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Bis{2,2′-[ethane-1,2-diylbis(iminomethylene)]diphenolato-κ^2O,N,N',O'}cerium(IV) chloroform solvate

Shu-Ping Yang,[a]* Li-Jun Han,[b] Da-Qi Wang[c] and Bo Wang[a]

[a]Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China, [b]Department of Mathematics and Science, Huaihai Institute of Technology, Lianyungang 222005, People's Republic of China, and [c]College of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, People's Republic of China
Correspondence e-mail: yangshuping@hhit.edu.cn

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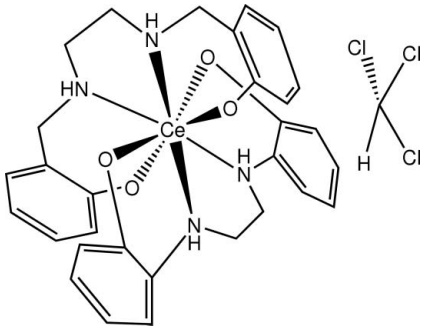
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.010 Å; R factor = 0.046; wR factor = 0.128; data-to-parameter ratio = 15.1.

In the title compound, $[Ce(C_{16}H_{18}N_2O_2)_2]\cdot CHCl_3$, the Ce^{IV} atom has an eight-coordinate geometry involving two tetradentate *N*,*N*′-(2-oxidobenzyl)ethane-1,2-diamine ligands. The asymmetric unit contains one molecule of the title complex and one chloroform molecule, linked by C—H···O and N—H···Cl hydrogen bonds. These neighbouring molecules are connected by two C—H···π interactions, and by N—H···Cl and C—H···Cl interactions, resulting in a three-dimensional network.

Related literature

For related literature, see: Branum *et al.* (2001); Franklin (2001); Komiyama *et al.* (1999); Liu *et al.* (2007); Takasaki & Chin (1994); Williams *et al.* (1999).



Experimental

Crystal data

$[Ce(C_{16}H_{18}N_2O_2)_2]\cdot CHCl_3$
M_r = 800.14
Monoclinic, $P2_1/n$
a = 12.493 (1) Å
b = 14.199 (2) Å
c = 20.253 (2) Å
β = 104.263 (2)°
V = 3481.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.58 mm^{-1}
T = 298 (2) K
0.57 × 0.51 × 0.39 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.466, T_{max} = 0.578
(expected range = 0.436–0.540)
17037 measured reflections
6130 independent reflections
3810 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.129
S = 1.06
6130 reflections
406 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ce1—O1	2.193 (4)	Ce1—N1	2.603 (4)
Ce1—O2	2.218 (4)	Ce1—N2	2.628 (4)
Ce1—O3	2.239 (4)	Ce1—N4	2.621 (4)
Ce1—O4	2.188 (4)	Ce1—N3	2.626 (5)
O4—Ce1—O1	95.7 (2)	N1—Ce1—N4	132.6 (2)
O4—Ce1—O2	90.7 (2)	N1—Ce1—N3	133.7 (1)
O1—Ce1—O2	149.1 (1)	N4—Ce1—N3	67.1 (1)
O4—Ce1—O3	147.2 (1)	N1—Ce1—N2	66.5 (1)
O1—Ce1—O3	95.1 (2)	N4—Ce1—N2	135.3 (1)
O2—Ce1—O3	95.7 (2)	N3—Ce1—N2	135.2 (2)

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

*Cg*1 is the centroid of the ring C9–C14 and *Cg*2 is the centroid of the ring C25–C30.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.91	2.73	3.604 (5)	162
C33—H33···O3	0.98	2.51	3.437 (7)	157
N2—H2···Cl2^{i}	0.91	2.94	3.762 (5)	151
C4—H4*A*···Cl3^{ii}	0.93	2.79	3.646 (7)	153
C29—H29···*Cg*1^{iii}	0.93	2.85	3.626 (7)	142
C31—H31*B*···*Cg*2^{iv}	0.97	2.79	3.712 (6)	158

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: AT2424).

References

Branum, M. E., Tipton, A. K., Zhu, S. & Que, L. Jr (2001). *J. Am. Chem. Soc.* **123**, 1898–1904.

Franklin, S. J. (2001). *Curr. Opin. Chem. Biol.* **5**, 201–208.

Komiyama, M., Takeda, N. & Shigekawa, H. (1999). *Chem. Commun.* pp. 1443–1451.

Liu, Y.-F., Xia, H.-T., Wang, D.-Q. & Yang, S.-P. (2007). *Acta Cryst.* E**63**, m484–m486.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Takasaki, B. K. & Chin, J. (1994). *J. Am. Chem. Soc.* **116**, 1121–1122.

Williams, N. H., Takasaki, B., Wall, M. & Chin, J. (1999). *Acc. Chem. Res.* **32**, 485–493.

supplementary materials

Acta Cryst. (2007). E**63**, m2777-m2778 [**doi:10.1107/S160053680705101X**]

Bis{2,2'-[ethane-1,2-diylbis(iminomethylene)]diphenolato-κ^2O,N,N',O'}cerium(IV) chloroform solvate

S.-P. Yang, L.-J. Han, D.-Q. Wang and B. Wang

Comment

Some Ce^{IV}complexs has been shown to hydrolyze DNA effectively at a reasonable rate (Franklin, 2001; Williams *et al.*,1999; Takasaki & Chin, 1994; Branum *et al.*, 2001; Komiyama *et al.*, 1999). We have reported recently the crystyl structure of a Ce^{IV} complex (Liu *et al.*, 2007). As part of our study of the Ce^{IV}complexes with the diamine derives, We report here the crystal structure of a new Ce^{IV}complex, bis[*N*,*N*'-bis(2-oxidobenzyl)ethane-1,2-diamine-κ^2N,N',O,O'] cerium(IV) chloroform disolvate, (I).

