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trans-Tetraaquabis{(*E*)-2-cyano-1-[(ethoxycarbonyl)methylsulfanyl]-2-(1-naphthylaminocarbonyl)ethene-1-thiolato}calcium(II) diethyl ether disolvate

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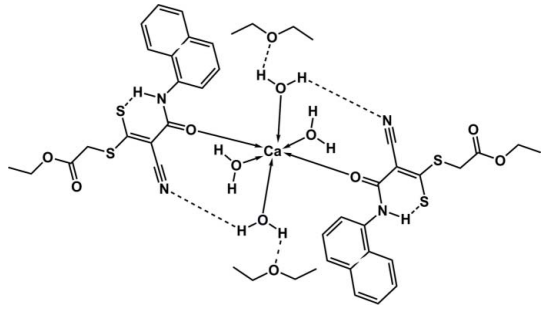
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.029; wR factor = 0.070; data-to-parameter ratio = 19.8.

In the title compound, $[Ca(C_{18}H_{15}N_2O_3S_2)(H_2O)_4]\cdot 2C_4H_{10}O$, the Ca atom, which lies on an inversion centre, is coordinated octahedrally by four water molecules and two anions of the ketene dithioacetal, the donor atoms of which are the amidic carbonyl O atoms. The central backbone of the ligands (excluding the naphthalene and oxoethyl groups) is essentially planar (r.m.s. deviation 0.035 Å). Intramolecular hydrogen bonds are observed from the NH group to the formally 'thiolate' S atom and from one coordinated water to the nitrile group and to the ether O atom. Intermolecular hydrogen bonds from the second independent water molecule to the thiolate S atom and the side-chain oxo group connect the molecules in chains parallel to the *a* axis.

Related literature

For our studies exploring the synthetic potential of ketene dithioacetals for synthesizing new classes of novel antimetabolic agents, see: Elgemeie & Sood (2006); Elgemeie *et al.* (2008, 2009). For our reports of successful approaches for the synthesis of mercaptopurine and pyrimidine analogues by the reaction of ketene dithioacetals with active methylene functions, see: Elgemeie (2003); Elgemeie *et al.* (2004, 2007).



Experimental

Crystal data

$[Ca(C_{18}H_{15}N_2O_3S_2)(H_2O)_4]\cdot 2C_4H_{10}O$
M_r = 1003.26
Triclinic, $P\overline{1}$
a = 7.8665 (3) Å
b = 12.4361 (5) Å
c = 13.8045 (6) Å
α = 103.692 (4)°
β = 99.963 (4)°
γ = 101.609 (3)°
V = 1250.24 (9) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 100 K
0.4 × 0.3 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.970, T_{max} = 1.000
26853 measured reflections
6443 independent reflections
4941 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 0.96
6443 reflections
326 parameters
18 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca—O1	2.2696 (9)	N1—C11	1.3448 (15)
Ca—O2*W*	2.3265 (10)	N1—C1	1.4184 (15)
Ca—O1*W*	2.3434 (10)	N2—C18	1.1518 (16)
S1—C13	1.7686 (12)	C11—C12	1.4684 (16)
S1—C14	1.7891 (12)	C12—C13	1.3996 (17)
S2—C13	1.7037 (12)	C12—C18	1.4325 (17)
O1—C11	1.2494 (14)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···S2	0.855 (16)	2.279 (16)	3.0274 (11)	146.2 (14)
O1*W*—H1*W*···O93	0.82 (1)	1.94 (1)	2.7531 (14)	171 (2)
O1*W*—H2*W*···N2^{i}	0.82 (1)	2.22 (1)	2.9902 (15)	157 (2)
O2*W*—H3*W*···O3^{ii}	0.82 (1)	2.03 (1)	2.7797 (13)	151 (2)
O2*W*—H4*W*···S2^{ii}	0.81 (1)	2.51 (1)	3.2666 (11)	157 (2)

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*;

program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5223).

