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Aquatris[1-(2,4-dioxo-2*H*-1-benzopyran-3-yl-idene)ethan-1-olato]ethanolgadolinium(III) ethanol monosolvate

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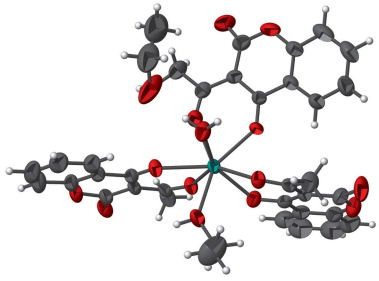
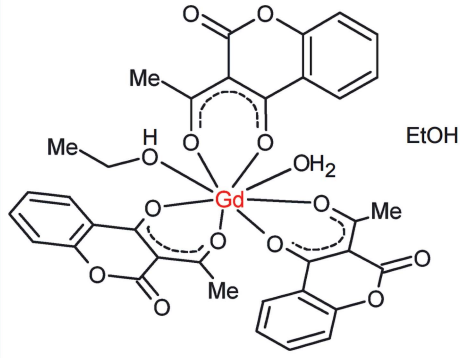
The title compound, $[Gd(C_{11}H_7O_4)_3(C_2H_5OH)(H_2O)]\cdot C_2H_5OH$, was crystallized from ethanol, affording a solvate. The main ligand in the complex results from deprotonation of the hydroxy group in 3-acetyl-4-hydroxycoumarin ($C_{11}H_8O_4$) and the resulting anionic ligands chelate the Gd^{III} centre. Three anions, one ethanol and one water molecule are bonded to the lanthanide, giving an eight-coordinate metal centre with a slightly distorted trigonal–prismatic square-face-bicapped coordination geometry. All water and ethanol molecules participate in an intricate three-dimensional framework of hydrogen bonds. The complex is isostructural to the Tb and Dy compounds reported previously [Guzmán-Méndez *et al.* (2018). *Inorg. Chem.* **57**, 908–911].

3D view



Chemical scheme



Structure description

We are currently probing the possibility of using a coumarin derivative, 3-acetyl-4-hydroxycoumarin, as an efficient luminescence sensitizer for lanthanide ions (Guzmán-Méndez *et al.*, 2018). Although the molecular structure of this coumarin derivative is very simple, with an essentially planar conformation (Traven *et al.*, 2000; Lyssenko & Antipin, 2001), weak intermolecular contacts in the solid state are known to promote polymorphism (Ghouili *et al.*, 2015). Such behaviour was previously studied in detail for a closely related system, 3-acetylcoumarin (Munshi *et al.*, 2004; Munshi & Guru Row, 2006). For our part, we determined that the coordination ability of 3-acetyl-4-hydroxycoumarin towards lanthanides is related to the chelating character of the acetyl and hydroxyl groups, once the hydroxyl group has been deprotonated. The same behaviour has been reported for this ligand with a transition metal (Co^{II}; Bejaoui *et al.*, 2018) and a

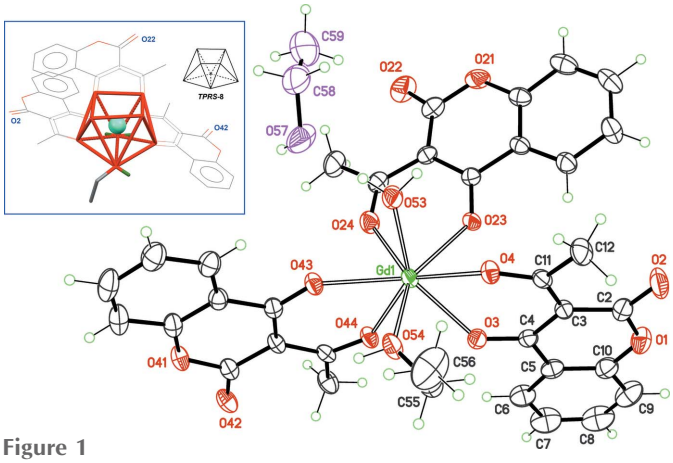


Figure 1
Structure of the title compound, with displacement ellipsoids for non-H atoms at the 30% probability level. The inset shows the Gd^{III} coordination polyhedron (red capped sticks), which is compared with the idealized TPRS-8 polyhedron (IUPAC, 2005).

main-group element (B; Manaev *et al.*, 2006). In the case of lanthanides, for which the coordination number is generally unpredictable, it is sometimes difficult to set up well-reproducible synthetic methods, especially when small coordinating molecules, such as water and alcohols, may be included in the coordination sphere. However, isotypic or partially isotypic series may be obtained along the lanthanide group. For example, compounds with reproducible formulae {[$LnL_3(H_2O)$(EtOH)]·EtOH}, where L is the anion obtained from 3-acetyl-4-hydroxycoumarin, can be crystallized in the space group $P2_1/c$ at least with Ln = Gd, Tb, Dy, Ho and Tm. The present report deals with the compound corresponding to Ln = Gd.

