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(*E*)-4-[4-(Dimethylamino)styryl]-1-methylpyridin-1-ium tetrakis[(*Z*)-4,4,4-trifluoro-3-oxo-1-(thiophen-2-yl)but-1-en-1-olato]gadolinate(III) with an unknown amount of water as solvate

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Keywords: crystal structure; Gd^{III} complex anion; 4-[4-(dimethylamino)styryl]-1-methylpyridin-1-ium cation; weak C—H···F interaction.

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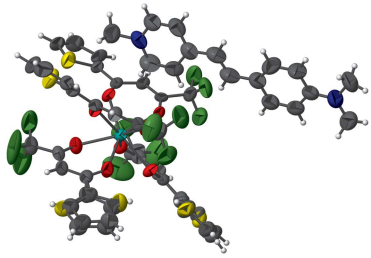
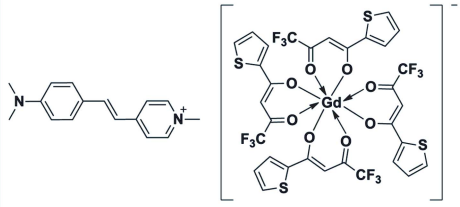
Structural data: full structural data are available from iucrdata.iucr.org

In the complex anion of the title salt, $(C_{16}H_{19}N_2)[Gd(C_8H_4F_3S)_4]$, the Ga^{III} cation is *O*,*O*′-chelated by four anionic 4,4,4-trifluoro-3-oxo-1-(thiophen-2-yl)but-1-en-1-olate ligands in a distorted square-antiprismatic geometry; the 4-[4-(dimethylamino)styryl]-1-methylpyridin-1-ium cation is nearly planar, with a dihedral angle of 9.6 (5)° between the planes of the pyridine and benzene rings. In the crystal, the cations are linked with the complex anions *via* weak C—H···F and C—H···π interactions. Two of the four independent thiophene rings are disordered over two sites; occupancies were refined to 0.662 (10):0.338 (10). The solvent water molecules are highly disordered in a solvent-accessible void of 54 (3) Å^3; the diffuse electron densities were removed from the data set using SQUEEZE [Spek (2015). *Acta Cryst.* C**71**, 9–16]. These solvent molecules are not considered in the given chemical formula and other crystal data.

3D view



Chemical scheme



Structure description

In recent decades, the construction of lanthanide-based metal–organic complexes has attracted widespread attention due to their essential photophysical properties which have potential applications in luminescent materials (Cui *et al.*, 2012), optical amplification (Bradley & Pollnau, 2011), magnetic materials, pressure and impact sensors, and biological systems. (Bünzli & Eliseeva, 2013). According to these excellent properties, a new pyridinium complex consisting of *p*-aminostyryl-pyridinium cation and a gadolinium(III) complex anion was synthesized by an ionic exchange reaction.

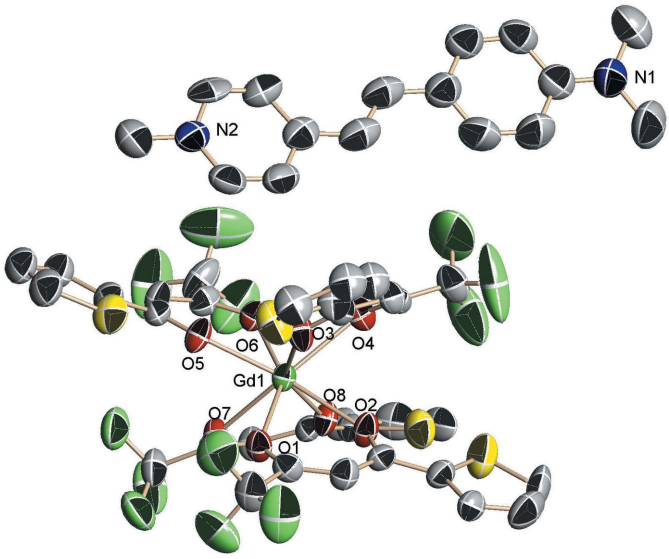


Figure 1
The molecular structure of the title complex, showing 30% probability displacement ellipsoids. The H atoms have been omitted for clarity.

