Ca1—O4	2.384 (3)
C7—H5A	0.9700	Ca1—O11	2.384 (3)
C7—H5B	0.9700	Ca1—O9	2.389 (3)
C8—N2	1.436 (6)	Ca1—O5	2.479 (3)
C8—N3	1.441 (6)	Cl1—Zn1	2.2471 (11)
C8—H3B	0.9700	Cl2—Zn1	2.2512 (13)
C8—H3C	0.9700	Cl3—Zn1	2.2871 (13)
C9—N4	1.426 (6)	Cl4—Zn1	2.2634 (12)
C9—N5	1.450 (6)	N6—C10^{i}	1.436 (6)
C9—H10A	0.9700	N12—C7^{i}	1.441 (6)
C9—H10B	0.9700	O7—H7C	0.8502
C10—N7	1.427 (6)	O7—H7D	0.8501
C10—N6^{i}	1.436 (6)	O8—H8C	0.9701
C10—H2B	0.9700	O8—H8D	0.9699

C10—H2C	0.9700	O9—H9B	0.8502
C11—N8	1.432 (6)	O9—H9C	0.8498
C11—N9	1.444 (6)	O10—H10C	0.8500
C11—H6A	0.9700	O10—H10D	0.8499
C11—H6B	0.9700	O11—H11B	0.9700
C12—N10	1.438 (6)	O11—H11C	0.9702
C12—N11	1.452 (6)	O12—H12D	0.9697
C12—H8A	0.9700	O12—H12C	0.9698
C12—H8B	0.9700	O1W—H1WA	0.8501
C13—N1	1.453 (5)	O1W—H1WB	0.8497
C13—N7	1.454 (5)	O2W—H2WA	0.8498
C13—C14	1.523 (6)	O2W—H2WC	0.8498
C13—H9A	0.9800	O3W—H3WA	0.9596
C14—N8	1.447 (5)	O3W—H3WB	0.9600
O1—C1—N1	125.9 (4)	O10—Ca1—O4	120.34 (12)
O1—C1—N2	125.8 (4)	O8—Ca1—O4	75.77 (11)
N1—C1—N2	108.2 (4)	O12—Ca1—O11	81.71 (12)
O2—C2—N3	126.8 (5)	O10—Ca1—O11	93.68 (12)
O2—C2—N4	125.2 (5)	O8—Ca1—O11	154.45 (12)
N3—C2—N4	108.0 (4)	O4—Ca1—O11	126.60 (11)
O3—C3—N5	126.1 (4)	O12—Ca1—O9	79.11 (12)
O3—C3—N6	126.0 (4)	O10—Ca1—O9	78.14 (12)
N5—C3—N6	107.8 (4)	O8—Ca1—O9	76.46 (12)
O4—C4—N8	125.7 (4)	O4—Ca1—O9	143.67 (12)
O4—C4—N7	125.4 (4)	O11—Ca1—O9	78.01 (11)
N8—C4—N7	108.9 (4)	O12—Ca1—O5	125.49 (12)
O5—C5—N9	127.3 (4)	O10—Ca1—O5	72.47 (11)
O5—C5—N10	125.5 (4)	O8—Ca1—O5	131.00 (12)
N9—C5—N10	107.2 (4)	O4—Ca1—O5	81.80 (11)
O6—C6—N11	125.2 (4)	O11—Ca1—O5	70.18 (11)
O6—C6—N12	124.9 (4)	O9—Ca1—O5	134.48 (11)
N11—C6—N12	109.9 (4)	O12—Ca1—H8C	81.2
N1—C7—N12^{i}	114.5 (3)	O10—Ca1—H8C	85.3
N1—C7—H5A	108.6	O8—Ca1—H8C	23.7
N12^{i}—C7—H5A	108.6	O4—Ca1—H8C	94.3
N1—C7—H5B	108.6	O11—Ca1—H8C	131.1
N12^{i}—C7—H5B	108.6	O9—Ca1—H8C	53.8
H5A—C7—H5B	107.6	O5—Ca1—H8C	151.0
N2—C8—N3	114.8 (4)	O12—Ca1—H11C	62.9
N2—C8—H3B	108.6	O10—Ca1—H11C	107.2
N3—C8—H3B	108.6	O8—Ca1—H11C	137.8
N2—C8—H3C	108.6	O4—Ca1—H11C	126.1
N3—C8—H3C	108.6	O11—Ca1—H11C	21.4
H3B—C8—H3C	107.6	O9—Ca1—H11C	66.1
N4—C9—N5	114.8 (4)	O5—Ca1—H11C	90.3
N4—C9—H10A	108.6	H8C—Ca1—H11C	114.4
N5—C9—H10A	108.6	C1—N1—C7	123.1 (4)
N4—C9—H10B	108.6	C1—N1—C13	112.7 (4)