The complex crystallizes with one uncoordinated ethanol molecule (O57) per complex, with no disordered parts (Fig. 1). The neutral complex [$GdL_3(H_2O)$(EtOH)] is built up of an eight-coordinate Gd^{III} ion, which is a common coordination number for this metal. Three coumarin ligands chelate the metal, with Gd—O bond lengths in the range 2.330 (2)–2.401 (2) Å, the coordination sphere being completed with one water molecule [Gd1—O53: 2.379 (3) Å] and one ethanol molecule [Gd—O54: 2.417 (3) Å]. The set of eight O atoms around the lanthanide is arranged to form a trigonal–prismatic square-face-bicapped polyhedron, corresponding to the TPRS-8 polyhedral symbol in the IUPAC nomenclature (IUPAC, 2005). The chelating fragment, O3—C4—C3—C11—O4 (and equivalent groups in other L ligands) displays geometric parameters consistent with a negative charge fully delocalized over the chelate, giving a strongly stabilizing six-membered metallacycle. Two ligands L are almost coplanar, forming a dihedral angle of 9.87 (8)°, while the third ligand bisects this plane, with dihedral angles of 80.05 (6) and 82.60 (5)° (mean planes are calculated using 15 non-H atoms for each ligand L; see Fig. 1, inset). This arrangement is similar to that observed for the eight-coordinate [$LnL_3(H_2O)$(EtOH)] and [$LnL_3(H_2O)$(MeOH)] complexes previously reported (Guzmán-Méndez *et al.*, 2018).

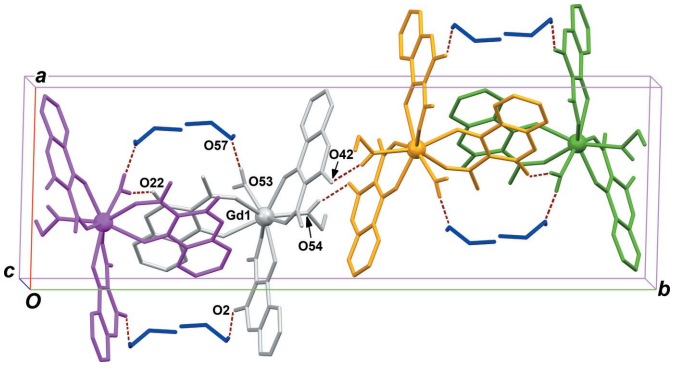


Figure 2
Part of the crystal structure of the title compound, showing the interactions between the lattice solvent (blue molecules) and the complexes, *via* hydrogen bonds (dashed lines). The colour scheme for the complexes indicates the symmetry operations in $P2_1/c$: grey: asymmetric unit; gold: inversion ($1-x$, $1-y$, $1-z$); green: screw axis ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$); magenta: glide plane (x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$).

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

D—H···A	D—H	H···A	D···A	D—H···A
O53—H53A···O22^{i}	0.84 (2)	2.01 (2)	2.840 (4)	169 (4)
O54—H54···O42^{ii}	0.85 (2)	1.95 (2)	2.768 (4)	163 (5)
O53—H53B···O57	0.84 (2)	1.80 (2)	2.634 (4)	173 (5)

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

Water and ethanol molecules participate in the building of a complex supramolecular structure based on O—H···O hydrogen bonds. The main feature is the formation of a one-dimensional frame along the [010] direction, in which molecules are connected using the non-coordinating carbonyl groups of two α-pyrone rings as acceptor to form bonds with coordinated water and ethanol molecules (Table 1, entries 1 and 2). The lattice ethanol molecule forms a third bond, with the coordinated water molecule (Table 1, entry 3). The resulting arrangement allows weak π–π interactions between coumarin ligands related by inversion, with a separation of 3.32 Å between the planes of these rings (Fig. 2).

Synthesis and crystallization

The synthesis was carried out using the methodology described in a previous publication (Guzmán-Méndez *et al.*, 2018). The title complex was synthesized by dissolving 0.75 mmol HL in 40 ml EtOH with 0.75 mmol of sodium methoxide. To this mixture, an ethanolic solution of 0.25 mmol of $Gd(NO_3)_3{\cdot}6H_2O$ was added dropwise. This mixture was allowed to react for 5 h at 333 K with vigorous stirring. After this time, the solvent was evaporated to 5 ml and water was added to precipitate the complex, which was then filtered and dried (yield: 89%). Colourless plate-shaped crystals were obtained from the slow evaporation of an ethanolic solution of the solid.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Gd(C_{11}H_7O_4)_3(C_2H_6O)(H_2O)]\cdot C_2H_6O$
M_r	876.90
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	250
a, b, c (Å)	11.5029 (3), 31.8022 (9), 10.8445 (3)
β (°)	113.840 (2)
V (Å^3)	3628.62 (18)
Z	4
Radiation type	Ag $K\alpha$, λ = 0.56083 Å
μ (mm^{-1})	1.02
Crystal size (mm)	0.50 × 0.30 × 0.06
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (*X-AREA*; Stoe & Cie, 2018)
T_{min}, T_{max}	0.583, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	45823, 7317, 5494
R_{int}	0.051
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.078, 1.01
No. of reflections	7317
No. of parameters	495
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, −0.65

Computer programs: *X-AREA* (Stoe & Cie, 2018), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *XP* in *SHELXTL-Plus* (Sheldrick, 2008),*Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2019). **4**, x190493 [https://doi.org/10.1107/S2414314619004930]