As shown in Fig. 1, the asymmetric unit of the title complex contains one Gd^{III} cation, four bidentate TTA^- (4,4,4-trifluoro-1,3-dioxo-1-(thiophen-2-yl)butan-2-ide) anions and one (*E*)-4-(4-(dimethylamino)styryl)-1-methylpyridin-1-ium cation. The central Gd^{III} cation is coordinated by eight oxygen atoms from four bidentate TTA^- anions, which presents typical O,*O*-chelates. The coordination environment of the Gd^{III} cation is shown in Fig. 2. The Gd—O bond lengths range from 2.366 (5) to 2.419 (4)°, which deviate from the average of 2.385°. Eight different bond lengths generate a distorted square antiprism with the two square planes comprising atoms (O1,O2,O8,O7) and (O3,O4,O6,O5). The dihedral angle between these planes is 0.269 (1)°.

Synthesis and crystallization

1,4-Dimethylpyridinium iodide and (*E*)-4-(4-(dimethylamino) styryl)-1-methylpyridin-1-ium iodide were prepared using established literature methods (Zhao *et al.*, 1995*a*,*b*). For the preparation of the title complex, $Gd(NO_3)_3{\cdot}6H_2O$ (0.45 g, 1 mmol) dissolved in ethanol solution was added dropwise into a 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione (HTTA, 0.89 g, 4 mmol) and aqueous NaOH (0.16 g, 4 mmol) solution that reacted to form the intermediate 4,4,4-trifluoro-1,3-dioxo-1-(thiophen-2-yl)butan-2-ide (TTA^-), then (*E*)-4-[4-(dimethylamino)styryl]-1-methylpyridin-1-ium iodide (0.37 g, 1 mmol) was added into the solution. After refluxing for half an hour, the precipitate was filtered off and recrystallized from ethanol solution. Single crystals of the title complex were gained by slow evaporation of methanol covered with acetonitrile at room temperature. ^{1}H NMR: (400 MHz, CD_3COCD_3-d_6), (p.p.m.): 10.30 (*d*, 2H), 8.90 (*d*,2*H*), 8.14 (*d*, 1H), 7.68 (*d*, 2H), 7.43 (*d*, 1H), 7.25 (*d*, 4H), 6.85 (*d*, 2H),6.73 (*d*, 4H), 6.67–6.60 (*m*, 4H), 5.69 (*s*, 4H), 4.05 (*s*, 3H), 3.11 (*s*, 6H).

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{16}H_{19}N_2)[Gd(C_8H_4F_3S)_4]$
M_r	1281.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	298
a, *b*, *c* (Å)	10.500 (5), 21.888 (5), 23.348 (5)
β (°)	101.145 (5)
V (Å^3)	5265 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.51
Crystal size (mm)	0.24 × 0.22 × 0.21
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Absorption correction	ψ scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.713, 0.742
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37288, 9781, 7812
R_{int}	0.056
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.143, 1.09
No. of reflections	9781
No. of parameters	770
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −1.42

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The residual solvent water molecules were highly disordered and could not be found and refined. The diffuse electron densities of these residual solvent molecules were removed from the data set by the SQUEEZE routine of *PLATON* (Spek, 2015) software, and then the generated data were used to further refine the structure.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161727 [https://doi.org/10.1107/S2414314616017272]

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Crystal data

$(C_{16}H_{19}N_2)[Gd(C_8H_4F_3S)_4]$
M_r = 1281.27
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 10.500 (5) Å
b = 21.888 (5) Å
c = 23.348 (5) Å
β = 101.145 (5)°
V = 5265 (3) Å^3
Z = 4
$F(000)$ = 2548
D_x = 1.616 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 9929 reflections
θ = 2.2–24.3°
μ = 1.51 mm^{-1}
T = 298 K
Block, red
0.24 × 0.22 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: ψ scan (SADABS; Bruker, 2007)
T_{min} = 0.713, T_{max} = 0.742
37288 measured reflections
9781 independent reflections
7812 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 25.5°, θ_{min} = 1.3°
h = −11→12
k = −25→26
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.143
S = 1.09
9781 reflections
770 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 26.1086P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.020
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 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.