Compound (I) crystallizes in the space group $P2_1/n$, and the asymmetric unit contains a title complex and one chloroform molecule, which are linked by one N—H···Cl and one C—H···O hydrogen bonds into a dimeric structure (Table 2 and Fig. 1). The Ce^{IV} atom is coordinated by four O atoms and four N atoms from two tetradentate ligand, *N*,*N*'-(2-oxidobenzyl)ethane-1,2-diamine, forming a complex eight-coordinated stereochemistry geometry (Fig. 1). Two least-squares planes are defined by the atoms Ce1/O1/O2/N1/N2 and Ce1/O3/O4/N3/N4, and which are approximately planar, the maximum deviation are −0.079 (3) Å for N2 and −0.118 (3) Å for N3, respectively. The dihedral angle between the two least-squares planes are 89.23 (9)°. The average Ce—O and Ce—N distance are 2.192 (4) Å and 2.620 (4) Å, these values are approximately similar to the Ce^{IV} complexes reported [2.199 (4)Å and 2.624 (4) Å; Liu *et al.*, 2007], and the bond angles ranges around Ce^{IV} atom are O—Ce—O of 95.1 (2)° − 149.1 (1)°, N—Ce—N of 66.5 (1)° − 135.3 (1)° (see in Table 1). The crystal structure of (I) is stabilized by two C—H···π, one N—H···Cl and one C—H···Cl interactions (Table. 2).

Experimental

To a solution containing *N*,*N*-bis(2-hydroxybenzyl)ethane-1,2-diamine (1.52 g, 5 mmol) and ethanol (20 ml), a solution of cerium nitrate (1.09 g, 5 mmol) and methanol (10 ml) was added with stirring for 3 h at 333–343 K; the solid obtained was filtered off, washed successively with ethanol, and dried at room temperature. Dark red crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation of a chloroform–ethanol (1:2) solution containing the product over a period of one week.

Refinement

All H atoms were located in difference Fourier maps and then treated as riding atoms, with C—H distances of 0.93 Å (aryl), 0.97 Å (methylene), 0.98 Å (methine), N—H distances of 0.91 Å (amine), and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ (aryl, methylene, methine, amine).

Figures

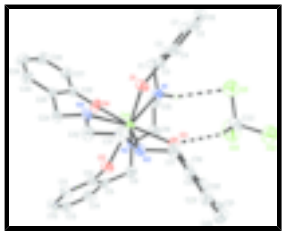

Fig. 1. The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms have been omitted.

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Crystal data

$[Ce(C_{16}H_{18}N_2O_2)_2]\cdot CHCl_3$	$F_{000} = 1616$
$M_r = 800.14$	$D_x = 1.526$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5182 reflections
$a = 12.493$ (1) Å	$\theta = 2.3$–25.4º
$b = 14.199$ (2) Å	$\mu = 1.58$ mm^{-1}
$c = 20.253$ (2) Å	$T = 298$ (2) K
$\beta = 104.263$ (2)º	Block, dark red
$V = 3481.8$ (7) Å^3	0.57 × 0.51 × 0.39 mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	6130 independent reflections
Radiation source: fine-focus sealed tube	3810 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.064$
$T = 298$(2) K	$\theta_{max} = 25.0$º
φ and ω scans	$\theta_{min} = 1.8$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13\rightarrow14$
$T_{min} = 0.466$, $T_{max} = 0.578$	$k = -16\rightarrow16$
17037 measured reflections	$l = -18\rightarrow24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.06	$(\Delta/\sigma)_{max} < 0.001$
6130 reflections	$\Delta\rho_{max}$ = 1.50 e Å^{-3}
406 parameters	$\Delta\rho_{min}$ = −0.77 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}
Ce1	0.49514 (2)	0.39970 (2)	0.249313 (17)	0.03636 (13)
N1	0.6295 (3)	0.3382 (3)	0.1791 (2)	0.0420 (12)
H1	0.6932	0.3713	0.1942	0.050*
N2	0.5780 (3)	0.2327 (3)	0.2880 (2)	0.0403 (12)
H2	0.5283	0.1900	0.2649	0.048*
N3	0.4776 (3)	0.5594 (3)	0.3112 (3)	0.0437 (12)
H3	0.4642	0.5447	0.3522	0.052*
N4	0.2960 (3)	0.4716 (3)	0.2136 (3)	0.0425 (12)
H4	0.2902	0.4974	0.1718	0.051*
O1	0.4930 (3)	0.4995 (3)	0.1663 (2)	0.0506 (11)
O2	0.4336 (3)	0.3579 (3)	0.3389 (2)	0.0499 (11)
O3	0.6658 (3)	0.4371 (3)	0.3088 (2)	0.0518 (11)
O4	0.3878 (3)	0.2954 (3)	0.1861 (2)	0.0473 (11)
C1	0.5930 (5)	0.3567 (4)	0.1052 (3)	0.0505 (16)
H1A	0.5171	0.3361	0.0885	0.061*
H1B	0.6384	0.3206	0.0817	0.061*
C2	0.6012 (4)	0.4591 (4)	0.0896 (3)	0.0451 (16)
C3	0.5489 (4)	0.5277 (4)	0.1208 (3)	0.0434 (15)
C4	0.5554 (5)	0.6209 (5)	0.1045 (3)	0.0536 (17)
H4A	0.5212	0.6665	0.1251	0.064*
C5	0.6131 (6)	0.6465 (6)	0.0573 (4)	0.066 (2)
H5	0.6156	0.7099	0.0461	0.079*
C6	0.6669 (6)	0.5825 (6)	0.0260 (4)	0.069 (2)
H6	0.7063	0.6017	−0.0051	0.083*
C7	0.6602 (5)	0.4894 (5)	0.0424 (3)	0.0632 (19)
H7	0.6957	0.4447	0.0217	0.076*
C8	0.5915 (5)	0.2124 (5)	0.3613 (3)	0.0563 (18)