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supporting information

Acta Cryst. (2010). E**66**, m554–m555 [https://doi.org/10.1107/S1600536810013024]

trans-Tetraaquabis{(*E*)-2-cyano-1-[(ethoxycarbonyl)methylsulfanyl]-2-(1-naphthylaminocarbonyl)ethene-1-thiolato}calcium(II) diethyl ether disolvate

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S1. Comment

During the course of our studies directed toward exploring the synthetic potential of ketene dithioacetals for synthesizing new classes of novel antimetabolic agents (Elgemeie & Sood, 2006; Elgemeie *et al.*, 2008, 2009), we have recently reported various successful approaches for synthesis of mercaptopurine and pyrimidine analogues by the reaction of ketene dithioacetals with active methylene functions (Elgemeie, 2003; Elgemeie *et al.*, 2004, 2007). In conjunction of this work, we report here a novel calcium salt (I) of a ketene dithioacetal. The structure of (I) was established on the basis of its elemental analysis and spectral data (see Experimental). In order to establish unambiguously the structure of the product, the crystal structure was determined. The X-ray analysis confirms the exclusive presence of the form (I) in the solid state (Figure 1).

The structure consists of a calcium ion on an inversion centre, coordinated octahedrally by four water molecules and two anions of the ketene dithioacetal; the latter coordinate via the amidic carbonyl oxygen O1, with Ca—O1 2.2696 (9) Å. The asymmetric unit also contains one molecule of diethyl ether.

Within the ligand, there is presumably extensive delocalization of the negative charge from its formal position at the "thiolate" sulfur S2 through the ligand backbone (see dimensions in Table 1), in which the ten atoms C1, C11–14, C18, N1, O1, S1 and S2 are approximately coplanar (r.m.s. deviation 0.035 Å). The backbone angles C11—C12—C13 and C12—C13—S2 are noticeably wide at 126.43 (9) and 129.48 (11)° respectively. The Ca atom lies 0.862 (1) Å out of the backbone plane,and the naphthalene plane subtends an interplanar angle to this plane of 29.03 (2)°.

Intramolecular hydrogen bonds (Table 2) are observed from the NH function to the formally thiolate sulfur and from a hydrogen of the coordinated water O1W to the nitrile N. Additionally, the ether molecules are connected by a hydrogen bond from the same water to the ether oxygen. Intramolecular H bonds from the second water to the thiolate sulfur and the 2-oxo function connect the molecules to form chains parallel to the *a* axis (Fig. 2).

S2. Experimental

The IR spectrum revealed the presence of cyano group at 2190 cm^{-1}. The ^1H NMR spectrum revealed signals at δ 1.06–1.24 ppm (t, CH_3), 2.51 (s, SCH_2), 4.08–4.15 (qua, ester CH_2) 7.43–8.37 (m, aromatic protons) and 8.40 (br s, NH).

S3. Refinement

NH and OH hydrogens were identified in difference syntheses. The NH hydrogen was refined freely, water H freely but with distance restraints (SADI) to O—H and H···H. Methyl protons were identified in difference syntheses, idealised and allowed to refine as rigid groups (C—H 0.98 Å, H—C—H 109.5°) allowed to rotate but not tip. Other H were included starting from calculated, idealised positions using a riding model with C—H 0.99 Å for methylene groups and 0.95 Å for sp^2 carbons. The ethyl group C16/17 is disordered over two positions with occupancies 0.738, 0.262 (4). Similarity

restraints to this group were used to improve stability of refinement.

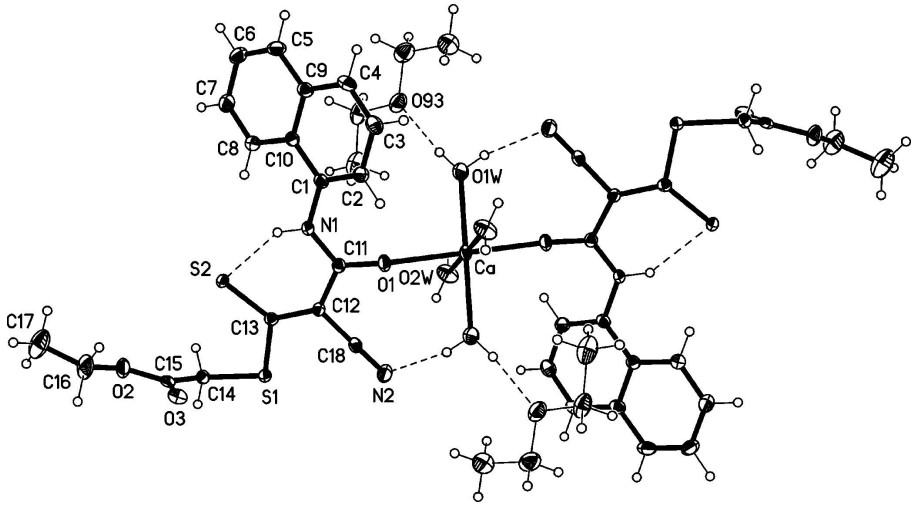

Figure 1

View of the title compound showing ellipsoids at the 50% probability level. Intramolecular hydrogen bonds are indicated by thin dashed lines.