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S2	0.5249 (17)	0.6856 (12)	0.4449 (8)	0.090 (3)	0.662 (10)
C41	0.494 (7)	0.6822 (17)	0.512 (3)	0.086 (10)	0.662 (10)
H41	0.4114	0.6758	0.5194	0.103*	0.662 (10)
C42	0.604 (9)	0.690 (3)	0.555 (4)	0.080 (12)	0.662 (10)
H42	0.6057	0.6901	0.5953	0.096*	0.662 (10)
C43	0.717 (5)	0.697 (3)	0.528 (2)	0.078 (14)	0.662 (10)
H43	0.8016	0.7027	0.5483	0.094*	0.662 (10)
C44	0.68 (2)	0.694 (9)	0.467 (10)	0.06 (2)	0.662 (10)
S2′	0.748 (3)	0.7062 (16)	0.5382 (12)	0.073 (5)	0.338 (10)
C42′	0.509 (13)	0.706 (3)	0.511 (6)	0.09 (2)	0.338 (10)
H42′	0.4243	0.7095	0.5173	0.105*	0.338 (10)
C41′	0.622 (19)	0.709 (5)	0.556 (9)	0.08 (2)	0.338 (10)
H41′	0.6164	0.7128	0.5955	0.099*	0.338 (10)
C43′	0.547 (11)	0.697 (7)	0.454 (5)	0.10 (4)	0.338 (10)
H43′	0.4921	0.6910	0.4181	0.114*	0.338 (10)
C44′	0.70 (4)	0.698 (18)	0.47 (2)	0.06 (5)	0.338 (10)
S4	0.311 (2)	0.7632 (9)	0.2735 (9)	0.077 (2)	0.662 (10)
C33	0.181 (8)	0.808 (3)	0.249 (3)	0.082 (17)	0.662 (10)
H33	0.1055	0.8057	0.2640	0.098*	0.662 (10)
C34	0.198 (6)	0.849 (3)	0.2038 (19)	0.082 (11)	0.662 (10)
H34	0.1338	0.8753	0.1855	0.099*	0.662 (10)
C35	0.326 (9)	0.844 (4)	0.190 (4)	0.08 (3)	0.662 (10)
H35	0.3586	0.8664	0.1620	0.098*	0.662 (10)
C36	0.392 (9)	0.796 (4)	0.226 (4)	0.06 (3)	0.662 (10)
S4′	0.308 (6)	0.852 (2)	0.1931 (19)	0.079 (6)	0.338 (10)
C34′	0.183 (18)	0.791 (7)	0.263 (7)	0.08 (2)	0.338 (10)
H34′	0.1202	0.7746	0.2821	0.093*	0.338 (10)
C33′	0.181 (11)	0.842 (5)	0.224 (3)	0.07 (2)	0.338 (10)
H33′	0.1099	0.8683	0.2167	0.087*	0.338 (10)
C35′	0.319 (14)	0.772 (6)	0.264 (6)	0.09 (5)	0.338 (10)
H35′	0.3538	0.7418	0.2905	0.109*	0.338 (10)
C36′	0.40 (2)	0.795 (8)	0.228 (8)	0.07 (6)	0.338 (10)
C1	−0.2577 (12)	0.3626 (6)	0.0335 (6)	0.123 (5)	
H1A	−0.2329	0.3472	−0.0012	0.184*	
H1B	−0.3507	0.3647	0.0278	0.184*	