H8A	0.6323	0.2633	0.3881	0.068*
H8B	0.6340	0.1550	0.3731	0.068*
C9	0.4812 (5)	0.2014 (4)	0.3783 (3)	0.0480 (15)
C10	0.4068 (5)	0.2771 (5)	0.3661 (3)	0.0470 (16)
C11	0.3065 (5)	0.2667 (5)	0.3833 (3)	0.0584 (18)
H11	0.2557	0.3158	0.3757	0.070*
C12	0.2818 (6)	0.1829 (6)	0.4119 (4)	0.070 (2)
H12	0.2142	0.1768	0.4230	0.084*
C13	0.3541 (7)	0.1099 (5)	0.4239 (4)	0.070 (2)
H13	0.3363	0.0542	0.4429	0.084*
C14	0.4530 (6)	0.1194 (5)	0.4076 (3)	0.0605 (18)
H14	0.5030	0.0697	0.4162	0.073*
C15	0.6596 (5)	0.2388 (4)	0.1918 (4)	0.0574 (19)
H15A	0.7254	0.2253	0.1762	0.069*
H15B	0.6003	0.1992	0.1665	0.069*
C16	0.6807 (5)	0.2169 (4)	0.2665 (3)	0.0523 (17)
H16A	0.7042	0.1520	0.2748	0.063*
H16B	0.7388	0.2574	0.2922	0.063*
C17	0.5802 (4)	0.6174 (4)	0.3255 (3)	0.0530 (17)
H17A	0.5643	0.6796	0.3405	0.064*
H17B	0.6046	0.6247	0.2839	0.064*
C18	0.6705 (5)	0.5735 (5)	0.3788 (3)	0.0476 (16)
C19	0.7083 (5)	0.4835 (5)	0.3672 (3)	0.0513 (17)
C20	0.7945 (5)	0.4448 (5)	0.4167 (4)	0.0617 (19)
H20	0.8211	0.3853	0.4100	0.074*
C21	0.8406 (6)	0.4933 (7)	0.4752 (4)	0.079 (3)
H21	0.8982	0.4659	0.5074	0.095*
C22	0.8046 (6)	0.5810 (6)	0.4876 (4)	0.080 (2)
H22	0.8368	0.6133	0.5275	0.096*
C23	0.7188 (6)	0.6199 (6)	0.4389 (4)	0.072 (2)
H23	0.6927	0.6791	0.4467	0.086*
C24	0.2056 (4)	0.4024 (4)	0.2043 (3)	0.0451 (16)
H24A	0.1363	0.4363	0.1972	0.054*
H24B	0.2149	0.3663	0.2460	0.054*
C25	0.1980 (4)	0.3355 (4)	0.1465 (3)	0.0422 (15)
C26	0.2905 (4)	0.2832 (4)	0.1421 (3)	0.0403 (14)
C27	0.2786 (5)	0.2156 (4)	0.0908 (3)	0.0548 (17)
H27	0.3396	0.1804	0.0871	0.066*
C28	0.1775 (6)	0.2002 (5)	0.0456 (4)	0.067 (2)
H28	0.1712	0.1545	0.0119	0.081*
C29	0.0880 (6)	0.2507 (5)	0.0496 (4)	0.065 (2)
H29	0.0201	0.2398	0.0192	0.078*
C30	0.0981 (5)	0.3193 (5)	0.0998 (3)	0.0573 (18)
H30	0.0367	0.3550	0.1021	0.069*
C31	0.3810 (5)	0.6138 (4)	0.2725 (4)	0.0549 (18)
H31A	0.3950	0.6367	0.2303	0.066*
H31B	0.3681	0.6676	0.2990	0.066*
C32	0.2805 (4)	0.5497 (4)	0.2573 (4)	0.0539 (18)
H32A	0.2686	0.5253	0.2996	0.065*