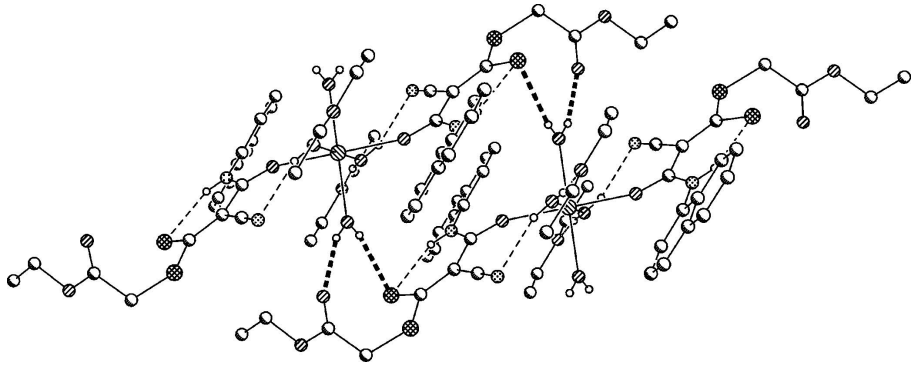

Figure 2

Packing diagram of the title compound showing two molecules connected by intermolecular hydrogen bonds (thick dashed lines).

trans-tetraaquabis{(*E*)-2-cyano-1- [(ethoxycarbonyl)methylsulfanyl]-2-(1-naphthylaminocarbonyl)ethene-1-thiolato}calcium(II) diethyl ether disolvate

Crystal data

$[Ca(C_{18}H_{15}N_2O_3S_2)(H_2O)_4]\cdot 2C_4H_{10}O$
$M_r = 1003.26$
Triclinic, $P\overline{1}$
$a = 7.8665\ (3)$ Å
$b = 12.4361\ (5)$ Å
$c = 13.8045\ (6)$ Å
$\alpha = 103.692\ (4)°$
$\beta = 99.963\ (4)°$
$\gamma = 101.609\ (3)°$
$V = 1250.24\ (9)$ Å^3
$Z = 1$
$F(000) = 530$
$D_x = 1.333$ Mg m^{-3}
Melting point = 479–481 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 11577 reflections
$\theta = 2.6–30.8°$
$\mu = 0.35$ mm^{-1}
$T = 100$ K
Irregular tablet, pale yellow
0.4 × 0.3 × 0.1 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1419 pixels mm^{-1}
ω–scan
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.970, T_{max} = 1.000

26853 measured reflections
6443 independent reflections
4941 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.7°, θ_{min} = 2.7°
h = −10→10
k = −16→16
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 0.96
6443 reflections
326 parameters
18 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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.
Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
5.7234 (0.0013) x - 5.6563 (0.0020) y + 7.4193 (0.0030) z = 5.4532 (0.0027)
* 0.0098 (0.0008) C1 * 0.0042 (0.0011) C11 * 0.0033 (0.0011) C12 * -0.0107 (0.0010) C13 * 0.0215 (0.0007) C14 * 0.0075 (0.0008) C18 * 0.0664 (0.0009) N1 * -0.0508 (0.0008) O1 * 0.0150 (0.0006) S1 * -0.0662 (0.0006) S2 -0.8620 (0.0010) Ca
Rms deviation of fitted atoms = 0.0351
7.5293 (0.0008) x - 5.2398 (0.0041) y + 0.8431 (0.0033) z = 1.0859 (0.0024)
Angle to previous plane (with approximate esd) = 29.03 (0.02)
* -0.0015 (0.0010) C1 * 0.0157 (0.0010) C2 * 0.0006 (0.0010) C3 * -0.0152 (0.0011) C4 * 0.0063 (0.0011) C5 * 0.0109 (0.0011) C6 * -0.0015 (0.0011) C7 * -0.0092 (0.0010) C8 * -0.0036 (0.0011) C9 * -0.0025 (0.0011) C10
Rms deviation of fitted atoms = 0.0086