H1C	−0.2255	0.3359	0.0656	0.184*
C2	−0.2884 (11)	0.4743 (6)	0.0322 (5)	0.110 (4)
H2A	−0.2806	0.5007	0.0655	0.166*
H2B	−0.3763	0.4602	0.0214	0.166*
H2C	−0.2653	0.4965	0.0002	0.166*
C3	−0.0744 (11)	0.4306 (5)	0.0667 (4)	0.080 (3)
C4	0.0107 (12)	0.3808 (5)	0.0796 (5)	0.103 (4)
H4	−0.0209	0.3412	0.0733	0.123*
C5	0.1423 (12)	0.3905 (5)	0.1016 (5)	0.103 (4)
H5	0.1952	0.3563	0.1105	0.123*
C6	0.1986 (11)	0.4468 (5)	0.1111 (4)	0.081 (3)
C7	0.1139 (11)	0.4955 (5)	0.0988 (4)	0.084 (3)
H7	0.1470	0.5348	0.1055	0.101*
C8	−0.0152 (11)	0.4888 (5)	0.0772 (4)	0.082 (3)
H8	−0.0665	0.5236	0.0692	0.099*
C9	0.3388 (12)	0.4575 (5)	0.1357 (4)	0.087 (3)
H9	0.3644	0.4976	0.1449	0.104*
C10	0.4279 (12)	0.4159 (5)	0.1454 (4)	0.087 (3)
H10	0.4043	0.3754	0.1373	0.104*
C11	0.5645 (11)	0.4299 (4)	0.1686 (4)	0.075 (3)
C12	0.6550 (12)	0.3826 (4)	0.1725 (4)	0.088 (3)
H12	0.6270	0.3433	0.1613	0.105*
C13	0.7826 (11)	0.3931 (4)	0.1923 (4)	0.083 (3)
H13	0.8412	0.3609	0.1952	0.100*
C14	0.7437 (11)	0.4988 (4)	0.2029 (4)	0.081 (3)
H14	0.7750	0.5383	0.2107	0.097*
C15	0.6147 (10)	0.4878 (4)	0.1862 (4)	0.077 (3)
H15	0.5571	0.5200	0.1864	0.092*
C16	0.9678 (10)	0.4600 (5)	0.2285 (5)	0.099 (3)
H16A	0.9879	0.4589	0.2704	0.148*
H16B	0.9915	0.4992	0.2152	0.148*
H16C	1.0154	0.4286	0.2131	0.148*
C17	1.1792 (11)	0.4745 (5)	0.4335 (5)	0.095 (3)
H17	1.2678	0.4666	0.4427	0.115*
C18	1.0904 (13)	0.4435 (5)	0.4554 (4)	0.092 (3)
H18	1.1132	0.4124	0.4825	0.111*
C19	0.9631 (8)	0.4601 (3)	0.4355 (3)	0.0549 (19)
H19	0.8910	0.4416	0.4457	0.066*
C20	0.9601 (8)	0.5110 (3)	0.3961 (3)	0.0546 (19)
C21	0.8490 (7)	0.5459 (3)	0.3634 (3)	0.0472 (17)
C22	0.7215 (7)	0.5298 (3)	0.3675 (3)	0.0545 (19)
H22	0.7091	0.5017	0.3957	0.065*
C23	0.6151 (7)	0.5539 (3)	0.3316 (3)	0.0532 (18)
C24	0.4809 (9)	0.5292 (5)	0.3360 (4)	0.073 (3)
C25	1.3133 (8)	0.6296 (4)	0.1907 (5)	0.073 (3)
H25	1.4007	0.6220	0.2053	0.087*
C26	1.2682 (10)	0.6534 (5)	0.1378 (5)	0.084 (3)
H26	1.3233	0.6646	0.1128	0.101*