H32B	0.2156	0.5856	0.2348	0.065*
Cl1	0.88566 (18)	0.46389 (19)	0.19706 (14)	0.1116 (8)
Cl2	1.02770 (19)	0.52366 (17)	0.32317 (13)	0.1072 (8)
Cl3	0.9785 (2)	0.32984 (16)	0.29798 (18)	0.1389 (12)
C33	0.9284 (6)	0.4425 (5)	0.2845 (4)	0.069 (2)
H33	0.8645	0.4487	0.3042	0.083*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.03244 (18)	0.0353 (2)	0.0427 (2)	0.00136 (14)	0.01173 (14)	−0.00221 (19)
N1	0.040 (3)	0.042 (3)	0.045 (3)	0.004 (2)	0.012 (2)	0.001 (3)
N2	0.037 (2)	0.044 (3)	0.040 (3)	0.003 (2)	0.010 (2)	0.000 (3)
N3	0.039 (3)	0.047 (3)	0.047 (3)	0.000 (2)	0.016 (2)	0.003 (3)
N4	0.036 (2)	0.039 (3)	0.054 (3)	0.000 (2)	0.014 (2)	0.005 (3)
O1	0.055 (2)	0.051 (3)	0.052 (3)	0.0118 (19)	0.025 (2)	0.007 (2)
O2	0.056 (2)	0.051 (3)	0.046 (3)	0.005 (2)	0.018 (2)	0.007 (2)
O3	0.041 (2)	0.054 (3)	0.057 (3)	−0.0004 (19)	0.005 (2)	−0.006 (3)
O4	0.035 (2)	0.045 (3)	0.058 (3)	0.0046 (18)	0.0031 (19)	−0.015 (2)
C1	0.064 (4)	0.048 (4)	0.041 (4)	0.008 (3)	0.016 (3)	−0.003 (3)
C2	0.043 (3)	0.055 (4)	0.035 (4)	−0.004 (3)	0.004 (3)	0.001 (3)
C3	0.042 (3)	0.051 (4)	0.036 (4)	−0.003 (3)	0.006 (3)	−0.003 (3)
C4	0.066 (4)	0.048 (4)	0.044 (4)	−0.009 (3)	0.007 (3)	−0.006 (4)
C5	0.076 (5)	0.061 (5)	0.050 (5)	−0.025 (4)	−0.005 (4)	0.008 (4)
C6	0.069 (5)	0.091 (6)	0.049 (5)	−0.024 (4)	0.016 (4)	0.000 (5)
C7	0.058 (4)	0.083 (6)	0.054 (5)	−0.004 (4)	0.022 (4)	−0.008 (4)
C8	0.050 (4)	0.055 (4)	0.059 (5)	0.007 (3)	0.005 (3)	0.009 (4)
C9	0.058 (4)	0.046 (4)	0.039 (4)	−0.007 (3)	0.009 (3)	−0.005 (3)
C10	0.054 (4)	0.053 (4)	0.034 (4)	−0.004 (3)	0.010 (3)	−0.005 (3)
C11	0.057 (4)	0.073 (5)	0.051 (4)	−0.002 (3)	0.025 (3)	0.002 (4)
C12	0.062 (4)	0.094 (6)	0.060 (5)	−0.025 (4)	0.028 (4)	−0.002 (5)
C13	0.095 (6)	0.064 (5)	0.055 (5)	−0.025 (4)	0.028 (5)	−0.009 (4)
C14	0.078 (5)	0.049 (4)	0.055 (5)	0.004 (3)	0.019 (4)	−0.002 (4)
C15	0.058 (4)	0.053 (4)	0.069 (5)	0.016 (3)	0.030 (4)	0.005 (4)
C16	0.049 (3)	0.048 (4)	0.065 (5)	0.018 (3)	0.023 (3)	0.014 (4)
C17	0.050 (4)	0.044 (4)	0.069 (5)	−0.013 (3)	0.022 (3)	−0.017 (4)
C18	0.040 (3)	0.051 (4)	0.053 (4)	−0.012 (3)	0.015 (3)	−0.008 (4)
C19	0.038 (3)	0.072 (5)	0.046 (4)	−0.016 (3)	0.016 (3)	0.001 (4)
C20	0.049 (4)	0.073 (5)	0.063 (5)	−0.008 (4)	0.014 (4)	0.006 (4)
C21	0.053 (4)	0.126 (8)	0.050 (5)	−0.021 (5)	−0.004 (4)	0.014 (6)
C22	0.078 (5)	0.094 (7)	0.065 (6)	−0.019 (5)	0.008 (5)	−0.026 (5)
C23	0.069 (5)	0.075 (5)	0.075 (6)	−0.020 (4)	0.025 (4)	−0.017 (5)
C24	0.030 (3)	0.051 (4)	0.056 (4)	0.001 (3)	0.014 (3)	−0.004 (3)
C25	0.040 (3)	0.039 (4)	0.049 (4)	−0.008 (3)	0.013 (3)	0.006 (3)
C26	0.041 (3)	0.039 (4)	0.041 (4)	−0.006 (3)	0.011 (3)	0.001 (3)
C27	0.059 (4)	0.049 (4)	0.058 (5)	0.000 (3)	0.015 (4)	0.005 (4)
C28	0.068 (5)	0.075 (5)	0.054 (5)	−0.008 (4)	0.005 (4)	−0.015 (4)
C29	0.064 (5)	0.074 (5)	0.048 (5)	−0.010 (4)	−0.003 (4)	0.002 (4)

C30	0.046 (4)	0.063 (5)	0.057 (5)	0.000 (3)	0.001 (3)	0.011 (4)
C31	0.054 (4)	0.041 (4)	0.070 (5)	0.007 (3)	0.016 (3)	−0.015 (4)
C32	0.040 (3)	0.053 (4)	0.072 (5)	0.014 (3)	0.019 (3)	−0.009 (4)
Cl1	0.0901 (15)	0.132 (2)	0.109 (2)	−0.0049 (14)	0.0177 (14)	0.0137 (18)
Cl2	0.1048 (16)	0.0996 (18)	0.113 (2)	−0.0105 (13)	0.0196 (15)	−0.0147 (16)
Cl3	0.133 (2)	0.0693 (16)	0.218 (4)	0.0123 (14)	0.049 (2)	0.036 (2)
C33	0.078 (5)	0.062 (5)	0.075 (6)	0.007 (4)	0.035 (4)	0.018 (5)

Geometric parameters (Å, °)