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Crystal data

$[Gd(C_{11}H_7O_4)_3(C_2H_6O)(H_2O)]\cdot C_2H_6O$
M_r = 876.90
Monoclinic, $P2_1/c$
a = 11.5029 (3) Å
b = 31.8022 (9) Å
c = 10.8445 (3) Å
β = 113.840 (2)°
V = 3628.62 (18) Å^3
Z = 4
$F(000)$ = 1764
D_x = 1.605 Mg m^{-3}
Ag $K\alpha$ radiation, λ = 0.56083 Å
Cell parameters from 36640 reflections
θ = 2.2–22.7°
μ = 1.02 mm^{-1}
T = 250 K
Plate, colourless
0.50 × 0.30 × 0.06 mm

Data collection

Stoe Stadivari diffractometer
Radiation source: Sealed X-ray tube, Axo Astix-f Microfocus source
Graded multilayer mirror monochromator
Detector resolution: 5.81 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (X-AREA; Stoe & Cie, 2018)
T_{min} = 0.583, T_{max} = 1.000
45823 measured reflections
7317 independent reflections
5494 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 20.5°, θ_{min} = 2.2°
h = −14→14
k = −39→39
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.078
S = 1.01
7317 reflections
495 parameters
6 restraints
0 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Special details

Refinement. H atoms bonded to C atoms were placed in idealized positions and refined as riding to their parent atoms, while remaining H atoms, for water and ethanol molecules, were placed using difference maps and refined with free coordinates. All O—H bond lengths were restrained to a distance target of 0.85 (2) Å, while H—O53—H angle for the water molecule was restrained with a target H···H = 1.34 (4) Å. Isotropic displacement parameters were calculated for all H atoms, as $U_{iso} = xU_{eq}$(carrier atom) where $x = 1.2$ or $x = 1.5$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Gd1	0.32396 (2)	0.38332 (2)	0.65440 (2)	0.03530 (7)
O1	−0.2286 (2)	0.36089 (11)	0.5373 (3)	0.0632 (8)
O2	−0.1432 (3)	0.34226 (12)	0.7479 (3)	0.0754 (10)
O3	0.1096 (2)	0.40002 (9)	0.5385 (2)	0.0458 (6)
O4	0.2153 (2)	0.38175 (9)	0.8025 (2)	0.0425 (6)
C2	−0.1229 (4)	0.35819 (15)	0.6576 (4)	0.0510 (10)
C3	−0.0025 (3)	0.37320 (12)	0.6643 (4)	0.0382 (9)
C4	0.0079 (3)	0.38814 (12)	0.5459 (4)	0.0380 (8)
C5	−0.1081 (4)	0.39009 (13)	0.4215 (4)	0.0463 (10)
C6	−0.1080 (4)	0.40423 (16)	0.3008 (4)	0.0605 (12)
H6	−0.031918	0.413900	0.297964	0.073*
C7	−0.2187 (6)	0.4043 (2)	0.1843 (5)	0.0825 (16)
H7	−0.218139	0.414098	0.102814	0.099*
C8	−0.3302 (6)	0.38977 (19)	0.1892 (6)	0.0872 (18)
H8	−0.405035	0.389533	0.109828	0.105*
C9	−0.3339 (4)	0.37599 (18)	0.3048 (6)	0.0756 (16)
H9	−0.410644	0.366535	0.306605	0.091*
C10	−0.2212 (4)	0.37593 (14)	0.4230 (5)	0.0543 (11)
C11	0.1068 (3)	0.37340 (12)	0.7928 (4)	0.0386 (9)
C12	0.0962 (4)	0.36405 (16)	0.9238 (4)	0.0558 (11)
H12A	0.026852	0.380229	0.929070	0.084*
H12B	0.174997	0.371584	0.998382	0.084*
H12C	0.079830	0.334292	0.928425	0.084*
O21	0.3255 (3)	0.19355 (9)	0.6550 (3)	0.0593 (8)
O22	0.4516 (3)	0.20264 (11)	0.5523 (4)	0.0754 (10)
O23	0.2292 (2)	0.31735 (8)	0.6307 (3)	0.0427 (6)
O24	0.4223 (2)	0.33318 (10)	0.5646 (3)	0.0505 (7)
C22	0.3833 (4)	0.22069 (15)	0.5968 (4)	0.0528 (11)
C23	0.3607 (3)	0.26510 (13)	0.5977 (4)	0.0397 (9)
C24	0.2634 (3)	0.27989 (12)	0.6364 (3)	0.0366 (8)
C25	0.1987 (3)	0.24889 (12)	0.6863 (4)	0.0397 (9)
C26	0.1059 (4)	0.26070 (14)	0.7297 (4)	0.0517 (10)
H26	0.078409	0.288814	0.720969	0.062*
C27	0.0533 (4)	0.23141 (16)	0.7858 (5)	0.0635 (12)
H27	−0.009484	0.239634	0.815633	0.076*
C28	0.0922 (4)	0.19063 (16)	0.7982 (4)	0.0635 (13)
H28	0.055881	0.170878	0.836663	0.076*
C29	0.1837 (4)	0.17797 (15)	0.7553 (4)	0.0624 (12)