C27	1.1305 (7)	0.6606 (3)	0.1221 (4)	0.060 (2)
H27	1.0840	0.6753	0.0868	0.071*
C28	1.0779 (7)	0.6407 (3)	0.1718 (3)	0.0489 (17)
C29	0.9424 (6)	0.6419 (3)	0.1792 (3)	0.0432 (15)
C30	0.8405 (7)	0.6459 (4)	0.1295 (3)	0.0506 (18)
H30	0.8608	0.6486	0.0925	0.061*
C31	0.7144 (7)	0.6457 (3)	0.1349 (3)	0.0474 (17)
C32	0.6096 (8)	0.6440 (5)	0.0784 (3)	0.066 (2)
C37	0.5247 (8)	0.7746 (3)	0.2253 (3)	0.0493 (17)
C38	0.5972 (8)	0.8030 (4)	0.1872 (3)	0.057 (2)
H38	0.5545	0.8292	0.1584	0.069*
C39	0.7265 (8)	0.7933 (3)	0.1912 (3)	0.0536 (19)
C40	0.7969 (11)	0.8301 (5)	0.1504 (5)	0.086 (3)
C45	0.7666 (7)	0.6981 (3)	0.4222 (3)	0.0520 (18)
C46	0.9019 (7)	0.7033 (4)	0.4371 (3)	0.0543 (19)
H46	0.9416	0.7006	0.4762	0.065*
C47	0.9790 (7)	0.7124 (3)	0.3960 (3)	0.0485 (17)
C48	1.1227 (9)	0.7182 (5)	0.4182 (4)	0.071 (2)
F1	0.4821 (6)	0.4883 (3)	0.3774 (3)	0.130 (3)
F2	0.4023 (5)	0.5737 (3)	0.3442 (3)	0.108 (2)
F3	0.4230 (6)	0.5022 (3)	0.2871 (3)	0.115 (2)
F4	1.1657 (6)	0.6989 (5)	0.4695 (3)	0.175 (4)
F5	1.1919 (6)	0.6924 (5)	0.3847 (4)	0.164 (4)
F6	1.1618 (8)	0.7730 (4)	0.4169 (5)	0.193 (5)
F7	0.8944 (7)	0.7999 (3)	0.1369 (3)	0.128 (3)
F8	0.8487 (10)	0.8796 (4)	0.1753 (4)	0.173 (4)
F9	0.7234 (8)	0.8450 (4)	0.1012 (3)	0.159 (4)
F10	0.5265 (6)	0.5973 (3)	0.0786 (2)	0.0957 (18)
F11	0.5367 (5)	0.6943 (3)	0.0729 (2)	0.0931 (17)
F12	0.6568 (5)	0.6376 (4)	0.0298 (2)	0.110 (2)
Gd1	0.76013 (3)	0.672150 (16)	0.279170 (14)	0.03944 (11)
N1	−0.2036 (9)	0.4232 (4)	0.0462 (4)	0.095 (3)
N2	0.8261 (8)	0.4500 (3)	0.2079 (3)	0.074 (2)
O1	0.6103 (4)	0.5937 (2)	0.2912 (2)	0.0522 (12)
O2	0.8757 (5)	0.5884 (2)	0.3318 (2)	0.0559 (13)
O3	0.7060 (5)	0.6942 (3)	0.3707 (2)	0.0621 (15)
O4	0.9438 (5)	0.7172 (2)	0.3414 (2)	0.0561 (13)
O5	0.5705 (4)	0.7338 (2)	0.2614 (2)	0.0519 (12)
O6	0.8026 (5)	0.7606 (2)	0.2270 (2)	0.0491 (12)
O7	0.6642 (4)	0.6448 (2)	0.17983 (18)	0.0455 (11)
O8	0.9229 (4)	0.6357 (2)	0.2300 (2)	0.0509 (12)
S1	1.1113 (2)	0.52987 (14)	0.38679 (13)	0.0916 (8)
S3	1.1934 (2)	0.61484 (13)	0.22812 (11)	0.0787 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.066 (4)	0.143 (9)	0.064 (4)	−0.006 (4)	0.022 (3)	−0.012 (4)