Ce1—O1	2.193 (4)	C12—C13	1.357 (9)
Ce1—O2	2.218 (4)	C12—H12	0.9300
Ce1—O3	2.239 (4)	C13—C14	1.362 (9)
Ce1—O4	2.188 (4)	C13—H13	0.9300
Ce1—N1	2.603 (4)	C14—H14	0.9300
Ce1—N2	2.628 (4)	C15—C16	1.501 (8)
Ce1—N4	2.621 (4)	C15—H15A	0.9700
Ce1—N3	2.626 (5)	C15—H15B	0.9700
N1—C15	1.467 (7)	C16—H16A	0.9700
N1—C1	1.478 (7)	C16—H16B	0.9700
N1—H1	0.9100	C17—C18	1.492 (8)
N2—C16	1.471 (6)	C17—H17A	0.9700
N2—C8	1.481 (7)	C17—H17B	0.9700
N2—H2	0.9100	C18—C23	1.385 (9)
N3—C31	1.484 (7)	C18—C19	1.402 (8)
N3—C17	1.491 (6)	C19—C20	1.391 (9)
N3—H3	0.9100	C20—C21	1.369 (9)
N4—C32	1.460 (7)	C20—H20	0.9300
N4—C24	1.473 (6)	C21—C22	1.37 (1)
N4—H4	0.9100	C21—H21	0.9300
O1—C3	1.347 (6)	C22—C23	1.38 (1)
O2—C10	1.350 (7)	C22—H22	0.9300
O3—C19	1.343 (7)	C23—H23	0.9300
O4—C26	1.330 (6)	C24—C25	1.491 (8)
C1—C2	1.497 (8)	C24—H24A	0.9700
C1—H1A	0.9700	C24—H24B	0.9700
C1—H1B	0.9700	C25—C30	1.387 (8)
C2—C3	1.407 (8)	C25—C26	1.396 (7)
C2—C7	1.410 (8)	C26—C27	1.394 (8)
C3—C4	1.372 (8)	C27—C28	1.383 (8)
C4—C5	1.380 (9)	C27—H27	0.9300
C4—H4A	0.9300	C28—C29	1.348 (9)
C5—C6	1.38 (1)	C28—H28	0.9300
C5—H5	0.9300	C29—C30	1.391 (9)
C6—C7	1.372 (9)	C29—H29	0.9300
C6—H6	0.9300	C30—H30	0.9300
C7—H7	0.9300	C31—C32	1.519 (8)
C8—C9	1.510 (8)	C31—H31A	0.9700
C8—H8A	0.9700	C31—H31B	0.9700

C8—H8B	0.9700	C32—H32A	0.9700
C9—C14	1.391 (8)	C32—H32B	0.9700
C9—C10	1.402 (8)	Cl1—C33	1.745 (7)
C10—C11	1.389 (8)	Cl2—C33	1.733 (8)
C11—C12	1.390 (9)	Cl3—C33	1.715 (7)
C11—H11	0.9300	C33—H33	0.9800
O4—Ce1—O1	95.7 (2)	C11—C10—C9	118.3 (6)
O4—Ce1—O2	90.7 (2)	C10—C11—C12	120.1 (7)
O1—Ce1—O2	149.1 (1)	C10—C11—H11	119.9
O4—Ce1—O3	147.2 (1)	C12—C11—H11	119.9
O1—Ce1—O3	95.1 (2)	C13—C12—C11	121.5 (7)
O2—Ce1—O3	95.7 (2)	C13—C12—H12	119.3
O4—Ce1—N1	80.7 (1)	C11—C12—H12	119.3
O1—Ce1—N1	71.7 (1)	C12—C13—C14	119.0 (7)
O2—Ce1—N1	139.2 (2)	C12—C13—H13	120.5
O3—Ce1—N1	73.6 (2)	C14—C13—H13	120.5
O4—Ce1—N4	72.5 (2)	C13—C14—C9	121.7 (7)
O1—Ce1—N4	72.9 (1)	C13—C14—H14	119.1
O2—Ce1—N4	80.4 (1)	C9—C14—H14	119.1
O3—Ce1—N4	140.3 (2)	N1—C15—C16	110.4 (5)
N1—Ce1—N4	132.6 (2)	N1—C15—H15A	109.6
O4—Ce1—N3	138.8 (1)	C16—C15—H15A	109.6
O1—Ce1—N3	79.7 (2)	N1—C15—H15B	109.6
O2—Ce1—N3	75.8 (2)	C16—C15—H15B	109.6
O3—Ce1—N3	73.7 (1)	H15A—C15—H15B	108.1
N1—Ce1—N3	133.7 (1)	N2—C16—C15	108.5 (5)
N4—Ce1—N3	67.1 (1)	N2—C16—H16A	110.0
O4—Ce1—N2	72.7 (1)	C15—C16—H16A	110.0
O1—Ce1—N2	137.8 (1)	N2—C16—H16B	110.0
O2—Ce1—N2	72.8 (1)	C15—C16—H16B	110.0
O3—Ce1—N2	78.5 (2)	H16A—C16—H16B	108.4
N1—Ce1—N2	66.5 (1)	N3—C17—C18	111.7 (5)
N4—Ce1—N2	135.3 (1)	N3—C17—H17A	109.3
N3—Ce1—N2	135.2 (2)	C18—C17—H17A	109.3
C15—N1—C1	110.5 (5)	N3—C17—H17B	109.3
C15—N1—Ce1	113.5 (3)	C18—C17—H17B	109.3
C1—N1—Ce1	114.5 (3)	H17A—C17—H17B	107.9
C15—N1—H1	105.8	C23—C18—C19	119.3 (7)
C1—N1—H1	105.8	C23—C18—C17	121.7 (6)
Ce1—N1—H1	105.8	C19—C18—C17	119.0 (6)
C16—N2—C8	112.0 (4)	O3—C19—C20	120.6 (7)
C16—N2—Ce1	110.9 (3)	O3—C19—C18	121.3 (6)
C8—N2—Ce1	114.4 (3)	C20—C19—C18	118.1 (7)
C16—N2—H2	106.3	C21—C20—C19	120.8 (7)
C8—N2—H2	106.3	C21—C20—H20	119.6
Ce1—N2—H2	106.3	C19—C20—H20	119.6
C31—N3—C17	111.2 (5)	C22—C21—C20	122.0 (8)
C31—N3—Ce1	110.5 (3)	C22—C21—H21	119.0
C17—N3—Ce1	113.6 (3)	C20—C21—H21	119.0