H29	0.210647	0.149802	0.764178	0.075*
C30	0.2355 (4)	0.20766 (13)	0.6984 (4)	0.0467 (9)
C31	0.4325 (3)	0.29467 (15)	0.5552 (4)	0.0461 (10)
C32	0.5275 (4)	0.28046 (17)	0.4999 (5)	0.0718 (14)
H32A	0.484305	0.264046	0.418714	0.108*
H32B	0.592455	0.263356	0.566673	0.108*
H32C	0.566722	0.304861	0.478848	0.108*
O41	0.6855 (2)	0.47924 (9)	0.4682 (3)	0.0523 (7)
O42	0.5149 (3)	0.48143 (10)	0.2835 (3)	0.0562 (7)
O43	0.5179 (2)	0.41424 (9)	0.6765 (2)	0.0425 (6)
O44	0.3049 (2)	0.41309 (9)	0.4466 (2)	0.0431 (6)
C42	0.5606 (3)	0.46792 (13)	0.3981 (4)	0.0440 (9)
C43	0.4987 (3)	0.44347 (12)	0.4673 (4)	0.0379 (8)
C44	0.5643 (3)	0.43375 (12)	0.6066 (4)	0.0390 (9)
C45	0.6956 (3)	0.44855 (13)	0.6745 (4)	0.0427 (9)
C46	0.7656 (4)	0.44179 (15)	0.8114 (4)	0.0522 (11)
H46	0.729631	0.426631	0.861698	0.063*
C47	0.8878 (4)	0.45728 (17)	0.8737 (5)	0.0654 (13)
H47	0.935060	0.452972	0.966420	0.079*
C48	0.9401 (4)	0.47921 (18)	0.7982 (5)	0.0711 (15)
H48	1.023669	0.489430	0.840589	0.085*
C49	0.8725 (4)	0.48642 (16)	0.6625 (5)	0.0660 (14)
H49	0.908613	0.501611	0.612360	0.079*
C50	0.7510 (3)	0.47080 (13)	0.6023 (4)	0.0471 (10)
C51	0.3681 (3)	0.43018 (12)	0.3907 (4)	0.0386 (8)
C52	0.3027 (4)	0.43506 (15)	0.2412 (4)	0.0551 (11)
H52A	0.351072	0.420692	0.198569	0.083*
H52B	0.296218	0.464690	0.218116	0.083*
H52C	0.218156	0.422977	0.209851	0.083*
O53	0.4721 (2)	0.35409 (11)	0.8598 (3)	0.0536 (8)
H53A	0.455 (4)	0.3378 (13)	0.911 (4)	0.080*
H53B	0.546 (2)	0.3478 (16)	0.871 (4)	0.080*
O54	0.3384 (3)	0.45345 (9)	0.7454 (3)	0.0535 (7)
H54	0.396 (4)	0.4704 (13)	0.748 (5)	0.080*
C55	0.2554 (4)	0.47760 (16)	0.7856 (5)	0.0677 (13)
H55A	0.174962	0.462504	0.761659	0.081*
H55B	0.237102	0.504482	0.737301	0.081*
C56	0.3133 (6)	0.4856 (2)	0.9332 (5)	0.111 (2)
H56A	0.254230	0.501409	0.958542	0.167*
H56B	0.391127	0.501553	0.956454	0.167*
H56C	0.332276	0.458980	0.981096	0.167*
O57	0.6984 (4)	0.33100 (18)	0.8778 (5)	0.124 (2)
H57	0.714 (6)	0.333 (2)	0.808 (4)	0.187*
C58	0.7719 (6)	0.2997 (3)	0.9692 (7)	0.109 (2)
H58A	0.740236	0.296023	1.039971	0.131*
H58B	0.860265	0.309275	1.012364	0.131*
C59	0.7684 (7)	0.2592 (3)	0.9043 (9)	0.140 (3)
H59A	0.810851	0.238156	0.972477	0.210*