C41	0.084 (17)	0.11 (3)	0.068 (13)	0.00 (2)	0.027 (12)	−0.01 (2)
C42	0.08 (2)	0.10 (4)	0.059 (13)	0.01 (3)	0.025 (14)	0.00 (3)
C43	0.08 (3)	0.09 (2)	0.07 (2)	0.005 (17)	0.019 (17)	−0.004 (15)
C44	0.06 (4)	0.09 (7)	0.05 (3)	0.01 (4)	0.02 (3)	0.00 (4)
S2′	0.078 (11)	0.088 (9)	0.057 (7)	0.005 (7)	0.024 (8)	0.002 (7)
C42′	0.08 (4)	0.10 (6)	0.08 (3)	0.00 (4)	0.03 (3)	−0.01 (5)
C41′	0.09 (5)	0.10 (6)	0.07 (3)	0.00 (5)	0.03 (3)	0.00 (5)
C43′	0.10 (8)	0.12 (6)	0.07 (6)	0.02 (5)	0.04 (5)	0.01 (5)
C44′	0.06 (8)	0.07 (7)	0.06 (8)	−0.01 (6)	0.01 (4)	0.00 (4)
S4	0.063 (4)	0.097 (5)	0.080 (4)	0.019 (4)	0.032 (4)	−0.007 (5)
C33	0.065 (14)	0.09 (5)	0.09 (5)	0.02 (3)	0.01 (3)	−0.01 (2)
C34	0.07 (2)	0.089 (18)	0.09 (3)	0.025 (14)	0.007 (19)	−0.02 (2)
C35	0.06 (4)	0.08 (3)	0.10 (3)	0.017 (18)	0.002 (18)	−0.011 (16)
C36	0.05 (4)	0.07 (4)	0.07 (4)	0.02 (3)	0.01 (3)	−0.02 (3)
S4′	0.060 (11)	0.082 (11)	0.088 (11)	0.013 (12)	0.000 (8)	0.002 (11)
C34′	0.07 (3)	0.08 (6)	0.08 (6)	0.02 (4)	0.01 (3)	0.00 (3)
C33′	0.06 (3)	0.08 (4)	0.07 (6)	0.03 (4)	0.01 (4)	−0.01 (4)
C35′	0.07 (5)	0.12 (7)	0.09 (7)	0.02 (4)	0.03 (4)	0.01 (4)
C36′	0.07 (9)	0.08 (9)	0.06 (7)	0.01 (6)	0.00 (6)	0.01 (5)
C1	0.116 (10)	0.117 (10)	0.120 (10)	−0.017 (8)	−0.016 (8)	−0.040 (8)
C2	0.104 (9)	0.125 (10)	0.094 (8)	0.030 (8)	−0.002 (7)	0.000 (7)
C3	0.095 (8)	0.070 (6)	0.072 (6)	0.009 (6)	0.011 (5)	−0.013 (5)
C4	0.103 (9)	0.061 (6)	0.140 (10)	0.005 (6)	0.009 (8)	−0.021 (6)
C5	0.095 (9)	0.074 (7)	0.135 (10)	0.024 (6)	0.013 (7)	0.009 (7)
C6	0.092 (8)	0.073 (7)	0.078 (6)	−0.004 (6)	0.014 (5)	−0.005 (5)
C7	0.100 (8)	0.067 (6)	0.083 (7)	0.004 (6)	0.013 (6)	−0.009 (5)
C8	0.100 (8)	0.072 (6)	0.072 (6)	0.021 (6)	0.010 (6)	−0.006 (5)
C9	0.122 (9)	0.057 (6)	0.085 (7)	−0.006 (6)	0.031 (6)	−0.006 (5)
C10	0.119 (9)	0.060 (6)	0.085 (7)	−0.011 (6)	0.031 (6)	−0.005 (5)
C11	0.098 (8)	0.073 (6)	0.055 (5)	−0.011 (6)	0.018 (5)	0.005 (4)
C12	0.121 (9)	0.056 (6)	0.075 (6)	−0.011 (6)	−0.005 (6)	0.005 (5)
C13	0.111 (9)	0.062 (6)	0.068 (6)	0.011 (6)	−0.004 (6)	0.011 (5)
C14	0.119 (9)	0.049 (5)	0.083 (6)	−0.013 (6)	0.039 (6)	0.026 (4)
C15	0.091 (7)	0.058 (6)	0.089 (7)	−0.008 (5)	0.036 (6)	−0.004 (5)
C16	0.094 (8)	0.097 (8)	0.096 (8)	0.007 (7)	−0.002 (6)	0.006 (6)
C17	0.073 (7)	0.115 (9)	0.088 (7)	0.051 (7)	−0.011 (6)	0.007 (7)
C18	0.126 (10)	0.074 (7)	0.073 (6)	0.039 (7)	0.011 (7)	0.019 (5)
C19	0.062 (5)	0.051 (4)	0.049 (4)	0.004 (4)	0.004 (4)	0.011 (3)
C20	0.064 (5)	0.047 (4)	0.052 (4)	0.010 (4)	0.007 (4)	0.003 (3)
C21	0.052 (4)	0.039 (4)	0.052 (4)	0.002 (3)	0.012 (3)	0.004 (3)
C22	0.055 (5)	0.052 (5)	0.058 (4)	0.000 (4)	0.013 (4)	0.015 (4)
C23	0.052 (5)	0.054 (5)	0.054 (4)	−0.008 (4)	0.013 (4)	0.002 (4)
C24	0.049 (5)	0.091 (7)	0.083 (6)	−0.006 (5)	0.022 (5)	0.017 (6)
C25	0.034 (4)	0.081 (6)	0.109 (8)	−0.004 (4)	0.029 (5)	−0.024 (6)
C26	0.072 (7)	0.094 (8)	0.099 (8)	−0.013 (5)	0.045 (6)	−0.010 (6)
C27	0.042 (4)	0.059 (5)	0.087 (6)	0.000 (4)	0.035 (4)	0.005 (4)
C28	0.036 (4)	0.050 (4)	0.062 (4)	0.004 (3)	0.014 (3)	−0.005 (4)
C29	0.040 (4)	0.040 (4)	0.051 (4)	0.006 (3)	0.013 (3)	0.002 (3)