C31—N3—H3	107.1	C21—C22—C23	117.7 (8)
C17—N3—H3	107.1	C21—C22—H22	121.2
Ce1—N3—H3	107.1	C23—C22—H22	121.2
C32—N4—C24	111.9 (4)	C22—C23—C18	122.1 (7)
C32—N4—Ce1	112.8 (3)	C22—C23—H23	118.9
C24—N4—Ce1	114.9 (3)	C18—C23—H23	118.9
C32—N4—H4	105.4	N4—C24—C25	115.1 (4)
C24—N4—H4	105.4	N4—C24—H24A	108.5
Ce1—N4—H4	105.4	C25—C24—H24A	108.5
C3—O1—Ce1	143.7 (4)	N4—C24—H24B	108.5
C10—O2—Ce1	137.1 (4)	C25—C24—H24B	108.5
C19—O3—Ce1	135.0 (3)	H24A—C24—H24B	107.5
C26—O4—Ce1	143.9 (3)	C30—C25—C26	119.2 (6)
N1—C1—C2	111.5 (5)	C30—C25—C24	120.9 (5)
N1—C1—H1A	109.3	C26—C25—C24	119.7 (5)
C2—C1—H1A	109.3	O4—C26—C27	120.0 (5)
N1—C1—H1B	109.3	O4—C26—C25	121.5 (5)
C2—C1—H1B	109.3	C27—C26—C25	118.5 (5)
H1A—C1—H1B	108.0	C28—C27—C26	121.0 (6)
C3—C2—C7	118.2 (6)	C28—C27—H27	119.5
C3—C2—C1	120.9 (5)	C26—C27—H27	119.5
C7—C2—C1	120.9 (6)	C29—C28—C27	120.7 (7)
O1—C3—C4	121.5 (6)	C29—C28—H28	119.6
O1—C3—C2	118.6 (5)	C27—C28—H28	119.6
C4—C3—C2	119.8 (6)	C28—C29—C30	119.3 (6)
C3—C4—C5	119.6 (7)	C28—C29—H29	120.3
C3—C4—H4A	120.2	C30—C29—H29	120.3
C5—C4—H4A	120.2	C25—C30—C29	121.3 (6)
C6—C5—C4	122.9 (7)	C25—C30—H30	119.3
C6—C5—H5	118.6	C29—C30—H30	119.3
C4—C5—H5	118.6	N3—C31—C32	108.6 (5)
C7—C6—C5	117.4 (7)	N3—C31—H31A	110.0
C7—C6—H6	121.3	C32—C31—H31A	110.0
C5—C6—H6	121.3	N3—C31—H31B	110.0
C6—C7—C2	122.1 (6)	C32—C31—H31B	110.0
C6—C7—H7	118.9	H31A—C31—H31B	108.3
C2—C7—H7	118.9	N4—C32—C31	110.6 (4)
N2—C8—C9	111.3 (5)	N4—C32—H32A	109.5
N2—C8—H8A	109.4	C31—C32—H32A	109.5
C9—C8—H8A	109.4	N4—C32—H32B	109.5
N2—C8—H8B	109.4	C31—C32—H32B	109.5
C9—C8—H8B	109.4	H32A—C32—H32B	108.1
H8A—C8—H8B	108.0	Cl3—C33—Cl2	110.8 (4)
C14—C9—C10	119.4 (6)	Cl3—C33—Cl1	109.4 (4)
C14—C9—C8	121.7 (6)	Cl2—C33—Cl1	110.4 (4)
C10—C9—C8	118.9 (6)	Cl3—C33—H33	108.7
O2—C10—C11	121.6 (6)	Cl2—C33—H33	108.7
O2—C10—C9	120.2 (5)	Cl1—C33—H33	108.7
O4—Ce1—N1—C15	−64.5 (4)	N4—Ce1—O4—C26	16.1 (6)