H59B	0.811209	0.261618	0.843785	0.210*
H59C	0.680693	0.250905	0.853506	0.210*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Gd1	0.03853 (10)	0.03460 (12)	0.03740 (11)	−0.00399 (9)	0.02013 (8)	0.00337 (9)
O1	0.0395 (15)	0.079 (3)	0.069 (2)	−0.0063 (15)	0.0202 (15)	−0.0025 (18)
O2	0.0566 (17)	0.105 (3)	0.076 (2)	−0.0144 (18)	0.0388 (16)	0.020 (2)
O3	0.0389 (13)	0.0559 (18)	0.0441 (15)	0.0055 (12)	0.0184 (12)	0.0157 (13)
O4	0.0419 (13)	0.0498 (18)	0.0401 (14)	−0.0059 (12)	0.0210 (11)	−0.0001 (12)
C2	0.043 (2)	0.057 (3)	0.056 (3)	0.004 (2)	0.024 (2)	0.003 (2)
C3	0.0394 (19)	0.034 (2)	0.045 (2)	0.0002 (15)	0.0215 (17)	0.0014 (17)
C4	0.0397 (19)	0.034 (2)	0.042 (2)	0.0045 (16)	0.0173 (16)	0.0016 (17)
C5	0.050 (2)	0.043 (3)	0.042 (2)	0.0073 (18)	0.0147 (18)	−0.0044 (18)
C6	0.064 (3)	0.066 (3)	0.043 (2)	0.009 (2)	0.013 (2)	0.003 (2)
C7	0.091 (4)	0.093 (5)	0.045 (3)	0.012 (3)	0.008 (3)	0.003 (3)
C8	0.081 (4)	0.085 (5)	0.061 (3)	0.010 (3)	−0.008 (3)	−0.013 (3)
C9	0.053 (3)	0.079 (4)	0.075 (4)	0.005 (3)	0.005 (3)	−0.022 (3)
C10	0.047 (2)	0.049 (3)	0.060 (3)	0.0019 (19)	0.014 (2)	−0.004 (2)
C11	0.048 (2)	0.032 (2)	0.043 (2)	0.0011 (16)	0.0259 (18)	0.0041 (16)
C12	0.061 (2)	0.072 (3)	0.044 (2)	−0.002 (2)	0.032 (2)	0.005 (2)
O21	0.0678 (18)	0.0345 (17)	0.072 (2)	0.0106 (15)	0.0253 (16)	−0.0012 (15)
O22	0.078 (2)	0.059 (2)	0.098 (2)	0.0106 (17)	0.0451 (19)	−0.0266 (19)
O23	0.0464 (14)	0.0250 (15)	0.0651 (17)	0.0008 (11)	0.0313 (13)	0.0029 (13)
O24	0.0552 (16)	0.049 (2)	0.0597 (17)	−0.0022 (14)	0.0361 (14)	−0.0020 (15)
C22	0.049 (2)	0.052 (3)	0.052 (2)	0.005 (2)	0.014 (2)	−0.011 (2)
C23	0.0400 (19)	0.038 (2)	0.039 (2)	0.0050 (17)	0.0143 (16)	−0.0045 (18)
C24	0.0380 (19)	0.033 (2)	0.036 (2)	−0.0010 (16)	0.0121 (15)	−0.0030 (17)
C25	0.044 (2)	0.034 (2)	0.037 (2)	−0.0042 (17)	0.0114 (16)	0.0013 (17)
C26	0.057 (2)	0.039 (3)	0.066 (3)	−0.003 (2)	0.032 (2)	0.002 (2)
C27	0.072 (3)	0.059 (3)	0.071 (3)	−0.014 (2)	0.042 (3)	0.000 (3)
C28	0.080 (3)	0.055 (3)	0.051 (3)	−0.024 (3)	0.022 (2)	0.006 (2)
C29	0.082 (3)	0.041 (3)	0.051 (3)	−0.009 (2)	0.013 (2)	0.002 (2)
C30	0.054 (2)	0.037 (3)	0.042 (2)	−0.0026 (19)	0.0122 (19)	−0.0013 (19)
C31	0.046 (2)	0.055 (3)	0.040 (2)	0.005 (2)	0.0202 (17)	−0.002 (2)
C32	0.070 (3)	0.077 (4)	0.090 (4)	0.010 (3)	0.055 (3)	−0.007 (3)
O41	0.0537 (16)	0.056 (2)	0.0558 (17)	−0.0166 (14)	0.0316 (14)	−0.0005 (14)
O42	0.0722 (18)	0.054 (2)	0.0529 (17)	−0.0137 (15)	0.0360 (15)	0.0057 (15)
O43	0.0412 (13)	0.0496 (18)	0.0381 (13)	−0.0098 (12)	0.0174 (11)	0.0044 (12)
O44	0.0465 (14)	0.0486 (18)	0.0377 (13)	−0.0094 (12)	0.0204 (11)	0.0069 (12)
C42	0.050 (2)	0.040 (2)	0.048 (2)	−0.0084 (18)	0.0268 (19)	−0.0050 (19)
C43	0.048 (2)	0.034 (2)	0.040 (2)	−0.0084 (17)	0.0252 (17)	−0.0029 (17)
C44	0.0405 (19)	0.037 (2)	0.044 (2)	−0.0041 (16)	0.0218 (17)	−0.0056 (18)
C45	0.041 (2)	0.041 (2)	0.048 (2)	−0.0049 (17)	0.0204 (18)	−0.0072 (18)
C46	0.046 (2)	0.057 (3)	0.051 (2)	−0.005 (2)	0.0170 (19)	−0.010 (2)
C47	0.052 (3)	0.070 (4)	0.068 (3)	−0.004 (2)	0.018 (2)	−0.015 (3)
C48	0.044 (2)	0.082 (4)	0.086 (4)	−0.018 (2)	0.024 (3)	−0.032 (3)

C49	0.053 (3)	0.073 (4)	0.081 (4)	−0.022 (2)	0.036 (3)	−0.021 (3)
C50	0.044 (2)	0.046 (3)	0.057 (3)	−0.0099 (19)	0.026 (2)	−0.012 (2)
C51	0.051 (2)	0.030 (2)	0.040 (2)	−0.0043 (17)	0.0236 (17)	0.0020 (17)
C52	0.066 (3)	0.061 (3)	0.039 (2)	−0.017 (2)	0.0212 (19)	0.002 (2)
O53	0.0438 (14)	0.072 (2)	0.0475 (16)	0.0016 (15)	0.0204 (13)	0.0185 (15)
O54	0.0657 (18)	0.0407 (18)	0.0727 (19)	−0.0148 (14)	0.0471 (16)	−0.0094 (15)
C55	0.077 (3)	0.058 (3)	0.084 (3)	−0.006 (3)	0.049 (3)	−0.006 (3)
C56	0.106 (4)	0.171 (8)	0.068 (4)	0.024 (4)	0.047 (3)	−0.016 (4)
O57	0.082 (2)	0.199 (6)	0.125 (3)	0.064 (3)	0.074 (2)	0.100 (4)
C58	0.069 (4)	0.154 (8)	0.101 (5)	0.013 (4)	0.030 (3)	0.055 (5)
C59	0.129 (6)	0.151 (9)	0.183 (9)	0.016 (6)	0.108 (6)	0.051 (7)

Geometric parameters (Å, º)