C30	0.043 (4)	0.071 (5)	0.042 (4)	0.009 (4)	0.020 (3)	0.001 (3)
C31	0.057 (4)	0.062 (4)	0.025 (3)	0.020 (4)	0.013 (3)	−0.011 (3)
C32	0.055 (5)	0.094 (7)	0.047 (4)	0.022 (5)	0.003 (4)	0.001 (4)
C37	0.048 (5)	0.045 (4)	0.053 (4)	0.007 (4)	0.004 (3)	−0.007 (3)
C38	0.053 (5)	0.057 (5)	0.060 (5)	0.013 (4)	0.007 (4)	0.017 (4)
C39	0.069 (5)	0.049 (4)	0.045 (4)	0.005 (4)	0.014 (4)	0.013 (3)
C40	0.101 (8)	0.080 (7)	0.087 (7)	0.036 (7)	0.042 (6)	0.040 (6)
C45	0.054 (5)	0.049 (4)	0.052 (4)	0.006 (4)	0.006 (4)	0.006 (3)
C46	0.053 (5)	0.066 (5)	0.041 (4)	0.000 (4)	0.002 (3)	0.003 (3)
C47	0.055 (4)	0.045 (4)	0.043 (4)	−0.011 (3)	0.004 (3)	0.005 (3)
C48	0.056 (5)	0.090 (7)	0.065 (5)	−0.020 (5)	0.009 (4)	0.008 (5)
F1	0.083 (4)	0.160 (6)	0.148 (6)	−0.026 (4)	0.028 (4)	0.086 (5)
F2	0.066 (4)	0.115 (5)	0.153 (6)	−0.001 (3)	0.046 (4)	0.003 (4)
F3	0.087 (4)	0.131 (6)	0.125 (5)	−0.054 (4)	0.014 (4)	−0.018 (4)
F4	0.058 (4)	0.350 (13)	0.104 (5)	−0.025 (5)	−0.014 (3)	0.093 (7)
F5	0.058 (4)	0.296 (12)	0.135 (6)	0.004 (5)	0.012 (4)	−0.064 (7)
F6	0.102 (6)	0.124 (7)	0.323 (14)	−0.062 (5)	−0.036 (7)	0.040 (8)
F7	0.132 (6)	0.137 (6)	0.139 (6)	0.033 (5)	0.086 (5)	0.067 (5)
F8	0.268 (11)	0.096 (5)	0.188 (8)	−0.078 (6)	0.125 (8)	0.002 (5)
F9	0.133 (6)	0.246 (10)	0.106 (5)	0.033 (6)	0.040 (5)	0.113 (6)
F10	0.086 (4)	0.109 (4)	0.079 (4)	−0.017 (4)	−0.017 (3)	−0.011 (3)
F11	0.087 (4)	0.109 (4)	0.072 (3)	0.032 (3)	−0.013 (3)	0.006 (3)
F12	0.084 (4)	0.202 (7)	0.043 (3)	0.021 (4)	0.008 (3)	−0.012 (3)
Gd1	0.03767 (18)	0.04414 (19)	0.03731 (17)	0.00276 (16)	0.00926 (12)	0.00810 (15)
N1	0.087 (6)	0.085 (6)	0.104 (7)	−0.003 (5)	−0.006 (5)	−0.013 (5)
N2	0.108 (7)	0.063 (5)	0.046 (4)	−0.012 (5)	0.000 (4)	0.007 (3)
O1	0.041 (3)	0.058 (3)	0.055 (3)	−0.005 (2)	0.005 (2)	0.014 (2)
O2	0.045 (3)	0.058 (3)	0.063 (3)	0.003 (2)	0.008 (2)	0.026 (3)
O3	0.045 (3)	0.102 (4)	0.039 (3)	0.005 (3)	0.007 (2)	0.001 (3)
O4	0.052 (3)	0.071 (3)	0.045 (3)	−0.017 (3)	0.009 (2)	0.011 (2)
O5	0.045 (3)	0.061 (3)	0.055 (3)	0.019 (2)	0.021 (2)	0.017 (2)
O6	0.047 (3)	0.049 (3)	0.053 (3)	0.002 (2)	0.016 (2)	0.013 (2)
O7	0.033 (2)	0.068 (3)	0.037 (2)	0.008 (2)	0.0113 (19)	0.000 (2)
O8	0.039 (3)	0.066 (3)	0.050 (3)	0.015 (2)	0.013 (2)	0.011 (2)
S1	0.0607 (15)	0.105 (2)	0.107 (2)	0.0156 (14)	0.0109 (14)	0.0301 (16)
S3	0.0507 (12)	0.0977 (19)	0.0861 (16)	0.0040 (12)	0.0097 (11)	−0.0017 (14)