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)
Ca	0.0000	0.5000	1.0000	0.01453 (8)	
S1	0.64002 (4)	0.90145 (3)	0.93054 (2)	0.01677 (8)	
S2	0.63380 (4)	0.69288 (3)	0.76538 (2)	0.01590 (8)	
O1	0.25364 (11)	0.53927 (7)	0.94360 (7)	0.0198 (2)	
O3	1.01513 (11)	0.87570 (7)	0.93853 (7)	0.0201 (2)	

N1	0.39935 (14)	0.49923 (9)	0.81647 (8)	0.0156 (2)	
H01	0.471 (2)	0.5286 (13)	0.7844 (11)	0.032 (4)*	
N2	0.36142 (15)	0.81149 (9)	1.07579 (8)	0.0225 (2)	
C1	0.32121 (15)	0.37980 (10)	0.77809 (9)	0.0152 (3)	
C2	0.27106 (16)	0.31450 (10)	0.84051 (10)	0.0173 (3)	
H2	0.2901	0.3491	0.9120	0.021*	
C3	0.19158 (17)	0.19658 (11)	0.79947 (10)	0.0211 (3)	
H3	0.1560	0.1523	0.8433	0.025*	
C4	0.16515 (17)	0.14516 (11)	0.69724 (10)	0.0210 (3)	
H4	0.1102	0.0656	0.6706	0.025*	
C5	0.19573 (17)	0.15718 (11)	0.52430 (10)	0.0236 (3)	
H5	0.1437	0.0773	0.4969	0.028*	
C6	0.24685 (18)	0.21949 (12)	0.46050 (10)	0.0256 (3)	
H6	0.2309	0.1830	0.3897	0.031*	
C7	0.32322 (17)	0.33790 (12)	0.49968 (10)	0.0240 (3)	
H7	0.3580	0.3813	0.4550	0.029*	
C8	0.34779 (17)	0.39113 (11)	0.60195 (9)	0.0193 (3)	
H8	0.3994	0.4712	0.6272	0.023*	
C9	0.21843 (16)	0.20880 (10)	0.63064 (10)	0.0178 (3)	
C10	0.29770 (15)	0.32891 (10)	0.67054 (9)	0.0153 (3)	
C11	0.36103 (16)	0.57231 (10)	0.89338 (9)	0.0143 (2)	
C12	0.44847 (15)	0.69477 (10)	0.91915 (9)	0.0139 (2)	
C13	0.56499 (15)	0.75240 (10)	0.87132 (9)	0.0137 (2)	
C14	0.78632 (16)	0.94911 (10)	0.85488 (9)	0.0147 (2)	
H14A	0.7223	0.9213	0.7818	0.018*	
H14B	0.8187	1.0338	0.8744	0.018*	
C15	0.95496 (16)	0.90825 (10)	0.86744 (9)	0.0152 (3)	
O2	1.03244 (11)	0.91600 (8)	0.78997 (7)	0.0246 (2)	
C16	1.1903 (3)	0.8657 (3)	0.7942 (2)	0.0354 (7)	0.738 (4)
H16A	1.2878	0.9141	0.8533	0.042*	0.738 (4)
H16B	1.1571	0.7883	0.8036	0.042*	0.738 (4)
C17	1.2505 (3)	0.8589 (2)	0.69962 (17)	0.0436 (8)	0.738 (4)
H17A	1.3527	0.8250	0.7021	0.065*	0.738 (4)
H17B	1.2859	0.9359	0.6916	0.065*	0.738 (4)
H17C	1.1533	0.8113	0.6414	0.065*	0.738 (4)
C16′	1.2112 (11)	0.9059 (6)	0.7918 (7)	0.029 (2)*	0.262 (4)
H16C	1.2780	0.9128	0.8616	0.034*	0.262 (4)
H16D	1.2780	0.9625	0.7633	0.034*	0.262 (4)
C17′	1.1676 (9)	0.7828 (6)	0.7206 (5)	0.044 (2)*	0.262 (4)
H17D	1.2788	0.7609	0.7139	0.066*	0.262 (4)
H17E	1.0996	0.7794	0.6529	0.066*	0.262 (4)
H17F	1.0967	0.7301	0.7499	0.066*	0.262 (4)
C18	0.40096 (16)	0.75993 (10)	1.00605 (9)	0.0152 (2)	
C91	−0.0616 (2)	0.49289 (14)	0.64737 (12)	0.0380 (4)	
H91A	0.0392	0.4925	0.7000	0.057*	
H91B	−0.1516	0.5204	0.6803	0.057*	
H91C	−0.0198	0.5436	0.6071	0.057*	
C92	−0.1421 (2)	0.37394 (14)	0.57815 (11)	0.0314 (3)	