O1—Ce1—N1—C15	−163.7 (4)	N3—Ce1—O4—C26	27.0 (7)
O2—Ce1—N1—C15	15.6 (5)	N2—Ce1—O4—C26	167.6 (6)
O3—Ce1—N1—C15	95.0 (4)	C15—N1—C1—C2	−159.3 (5)
N4—Ce1—N1—C15	−120.1 (4)	Ce1—N1—C1—C2	71.0 (5)
N3—Ce1—N1—C15	141.5 (4)	N1—C1—C2—C3	−54.8 (7)
N2—Ce1—N1—C15	10.7 (4)	N1—C1—C2—C7	126.2 (6)
O4—Ce1—N1—C1	63.7 (4)	Ce1—O1—C3—C4	−141.8 (5)
O1—Ce1—N1—C1	−35.5 (4)	Ce1—O1—C3—C2	38.4 (9)
O2—Ce1—N1—C1	143.8 (4)	C7—C2—C3—O1	−179.6 (5)
O3—Ce1—N1—C1	−136.8 (4)	C1—C2—C3—O1	1.4 (8)
N4—Ce1—N1—C1	8.1 (5)	C7—C2—C3—C4	0.6 (8)
N3—Ce1—N1—C1	−90.3 (4)	C1—C2—C3—C4	−178.4 (5)
N2—Ce1—N1—C1	138.9 (4)	O1—C3—C4—C5	−179.6 (5)
O4—Ce1—N2—C16	108.5 (4)	C2—C3—C4—C5	0.2 (9)
O1—Ce1—N2—C16	29.4 (5)	C3—C4—C5—C6	−1(1)
O2—Ce1—N2—C16	−155.2 (4)	C4—C5—C6—C7	1(1)
O3—Ce1—N2—C16	−55.5 (4)	C5—C6—C7—C2	0(1)
N1—Ce1—N2—C16	21.4 (4)	C3—C2—C7—C6	−0.6 (9)
N4—Ce1—N2—C16	148.9 (4)	C1—C2—C7—C6	178.5 (6)
N3—Ce1—N2—C16	−107.8 (4)	C16—N2—C8—C9	−163.6 (5)
O4—Ce1—N2—C8	−123.6 (4)	Ce1—N2—C8—C9	69.0 (6)
O1—Ce1—N2—C8	157.3 (3)	N2—C8—C9—C14	122.0 (6)
O2—Ce1—N2—C8	−27.3 (3)	N2—C8—C9—C10	−59.9 (7)
O3—Ce1—N2—C8	72.4 (4)	Ce1—O2—C10—C11	−129.1 (5)
N1—Ce1—N2—C8	149.3 (4)	Ce1—O2—C10—C9	51.5 (8)
N4—Ce1—N2—C8	−83.2 (4)	C14—C9—C10—O2	178.8 (5)
N3—Ce1—N2—C8	20.1 (4)	C8—C9—C10—O2	0.7 (9)
O4—Ce1—N3—C31	−32.3 (5)	C14—C9—C10—C11	−0.6 (9)
O1—Ce1—N3—C31	54.6 (4)	C8—C9—C10—C11	−178.7 (6)
O2—Ce1—N3—C31	−106.5 (4)	O2—C10—C11—C12	−179.4 (6)
O3—Ce1—N3—C31	153.1 (4)	C9—C10—C11—C12	0.0 (9)
N1—Ce1—N3—C31	106.6 (4)	C10—C11—C12—C13	0(1)
N4—Ce1—N3—C31	−21.1 (3)	C11—C12—C13—C14	0(1)
N2—Ce1—N3—C31	−153.1 (3)	C12—C13—C14—C9	0(1)
O4—Ce1—N3—C17	−158.1 (4)	C10—C9—C14—C13	1(1)
O1—Ce1—N3—C17	−71.2 (4)	C8—C9—C14—C13	179.0 (6)
O2—Ce1—N3—C17	127.7 (4)	C1—N1—C15—C16	−171.8 (5)
O3—Ce1—N3—C17	27.3 (4)	Ce1—N1—C15—C16	−41.6 (6)
N1—Ce1—N3—C17	−19.2 (5)	C8—N2—C16—C15	179.8 (5)
N4—Ce1—N3—C17	−146.9 (4)	Ce1—N2—C16—C15	−50.9 (6)
N2—Ce1—N3—C17	81.1 (4)	N1—C15—C16—N2	62.5 (6)
O4—Ce1—N4—C32	161.1 (4)	C31—N3—C17—C18	165.2 (5)
O1—Ce1—N4—C32	−97.0 (4)	Ce1—N3—C17—C18	−69.4 (6)
O2—Ce1—N4—C32	67.3 (4)	N3—C17—C18—C23	−121.0 (6)
O3—Ce1—N4—C32	−20.0 (5)	N3—C17—C18—C19	60.0 (7)
N1—Ce1—N4—C32	−140.3 (4)	Ce1—O3—C19—C20	131.1 (5)
N3—Ce1—N4—C32	−11.2 (4)	Ce1—O3—C19—C18	−51.5 (8)
N2—Ce1—N4—C32	120.7 (4)	C23—C18—C19—O3	−178.2 (5)
O4—Ce1—N4—C24	31.2 (4)	C17—C18—C19—O3	0.8 (8)