Gd1—O23	2.330 (2)	C29—C30	1.387 (6)
Gd1—O3	2.331 (2)	C29—H29	0.9400
Gd1—O43	2.360 (2)	C31—C32	1.513 (5)
Gd1—O44	2.372 (2)	C32—H32A	0.9700
Gd1—O53	2.379 (3)	C32—H32B	0.9700
Gd1—O24	2.380 (3)	C32—H32C	0.9700
Gd1—O4	2.401 (2)	O41—C50	1.367 (5)
Gd1—O54	2.417 (3)	O41—C42	1.374 (4)
O1—C10	1.363 (5)	O42—C42	1.215 (4)
O1—C2	1.381 (5)	O43—C44	1.254 (4)
O2—C2	1.206 (5)	O44—C51	1.244 (4)
O3—C4	1.262 (4)	C42—C43	1.451 (5)
O4—C11	1.238 (4)	C43—C44	1.423 (5)
C2—C3	1.438 (5)	C43—C51	1.455 (5)
C3—C4	1.419 (5)	C44—C45	1.465 (5)
C3—C11	1.451 (5)	C45—C50	1.387 (5)
C4—C5	1.466 (5)	C45—C46	1.390 (5)
C5—C10	1.383 (6)	C46—C47	1.382 (6)
C5—C6	1.384 (6)	C46—H46	0.9400
C6—C7	1.385 (6)	C47—C48	1.384 (7)
C6—H6	0.9400	C47—H47	0.9400
C7—C8	1.384 (8)	C48—C49	1.378 (7)
C7—H7	0.9400	C48—H48	0.9400
C8—C9	1.345 (8)	C49—C50	1.375 (6)
C8—H8	0.9400	C49—H49	0.9400
C9—C10	1.407 (6)	C51—C52	1.494 (5)
C9—H9	0.9400	C52—H52A	0.9700
C11—C12	1.504 (5)	C52—H52B	0.9700
C12—H12A	0.9700	C52—H52C	0.9700
C12—H12B	0.9700	O53—H53A	0.840 (19)
C12—H12C	0.9700	O53—H53B	0.835 (19)
O21—C30	1.375 (5)	O54—C55	1.424 (5)
O21—C22	1.388 (5)	O54—H54	0.847 (19)
O22—C22	1.219 (5)	C55—C56	1.486 (7)

O23—C24	1.248 (4)	C55—H55A	0.9800
O24—C31	1.238 (5)	C55—H55B	0.9800
C22—C23	1.437 (6)	C56—H56A	0.9700
C23—C24	1.426 (5)	C56—H56B	0.9700
C23—C31	1.444 (5)	C56—H56C	0.9700
C24—C25	1.464 (5)	O57—C58	1.419 (7)
C25—C30	1.368 (5)	O57—H57	0.84 (2)
C25—C26	1.382 (5)	C58—C59	1.461 (10)
C26—C27	1.378 (6)	C58—H58A	0.9800
C26—H26	0.9400	C58—H58B	0.9800
C27—C28	1.361 (7)	C59—H59A	0.9700
C27—H27	0.9400	C59—H59B	0.9700
C28—C29	1.372 (7)	C59—H59C	0.9700
C28—H28	0.9400		

O23—Gd1—O3	78.45 (9)	C27—C28—C29	120.8 (4)
O23—Gd1—O43	140.12 (9)	C27—C28—H28	119.6
O3—Gd1—O43	135.25 (9)	C29—C28—H28	119.6
O23—Gd1—O44	113.27 (9)	C28—C29—C30	118.5 (5)
O3—Gd1—O44	74.08 (8)	C28—C29—H29	120.7
O43—Gd1—O44	69.55 (8)	C30—C29—H29	120.7
O23—Gd1—O53	82.98 (10)	C25—C30—O21	121.8 (4)
O3—Gd1—O53	142.64 (8)	C25—C30—C29	121.6 (4)
O43—Gd1—O53	77.15 (9)	O21—C30—C29	116.6 (4)
O44—Gd1—O53	143.28 (8)	O24—C31—C23	122.2 (3)
O23—Gd1—O24	68.30 (8)	O24—C31—C32	115.8 (4)
O3—Gd1—O24	120.42 (10)	C23—C31—C32	122.0 (4)
O43—Gd1—O24	74.59 (9)	C31—C32—H32A	109.5
O44—Gd1—O24	75.82 (9)	C31—C32—H32B	109.5
O53—Gd1—O24	80.92 (10)	H32A—C32—H32B	109.5
O23—Gd1—O4	73.04 (9)	C31—C32—H32C	109.5
O3—Gd1—O4	69.03 (8)	H32A—C32—H32C	109.5
O43—Gd1—O4	131.84 (8)	H32B—C32—H32C	109.5
O44—Gd1—O4	140.41 (9)	C50—O41—C42	122.7 (3)
O53—Gd1—O4	74.66 (8)	C44—O43—Gd1	139.5 (2)
O24—Gd1—O4	136.22 (9)	C51—O44—Gd1	142.2 (2)
O23—Gd1—O54	145.86 (8)	O42—C42—O41	113.4 (3)
O3—Gd1—O54	83.85 (10)	O42—C42—C43	128.2 (3)
O43—Gd1—O54	70.61 (9)	O41—C42—C43	118.4 (3)
O44—Gd1—O54	89.10 (9)	C44—C43—C42	120.3 (3)
O53—Gd1—O54	94.21 (11)	C44—C43—C51	121.7 (3)
O24—Gd1—O54	145.06 (8)	C42—C43—C51	118.0 (3)
O4—Gd1—O54	73.42 (9)	O43—C44—C43	125.2 (3)
C10—O1—C2	121.8 (3)	O43—C44—C45	117.3 (3)
C4—O3—Gd1	134.7 (2)	C43—C44—C45	117.4 (3)
C11—O4—Gd1	136.6 (2)	C50—C45—C46	118.8 (3)
O2—C2—O1	114.1 (3)	C50—C45—C44	119.7 (3)
O2—C2—C3	126.6 (4)	C46—C45—C44	121.4 (3)