H92A	−0.2440	0.3737	0.5247	0.038*
H92B	−0.0523	0.3460	0.5439	0.038*
O93	−0.20128 (13)	0.30117 (9)	0.63788 (7)	0.0283 (2)
C94	−0.2807 (2)	0.18547 (13)	0.57820 (11)	0.0332 (4)
H94A	−0.1931	0.1539	0.5444	0.040*
H94B	−0.3842	0.1823	0.5244	0.040*
C95	−0.3405 (2)	0.11591 (14)	0.64723 (12)	0.0375 (4)
H95A	−0.4274	0.1474	0.6803	0.056*
H95B	−0.2373	0.1185	0.6997	0.056*
H95C	−0.3959	0.0364	0.6067	0.056*
O1W	−0.17859 (14)	0.37346 (9)	0.84531 (8)	0.0318 (3)
H1W	−0.173 (2)	0.3536 (15)	0.7848 (10)	0.051 (6)*
H2W	−0.252 (2)	0.3209 (14)	0.8526 (14)	0.064 (7)*
O2W	−0.07611 (14)	0.64913 (9)	0.94233 (8)	0.0277 (2)
H3W	−0.023 (2)	0.7169 (11)	0.9595 (12)	0.044 (5)*
H4W	−0.155 (2)	0.6389 (15)	0.8925 (11)	0.048 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	0.01563 (18)	0.01361 (17)	0.01734 (18)	0.00374 (13)	0.00750 (14)	0.00726 (13)
S1	0.01826 (16)	0.01288 (15)	0.01747 (16)	0.00078 (12)	0.00818 (12)	0.00085 (12)
S2	0.01890 (16)	0.01387 (15)	0.01454 (15)	0.00153 (12)	0.00815 (12)	0.00241 (11)
O1	0.0199 (5)	0.0174 (4)	0.0240 (5)	0.0023 (4)	0.0127 (4)	0.0061 (4)
O3	0.0200 (5)	0.0161 (4)	0.0215 (5)	0.0033 (4)	−0.0013 (4)	0.0058 (4)
N1	0.0165 (5)	0.0134 (5)	0.0162 (5)	0.0004 (4)	0.0076 (4)	0.0032 (4)
N2	0.0280 (6)	0.0196 (6)	0.0241 (6)	0.0076 (5)	0.0136 (5)	0.0074 (5)
C1	0.0118 (6)	0.0143 (6)	0.0184 (6)	0.0025 (5)	0.0029 (5)	0.0036 (5)
C2	0.0182 (6)	0.0168 (6)	0.0167 (6)	0.0039 (5)	0.0037 (5)	0.0050 (5)
C3	0.0216 (7)	0.0176 (6)	0.0262 (7)	0.0036 (5)	0.0064 (6)	0.0107 (5)
C4	0.0184 (7)	0.0131 (6)	0.0277 (7)	0.0004 (5)	0.0020 (5)	0.0038 (5)
C5	0.0192 (7)	0.0198 (7)	0.0242 (7)	0.0025 (5)	0.0018 (6)	−0.0037 (5)
C6	0.0244 (7)	0.0304 (8)	0.0165 (7)	0.0049 (6)	0.0045 (6)	−0.0017 (6)
C7	0.0243 (7)	0.0288 (7)	0.0189 (7)	0.0048 (6)	0.0079 (6)	0.0063 (6)
C8	0.0201 (7)	0.0181 (6)	0.0179 (6)	0.0017 (5)	0.0056 (5)	0.0032 (5)
C9	0.0133 (6)	0.0166 (6)	0.0211 (7)	0.0035 (5)	0.0022 (5)	0.0022 (5)
C10	0.0111 (6)	0.0168 (6)	0.0166 (6)	0.0032 (5)	0.0024 (5)	0.0031 (5)
C11	0.0129 (6)	0.0166 (6)	0.0142 (6)	0.0043 (5)	0.0035 (5)	0.0050 (5)
C12	0.0128 (6)	0.0154 (6)	0.0135 (6)	0.0036 (5)	0.0041 (5)	0.0030 (5)
C13	0.0121 (6)	0.0143 (6)	0.0135 (6)	0.0034 (5)	0.0013 (5)	0.0029 (5)
C14	0.0165 (6)	0.0130 (6)	0.0155 (6)	0.0029 (5)	0.0051 (5)	0.0050 (5)
C15	0.0152 (6)	0.0091 (5)	0.0174 (6)	−0.0010 (5)	0.0025 (5)	0.0008 (5)
O2	0.0161 (5)	0.0383 (6)	0.0213 (5)	0.0076 (4)	0.0079 (4)	0.0089 (4)
C16	0.0198 (12)	0.055 (2)	0.0368 (14)	0.0198 (14)	0.0121 (10)	0.0105 (15)
C17	0.0438 (15)	0.0669 (19)	0.0368 (13)	0.0383 (13)	0.0182 (11)	0.0195 (12)
C18	0.0151 (6)	0.0138 (6)	0.0184 (6)	0.0032 (5)	0.0056 (5)	0.0072 (5)
C91	0.0465 (10)	0.0441 (10)	0.0394 (9)	0.0246 (8)	0.0220 (8)	0.0223 (8)
C92	0.0300 (8)	0.0499 (10)	0.0230 (7)	0.0173 (7)	0.0103 (6)	0.0173 (7)