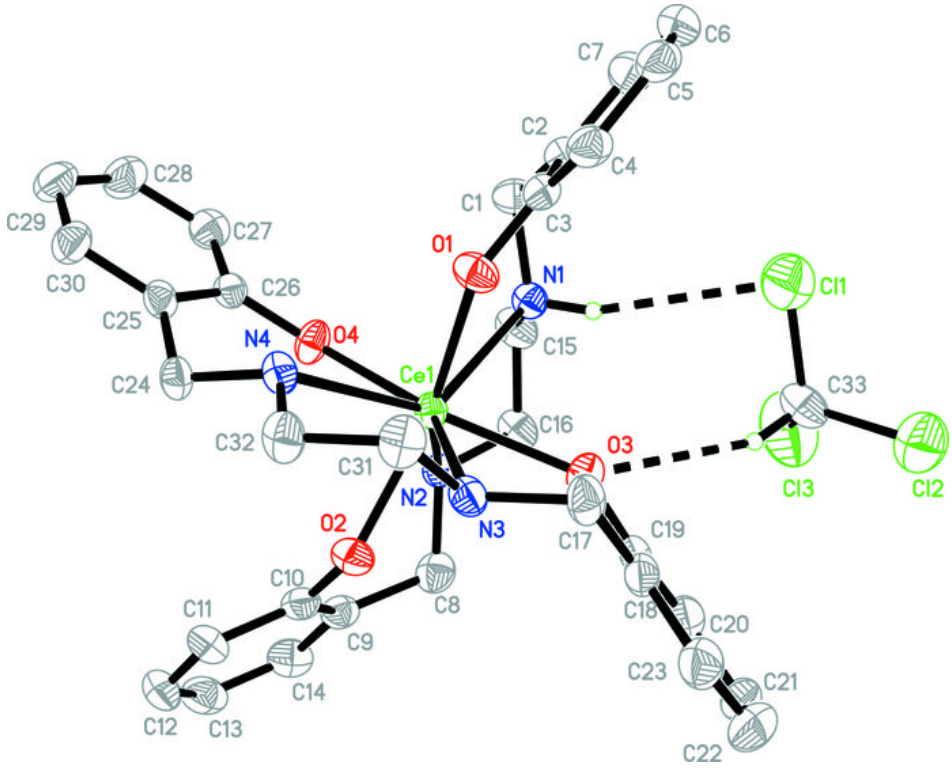
O1—Ce1—N4—C24	133.1 (4)	C23—C18—C19—C20	−0.7 (9)
O2—Ce1—N4—C24	−62.6 (4)	C17—C18—C19—C20	178.3 (5)
O3—Ce1—N4—C24	−149.9 (4)	O3—C19—C20—C21	177.7 (6)
N1—Ce1—N4—C24	89.8 (4)	C18—C19—C20—C21	0.2 (9)
N3—Ce1—N4—C24	−141.1 (4)	C19—C20—C21—C22	0(1)
N2—Ce1—N4—C24	−9.2 (5)	C20—C21—C22—C23	0(1)
O4—Ce1—O1—C3	−96.5 (6)	C21—C22—C23—C18	0(1)
O2—Ce1—O1—C3	162.6 (5)	C19—C18—C23—C22	1(1)
O3—Ce1—O1—C3	52.5 (6)	C17—C18—C23—C22	−178.0 (6)
N1—Ce1—O1—C3	−18.3 (6)	C32—N4—C24—C25	163.9 (5)
N4—Ce1—O1—C3	−166.2 (7)	Ce1—N4—C24—C25	−65.7 (6)
N3—Ce1—O1—C3	124.8 (6)	N4—C24—C25—C30	−131.3 (5)
N2—Ce1—O1—C3	−26.1 (7)	N4—C24—C25—C26	53.5 (7)
O4—Ce1—O2—C10	39.8 (5)	Ce1—O4—C26—C27	148.5 (5)
O1—Ce1—O2—C10	142.1 (5)	Ce1—O4—C26—C25	−32.8 (9)
O3—Ce1—O2—C10	−107.9 (5)	C30—C25—C26—O4	−179.3 (5)
N1—Ce1—O2—C10	−36.6 (6)	C24—C25—C26—O4	−4.0 (8)
N4—Ce1—O2—C10	111.9 (5)	C30—C25—C26—C27	−0.5 (8)
N3—Ce1—O2—C10	−179.5 (5)	C24—C25—C26—C27	174.7 (5)
N2—Ce1—O2—C10	−31.8 (5)	O4—C26—C27—C28	178.4 (6)
O4—Ce1—O3—C19	−142.9 (5)	C25—C26—C27—C28	−0.3 (9)
O1—Ce1—O3—C19	108.3 (6)	C26—C27—C28—C29	0(1)
O2—Ce1—O3—C19	−42.8 (6)	C27—C28—C29—C30	0(1)
N1—Ce1—O3—C19	177.5 (6)	C26—C25—C30—C29	1.3 (9)
N4—Ce1—O3—C19	39.0 (7)	C24—C25—C30—C29	−173.9 (6)
N3—Ce1—O3—C19	30.6 (6)	C28—C29—C30—C25	−1(1)
N2—Ce1—O3—C19	−113.9 (6)	C17—N3—C31—C32	177.8 (5)
O1—Ce1—O4—C26	−53.9 (6)	Ce1—N3—C31—C32	50.6 (6)
O2—Ce1—O4—C26	95.9 (6)	C24—N4—C32—C31	173.5 (5)
O3—Ce1—O4—C26	−162.6 (5)	Ce1—N4—C32—C31	42.1 (6)
N1—Ce1—O4—C26	−124.3 (6)	N3—C31—C32—N4	−63.2 (7)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.91	2.73	3.604 (5)	162
C33—H33···O3	0.98	2.51	3.437 (7)	157
N2—H2···Cl2^{i}	0.91	2.94	3.762 (5)	151
C4—H4A···Cl3^{ii}	0.93	2.79	3.646 (7)	153
C29—H29···Cg1^{iii}	0.93	2.85	3.626 (7)	142
C31—H31B···Cg2^{iv}	0.97	2.79	3.712 (6)	158

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

Fig. 1


C6
C7
C5
C2
C4
C28
C1
C3
C29
C27
O1
N1
Cl1
C30
C26
C25
N4
O4
C15
Ce1
C33
C24
C16
C32
O3
C31
Cl3
Cl2
N2
N3
O2
C19
C17
C10
C8
C18
C20
C11
C9
C23
C21
C14
C12
C13
C22