N5—C9—H10B	108.6	C7—N1—C13	124.2 (4)
H10A—C9—H10B	107.6	C1—N2—C8	122.3 (4)
N7—C10—N6^{i}	113.9 (4)	C1—N2—C14	111.8 (4)
N7—C10—H2B	108.8	C8—N2—C14	124.2 (4)
N6^{i}—C10—H2B	108.8	C2—N3—C8	121.1 (4)
N7—C10—H2C	108.8	C2—N3—C15	112.5 (4)
N6^{i}—C10—H2C	108.8	C8—N3—C15	125.1 (4)
H2B—C10—H2C	107.7	C2—N4—C9	122.9 (4)
N8—C11—N9	114.2 (4)	C2—N4—C16	111.9 (4)
N8—C11—H6A	108.7	C9—N4—C16	124.4 (4)
N9—C11—H6A	108.7	C3—N5—C17	113.3 (4)
N8—C11—H6B	108.7	C3—N5—C9	122.7 (4)
N9—C11—H6B	108.7	C17—N5—C9	123.6 (4)
H6A—C11—H6B	107.6	C3—N6—C10^{i}	122.2 (3)
N10—C12—N11	114.1 (4)	C3—N6—C18	112.4 (4)
N10—C12—H8A	108.7	C10^{i}—N6—C18	125.0 (4)
N11—C12—H8A	108.7	C4—N7—C10	121.7 (4)
N10—C12—H8B	108.7	C4—N7—C13	110.9 (3)
N11—C12—H8B	108.7	C10—N7—C13	124.4 (4)
H8A—C12—H8B	107.6	C4—N8—C11	123.6 (4)
N1—C13—N7	114.5 (3)	C4—N8—C14	112.5 (4)
N1—C13—C14	103.0 (4)	C11—N8—C14	123.7 (4)
N7—C13—C14	103.8 (3)	C5—N9—C11	122.1 (4)
N1—C13—H9A	111.6	C5—N9—C15	113.2 (4)
N7—C13—H9A	111.6	C11—N9—C15	124.3 (4)
C14—C13—H9A	111.6	C5—N10—C12	123.0 (4)
N8—C14—N2	114.7 (3)	C5—N10—C16	112.5 (4)
N8—C14—C13	103.4 (3)	C12—N10—C16	123.1 (4)
N2—C14—C13	104.0 (3)	C6—N11—C12	122.8 (4)
N8—C14—H14A	111.4	C6—N11—C17	111.7 (4)
N2—C14—H14A	111.4	C12—N11—C17	124.5 (4)
C13—C14—H14A	111.4	C6—N12—C7^{i}	122.5 (4)
N3—C15—N9	113.4 (4)	C6—N12—C18	111.0 (4)
N3—C15—C16	103.7 (4)	C7^{i}—N12—C18	124.1 (4)
N9—C15—C16	103.5 (4)	C4—O4—Ca1	153.9 (3)
N3—C15—H4A	111.9	C5—O5—Ca1	151.6 (3)
N9—C15—H4A	111.9	H7C—O7—H7D	103.2
C16—C15—H4A	111.9	Ca1—O8—H8C	75.3
N10—C16—N4	113.9 (4)	Ca1—O8—H8D	130.5
N10—C16—C15	103.4 (4)	H8C—O8—H8D	117.1
N4—C16—C15	103.5 (4)	Ca1—O9—H9B	119.6
N10—C16—H7A	111.8	Ca1—O9—H9C	119.5
N4—C16—H7A	111.8	H9B—O9—H9C	117.4
C15—C16—H7A	111.8	Ca1—O10—H10C	116.1
N5—C17—N11	115.6 (4)	Ca1—O10—H10D	117.1
N5—C17—C18	103.2 (3)	H10C—O10—H10D	113.8
N11—C17—C18	102.9 (3)	Ca1—O11—H11B	159.4