O93	0.0310 (6)	0.0366 (6)	0.0186 (5)	0.0095 (4)	0.0078 (4)	0.0078 (4)
C94	0.0259 (8)	0.0439 (9)	0.0240 (8)	0.0094 (7)	0.0017 (6)	0.0011 (7)
C95	0.0320 (9)	0.0389 (9)	0.0366 (9)	0.0044 (7)	0.0073 (7)	0.0056 (7)
O1W	0.0370 (6)	0.0330 (6)	0.0181 (5)	−0.0079 (5)	0.0103 (5)	0.0050 (5)
O2W	0.0291 (6)	0.0183 (5)	0.0353 (6)	0.0044 (4)	0.0007 (5)	0.0133 (5)

Geometric parameters (Å, º)

Ca—O1	2.2696 (9)	N1—H01	0.855 (16)
Ca—O2W	2.3265 (10)	C2—H2	0.9500
Ca—O1W	2.3434 (10)	C3—H3	0.9500
S1—C13	1.7686 (12)	C4—H4	0.9500
S1—C14	1.7891 (12)	C5—H5	0.9500
S2—C13	1.7037 (12)	C6—H6	0.9500
O1—C11	1.2494 (14)	C7—H7	0.9500
O3—C15	1.2064 (15)	C8—H8	0.9500
N1—C11	1.3448 (15)	C14—H14A	0.9900
N1—C1	1.4184 (15)	C14—H14B	0.9900
N2—C18	1.1518 (16)	C16—H16A	0.9900
C1—C2	1.3702 (17)	C16—H16B	0.9900
C1—C10	1.4325 (17)	C17—H17A	0.9800
C2—C3	1.4063 (17)	C17—H17B	0.9800
C3—C4	1.3643 (18)	C17—H17C	0.9800
C4—C9	1.4113 (18)	C16′—H16C	0.9900
C5—C6	1.3631 (19)	C16′—H16D	0.9900
C5—C9	1.4199 (18)	C17′—H17D	0.9800
C6—C7	1.4059 (19)	C17′—H17E	0.9800
C7—C8	1.3713 (17)	C17′—H17F	0.9800
C8—C10	1.4156 (17)	C91—H91A	0.9800
C9—C10	1.4284 (16)	C91—H91B	0.9800
C11—C12	1.4684 (16)	C91—H91C	0.9800
C12—C13	1.3996 (17)	C92—H92A	0.9900
C12—C18	1.4325 (17)	C92—H92B	0.9900
C14—C15	1.5105 (17)	C94—H94A	0.9900
C15—O2	1.3323 (15)	C94—H94B	0.9900
O2—C16′	1.433 (9)	C95—H95A	0.9800
O2—C16	1.497 (3)	C95—H95B	0.9800
C16—C17	1.455 (3)	C95—H95C	0.9800
C16′—C17′	1.545 (8)	O1W—H1W	0.824 (13)
C91—C92	1.499 (2)	O1W—H2W	0.820 (13)
C92—O93	1.4255 (17)	O2W—H3W	0.819 (13)
O93—C94	1.4277 (17)	O2W—H4W	0.810 (13)
C94—C95	1.503 (2)		
O1^{i}—Ca—O1	180.0	C9—C5—H5	119.2
O1—Ca—O2W^{i}	92.96 (4)	C5—C6—H6	120.1
O1^{i}—Ca—O2W	92.96 (4)	C7—C6—H6	120.1
O1—Ca—O2W	87.04 (4)	C8—C7—H7	119.8