O1—C2—C3	119.3 (3)	C47—C46—C45	120.2 (4)
C4—C3—C2	119.8 (3)	C47—C46—H46	119.9
C4—C3—C11	120.6 (3)	C45—C46—H46	119.9
C2—C3—C11	119.5 (3)	C46—C47—C48	119.4 (4)
O3—C4—C3	125.2 (3)	C46—C47—H47	120.3
O3—C4—C5	116.8 (3)	C48—C47—H47	120.3
C3—C4—C5	117.9 (3)	C49—C48—C47	121.5 (4)
C10—C5—C6	118.5 (4)	C49—C48—H48	119.2
C10—C5—C4	119.1 (4)	C47—C48—H48	119.2
C6—C5—C4	122.4 (4)	C50—C49—C48	118.3 (4)
C5—C6—C7	120.7 (5)	C50—C49—H49	120.9
C5—C6—H6	119.6	C48—C49—H49	120.9
C7—C6—H6	119.6	O41—C50—C49	116.9 (4)
C8—C7—C6	119.3 (5)	O41—C50—C45	121.3 (3)
C8—C7—H7	120.4	C49—C50—C45	121.8 (4)
C6—C7—H7	120.4	O44—C51—C43	121.4 (3)
C9—C8—C7	121.6 (5)	O44—C51—C52	115.9 (3)
C9—C8—H8	119.2	C43—C51—C52	122.7 (3)
C7—C8—H8	119.2	C51—C52—H52A	109.5
C8—C9—C10	119.0 (5)	C51—C52—H52B	109.5
C8—C9—H9	120.5	H52A—C52—H52B	109.5
C10—C9—H9	120.5	C51—C52—H52C	109.5
O1—C10—C5	122.0 (4)	H52A—C52—H52C	109.5
O1—C10—C9	117.1 (4)	H52B—C52—H52C	109.5
C5—C10—C9	120.9 (5)	Gd1—O53—H53A	126 (3)
O4—C11—C3	122.3 (3)	Gd1—O53—H53B	122 (3)
O4—C11—C12	115.2 (3)	H53A—O53—H53B	104 (3)
C3—C11—C12	122.4 (3)	C55—O54—Gd1	132.7 (2)
C11—C12—H12A	109.5	C55—O54—H54	105 (3)
C11—C12—H12B	109.5	Gd1—O54—H54	122 (3)
H12A—C12—H12B	109.5	O54—C55—C56	111.0 (4)
C11—C12—H12C	109.5	O54—C55—H55A	109.4
H12A—C12—H12C	109.5	C56—C55—H55A	109.4
H12B—C12—H12C	109.5	O54—C55—H55B	109.4
C30—O21—C22	121.2 (3)	C56—C55—H55B	109.4
C24—O23—Gd1	136.9 (2)	H55A—C55—H55B	108.0
C31—O24—Gd1	140.6 (2)	C55—C56—H56A	109.5
O22—C22—O21	113.0 (4)	C55—C56—H56B	109.5
O22—C22—C23	127.8 (4)	H56A—C56—H56B	109.5
O21—C22—C23	119.2 (3)	C55—C56—H56C	109.5
C24—C23—C22	119.5 (3)	H56A—C56—H56C	109.5
C24—C23—C31	119.8 (3)	H56B—C56—H56C	109.5
C22—C23—C31	120.6 (3)	C58—O57—H57	113 (4)
O23—C24—C23	124.7 (3)	O57—C58—C59	112.9 (7)
O23—C24—C25	117.6 (3)	O57—C58—H58A	109.0
C23—C24—C25	117.6 (3)	C59—C58—H58A	109.0
C30—C25—C26	118.7 (4)	O57—C58—H58B	109.0
C30—C25—C24	119.8 (3)	C59—C58—H58B	109.0

C26—C25—C24	121.4 (4)	H58A—C58—H58B	107.8
C27—C26—C25	120.2 (4)	C58—C59—H59A	109.5
C27—C26—H26	119.9	C58—C59—H59B	109.5
C25—C26—H26	119.9	H59A—C59—H59B	109.5
C28—C27—C26	120.2 (4)	C58—C59—H59C	109.5
C28—C27—H27	119.9	H59A—C59—H59C	109.5
C26—C27—H27	119.9	H59B—C59—H59C	109.5