N5—C17—H11A	111.5	H11B—O11—H11C	117.8
N11—C17—H11A	111.5	Ca1—O12—H12D	119.5
C18—C17—H11A	111.5	Ca1—O12—H12C	118.9
N12—C18—N6	114.0 (4)	H12D—O12—H12C	118.2
N12—C18—C17	103.9 (3)	H1WA—O1W—H1WB	109.5
N6—C18—C17	103.2 (4)	H2WA—O2W—H2WC	109.5
N12—C18—H17A	111.7	H3WA—O3W—H3WB	109.5
N6—C18—H17A	111.7	Cl1—Zn1—Cl2	112.69 (5)
C17—C18—H17A	111.7	Cl1—Zn1—Cl4	106.08 (5)
O12—Ca1—O10	157.25 (11)	Cl2—Zn1—Cl4	111.50 (6)
O12—Ca1—O8	92.29 (12)	Cl1—Zn1—Cl3	109.46 (5)
O10—Ca1—O8	82.28 (12)	Cl2—Zn1—Cl3	107.18 (5)
O12—Ca1—O4	79.07 (11)	Cl4—Zn1—Cl3	109.93 (5)

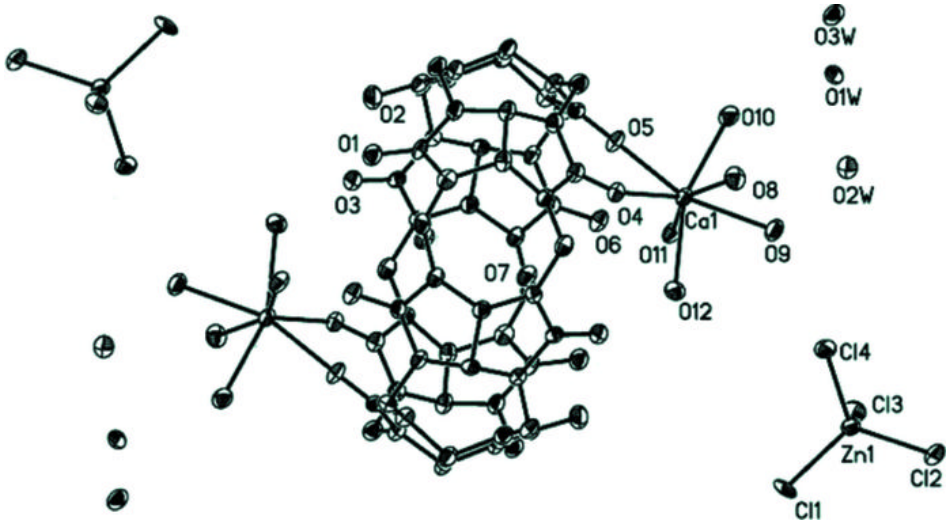
Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8C···O9	0.97	2.14	2.950 (5)	141
O8—H8D···Cl2^{ii}	0.97	2.36	3.137 (4)	136
O9—H9B···O11^{iii}	0.85	2.41	2.840 (5)	112
O11—H11B···O1W^{iii}	0.97	1.97	2.742 (4)	135
O12—H12D···O3W^{iii}	0.97	2.05	2.940 (5)	152
O2W—H2WA···O6^{iii}	0.85	2.23	2.961 (5)	145
O3W—H3WA···Cl1^{iii}	0.96	2.64	3.271 (4)	124
O9—H9C···Cl4	0.85	2.72	3.173 (4)	115
O10—H10C···O1W	0.85	2.41	2.833 (4)	112
O11—H11C···O12	0.97	2.22	3.107 (4)	151
O11—H11C···O9	0.97	2.33	3.004 (5)	126
O1W—H1WA···O3W	0.85	1.91	2.750 (5)	173
O12—H12C···O3^{i}	0.97	2.09	2.710 (4)	120
O1W—H1WB···O1^{iv}	0.85	2.15	2.737 (4)	126
O3W—H3WB···O2^{iv}	0.96	1.79	2.704 (5)	158
O2W—H2WC···Cl3^{v}	0.85	2.76	3.248 (4)	118

Symmetry codes: (ii) *x*−1/2, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*+1; (i) −*x*, −*y*, −*z*+1; (iv) *x*+1, *y*, *z*; (v) −*x*+3/2, *y*+1/2, −*z*+3/2.

Fig. 1


O3W
O1W
O2W
O2
O1
O3
O5
O10
O8
O4
O6
Ca1
O11
O9
O7
O12
Cl4
Cl3
Zn1
Cl2
Cl1