O2W^{i}—Ca—O2W	180.0	C6—C7—H7	119.8
O1—Ca—O1W^{i}	83.15 (3)	C7—C8—H8	119.4
O2W—Ca—O1W^{i}	91.93 (4)	C10—C8—H8	119.4
O1^{i}—Ca—O1W	83.15 (4)	C15—C14—H14A	109.0
O1—Ca—O1W	96.85 (3)	S1—C14—H14A	109.0
O2W^{i}—Ca—O1W	91.93 (4)	C15—C14—H14B	109.0
O2W—Ca—O1W	88.07 (4)	S1—C14—H14B	109.0
O1W^{i}—Ca—O1W	180.0	H14A—C14—H14B	107.8
C13—S1—C14	103.00 (6)	C17—C16—H16A	109.8
C11—O1—Ca	161.36 (9)	O2—C16—H16A	109.8
C11—N1—C1	126.41 (11)	C17—C16—H16B	109.8
C2—C1—N1	122.01 (11)	O2—C16—H16B	109.8
C2—C1—C10	120.73 (11)	H16A—C16—H16B	108.2
N1—C1—C10	117.26 (11)	C16—C17—H17A	109.5
C1—C2—C3	120.42 (12)	C16—C17—H17B	109.5
C4—C3—C2	120.61 (12)	H17A—C17—H17B	109.5
C3—C4—C9	120.80 (12)	C16—C17—H17C	109.5
C6—C5—C9	121.59 (12)	H17A—C17—H17C	109.5
C5—C6—C7	119.90 (12)	H17B—C17—H17C	109.5
C8—C7—C6	120.40 (13)	O2—C16′—H16C	112.1
C7—C8—C10	121.21 (12)	C17′—C16′—H16C	112.1
C4—C9—C5	122.03 (12)	O2—C16′—H16D	112.1
C4—C9—C10	119.51 (11)	C17′—C16′—H16D	112.1
C5—C9—C10	118.46 (12)	H16C—C16′—H16D	109.7
C8—C10—C9	118.44 (11)	C16′—C17′—H17D	109.5
C8—C10—C1	123.63 (11)	C16′—C17′—H17E	109.5
C9—C10—C1	117.93 (11)	H17D—C17′—H17E	109.5
O1—C11—N1	122.08 (11)	C16′—C17′—H17F	109.5
O1—C11—C12	119.03 (11)	H17D—C17′—H17F	109.5
N1—C11—C12	118.89 (11)	H17E—C17′—H17F	109.5
C13—C12—C18	118.58 (11)	C92—C91—H91A	109.5
C13—C12—C11	129.48 (11)	C92—C91—H91B	109.5
C18—C12—C11	111.94 (10)	H91A—C91—H91B	109.5
C12—C13—S2	126.43 (9)	C92—C91—H91C	109.5
C12—C13—S1	113.61 (9)	H91A—C91—H91C	109.5
S2—C13—S1	119.95 (7)	H91B—C91—H91C	109.5
C15—C14—S1	113.08 (9)	O93—C92—H92A	109.9
O3—C15—O2	124.07 (12)	C91—C92—H92A	109.9
O3—C15—C14	125.39 (12)	O93—C92—H92B	109.9
O2—C15—C14	110.52 (10)	C91—C92—H92B	109.9
C15—O2—C16′	122.7 (4)	H92A—C92—H92B	108.3
C15—O2—C16	112.09 (14)	O93—C94—H94A	109.9
C16′—O2—C16	19.7 (3)	C95—C94—H94A	109.9
C17—C16—O2	109.5 (2)	O93—C94—H94B	109.9
O2—C16′—C17′	98.6 (5)	C95—C94—H94B	109.9
N2—C18—C12	179.36 (14)	H94A—C94—H94B	108.3
O93—C92—C91	108.82 (12)	C94—C95—H95A	109.5
C92—O93—C94	112.91 (11)	C94—C95—H95B	109.5