C10—O1—C2—O2	−176.4 (4)	C25—C26—C27—C28	−0.3 (7)
C10—O1—C2—C3	2.6 (6)	C26—C27—C28—C29	−0.1 (7)
O2—C2—C3—C4	174.9 (4)	C27—C28—C29—C30	−0.2 (7)
O1—C2—C3—C4	−3.9 (6)	C26—C25—C30—O21	178.7 (4)
O2—C2—C3—C11	−5.9 (7)	C24—C25—C30—O21	−5.2 (6)
O1—C2—C3—C11	175.3 (4)	C26—C25—C30—C29	−1.3 (6)
Gd1—O3—C4—C3	28.2 (6)	C24—C25—C30—C29	174.8 (4)
Gd1—O3—C4—C5	−151.8 (3)	C22—O21—C30—C25	0.0 (5)
C2—C3—C4—O3	−176.2 (4)	C22—O21—C30—C29	−179.9 (4)
C11—C3—C4—O3	4.5 (6)	C28—C29—C30—C25	0.9 (6)
C2—C3—C4—C5	3.8 (5)	C28—C29—C30—O21	−179.1 (4)
C11—C3—C4—C5	−175.4 (3)	Gd1—O24—C31—C23	6.9 (7)
O3—C4—C5—C10	177.6 (4)	Gd1—O24—C31—C32	−171.6 (3)
C3—C4—C5—C10	−2.5 (5)	C24—C23—C31—O24	7.9 (6)
O3—C4—C5—C6	−0.1 (6)	C22—C23—C31—O24	−174.3 (4)
C3—C4—C5—C6	179.9 (4)	C24—C23—C31—C32	−173.8 (4)
C10—C5—C6—C7	0.2 (7)	C22—C23—C31—C32	4.0 (6)
C4—C5—C6—C7	177.8 (5)	C50—O41—C42—O42	173.5 (4)
C5—C6—C7—C8	−0.4 (8)	C50—O41—C42—C43	−4.4 (5)
C6—C7—C8—C9	0.7 (9)	O42—C42—C43—C44	−173.9 (4)
C7—C8—C9—C10	−0.8 (9)	O41—C42—C43—C44	3.6 (5)
C2—O1—C10—C5	−1.3 (6)	O42—C42—C43—C51	4.9 (6)
C2—O1—C10—C9	177.9 (4)	O41—C42—C43—C51	−177.5 (3)
C6—C5—C10—O1	178.9 (4)	Gd1—O43—C44—C43	−1.5 (6)
C4—C5—C10—O1	1.2 (6)	Gd1—O43—C44—C45	177.1 (3)
C6—C5—C10—C9	−0.2 (6)	C42—C43—C44—O43	177.3 (4)
C4—C5—C10—C9	−177.9 (4)	C51—C43—C44—O43	−1.5 (6)
C8—C9—C10—O1	−178.6 (5)	C42—C43—C44—C45	−1.3 (5)
C8—C9—C10—C5	0.5 (7)	C51—C43—C44—C45	179.9 (3)
Gd1—O4—C11—C3	−19.3 (6)	O43—C44—C45—C50	−179.1 (4)
Gd1—O4—C11—C12	161.5 (3)	C43—C44—C45—C50	−0.5 (5)
C4—C3—C11—O4	−8.5 (6)	O43—C44—C45—C46	−0.9 (6)
C2—C3—C11—O4	172.3 (4)	C43—C44—C45—C46	177.8 (4)
C4—C3—C11—C12	170.7 (4)	C50—C45—C46—C47	0.4 (6)
C2—C3—C11—C12	−8.6 (6)	C44—C45—C46—C47	−177.9 (4)
C30—O21—C22—O22	−173.4 (4)	C45—C46—C47—C48	−0.6 (7)
C30—O21—C22—C23	8.0 (5)	C46—C47—C48—C49	0.8 (8)
O22—C22—C23—C24	170.9 (4)	C47—C48—C49—C50	−0.7 (8)
O21—C22—C23—C24	−10.8 (5)	C42—O41—C50—C49	−175.6 (4)
O22—C22—C23—C31	−6.9 (6)	C42—O41—C50—C45	2.7 (6)

O21—C22—C23—C31	171.4 (3)	C48—C49—C50—O41	178.6 (4)
Gd1—O23—C24—C23	−32.4 (6)	C48—C49—C50—C45	0.4 (7)
Gd1—O23—C24—C25	147.7 (3)	C46—C45—C50—O41	−178.4 (4)
C22—C23—C24—O23	−174.1 (3)	C44—C45—C50—O41	−0.1 (6)
C31—C23—C24—O23	3.7 (6)	C46—C45—C50—C49	−0.3 (6)
C22—C23—C24—C25	5.8 (5)	C44—C45—C50—C49	178.0 (4)
C31—C23—C24—C25	−176.4 (3)	Gd1—O44—C51—C43	−10.3 (6)
O23—C24—C25—C30	−178.0 (3)	Gd1—O44—C51—C52	168.2 (3)
C23—C24—C25—C30	2.1 (5)	C44—C43—C51—O44	6.5 (6)
O23—C24—C25—C26	−2.0 (5)	C42—C43—C51—O44	−172.3 (3)
C23—C24—C25—C26	178.1 (4)	C44—C43—C51—C52	−171.9 (4)
C30—C25—C26—C27	1.0 (6)	C42—C43—C51—C52	9.3 (5)
C24—C25—C26—C27	−175.0 (4)	Gd1—O54—C55—C56	114.2 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O53—H53*A*···O22^{i}	0.84 (2)	2.01 (2)	2.840 (4)	169 (4)
O54—H54···O42^{ii}	0.85 (2)	1.95 (2)	2.768 (4)	163 (5)
O53—H53*B*···O57	0.84 (2)	1.80 (2)	2.634 (4)	173 (5)
O57—H57···O2^{iii}	0.84 (2)	2.02 (5)	2.740 (4)	143 (7)

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