O93—C94—C95	109.05 (12)	H95A—C95—H95B	109.5
C11—N1—H01	116.6 (10)	C94—C95—H95C	109.5
C1—N1—H01	116.8 (10)	H95A—C95—H95C	109.5
C1—C2—H2	119.8	H95B—C95—H95C	109.5
C3—C2—H2	119.8	Ca—O1W—H1W	138.0 (12)
C4—C3—H3	119.7	Ca—O1W—H2W	113.9 (13)
C2—C3—H3	119.7	H1W—O1W—H2W	105.2 (16)
C3—C4—H4	119.6	Ca—O2W—H3W	129.2 (12)
C9—C4—H4	119.6	Ca—O2W—H4W	122.9 (13)
C6—C5—H5	119.2	H3W—O2W—H4W	107.1 (16)

O1^{i}—Ca—O1—C11	71 (6)	Ca—O1—C11—C12	79.9 (3)
O2W^{i}—Ca—O1—C11	153.0 (3)	C1—N1—C11—O1	3.5 (2)
O2W—Ca—O1—C11	−27.0 (3)	C1—N1—C11—C12	−176.62 (11)
O1W^{i}—Ca—O1—C11	−119.3 (3)	O1—C11—C12—C13	−176.38 (12)
O1W—Ca—O1—C11	60.7 (3)	N1—C11—C12—C13	3.71 (19)
C11—N1—C1—C2	−34.63 (18)	O1—C11—C12—C18	3.10 (16)
C11—N1—C1—C10	145.94 (12)	N1—C11—C12—C18	−176.80 (11)
N1—C1—C2—C3	179.07 (11)	C18—C12—C13—S2	−177.98 (9)
C10—C1—C2—C3	−1.52 (19)	C11—C12—C13—S2	1.48 (19)
C1—C2—C3—C4	0.79 (19)	C18—C12—C13—S1	1.28 (15)
C2—C3—C4—C9	0.62 (19)	C11—C12—C13—S1	−179.27 (10)
C9—C5—C6—C7	−0.3 (2)	C14—S1—C13—C12	178.99 (9)
C5—C6—C7—C8	0.4 (2)	C14—S1—C13—S2	−1.70 (9)
C6—C7—C8—C10	0.1 (2)	C13—S1—C14—C15	−68.69 (9)
C3—C4—C9—C5	178.77 (13)	S1—C14—C15—O3	−20.07 (15)
C3—C4—C9—C10	−1.27 (19)	S1—C14—C15—O2	161.69 (8)
C6—C5—C9—C4	179.68 (13)	O3—C15—O2—C16′	−11.5 (4)
C6—C5—C9—C10	−0.29 (19)	C14—C15—O2—C16′	166.8 (3)
C7—C8—C10—C9	−0.74 (19)	O3—C15—O2—C16	7.3 (2)
C7—C8—C10—C1	179.59 (12)	C14—C15—O2—C16	−174.45 (16)
C4—C9—C10—C8	−179.15 (12)	C15—O2—C16—C17	170.4 (2)
C5—C9—C10—C8	0.82 (17)	C16′—O2—C16—C17	−63.0 (12)
C4—C9—C10—C1	0.53 (17)	C15—O2—C16′—C17′	103.4 (5)
C5—C9—C10—C1	−179.50 (12)	C16—O2—C16′—C17′	41.3 (9)
C2—C1—C10—C8	−179.49 (12)	C13—C12—C18—N2	162 (14)
N1—C1—C10—C8	−0.05 (18)	C11—C12—C18—N2	−17 (14)
C2—C1—C10—C9	0.84 (17)	C91—C92—O93—C94	179.86 (11)
N1—C1—C10—C9	−179.72 (10)	C92—O93—C94—C95	−179.38 (12)
Ca—O1—C11—N1	−100.2 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···S2	0.855 (16)	2.279 (16)	3.0274 (11)	146.2 (14)
O1*W*—H1*W*···O93	0.82 (1)	1.94 (1)	2.7531 (14)	171 (2)

O1*W*—H2*W*···N2^{i}	0.82 (1)	2.22 (1)	2.9902 (15)	157 (2)
O2*W*—H3*W*···O3^{ii}	0.82 (1)	2.03 (1)	2.7797 (13)	151 (2)
O2*W*—H4*W*···S2^{ii}	0.81 (1)	2.51 (1)	3.2666 (11)	157 (2)

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