Geometric parameters (Å, º)

S2—C44	1.6 (2)	C14—H14	0.9300
S2—C41	1.65 (6)	C15—H15	0.9300
C41—C42	1.40 (12)	C16—N2	1.489 (12)
C41—H41	0.9300	C16—H16A	0.9600
C42—C43	1.46 (11)	C16—H16B	0.9600
C42—H42	0.9300	C16—H16C	0.9600
C43—C44	1.4 (2)	C17—C18	1.332 (15)
C43—H43	0.9300	C17—S1	1.693 (10)
C44—C45	1.51 (19)	C17—H17	0.9300

S2′—C41′	1.5 (2)	C18—C19	1.377 (13)
S2′—C44′	1.7 (5)	C18—H18	0.9300
C42′—C41′	1.4 (2)	C19—C20	1.441 (10)
C42′—C43′	1.48 (17)	C19—H19	0.9300
C42′—H42′	0.9300	C20—C21	1.477 (10)
C41′—H41′	0.9300	C20—S1	1.694 (8)
C43′—C44′	1.5 (4)	C21—O2	1.253 (8)
C43′—H43′	0.9300	C21—C22	1.405 (10)
C44′—C45	1.4 (4)	C22—C23	1.366 (10)
S4—C36	1.68 (11)	C22—H22	0.9300
S4—C33	1.68 (7)	C23—O1	1.276 (8)
C33—C34	1.42 (6)	C23—C24	1.532 (11)
C33—H33	0.9300	C24—F1	1.314 (10)
C34—C35	1.45 (11)	C24—F2	1.316 (11)
C34—H34	0.9300	C24—F3	1.323 (11)
C35—C36	1.44 (12)	C25—C26	1.339 (13)
C35—H35	0.9300	C25—S3	1.697 (9)
C36—C37	1.48 (8)	C25—H25	0.9300
S4′—C33′	1.65 (10)	C26—C27	1.430 (12)
S4′—C36′	1.66 (17)	C26—H26	0.9300
C34′—C33′	1.44 (12)	C27—C28	1.446 (10)
C34′—C35′	1.5 (2)	C27—H27	0.9300
C34′—H34′	0.9300	C28—C29	1.467 (9)
C33′—H33′	0.9300	C28—S3	1.704 (8)
C35′—C36′	1.4 (3)	C29—O8	1.249 (8)
C35′—H35′	0.9300	C29—C30	1.421 (9)
C36′—C37	1.43 (18)	C30—C31	1.354 (10)
C1—N1	1.451 (13)	C30—H30	0.9300
C1—H1A	0.9600	C31—O7	1.261 (7)
C1—H1B	0.9600	C31—C32	1.546 (10)
C1—H1C	0.9600	C32—F12	1.331 (9)
C2—N1	1.427 (13)	C32—F11	1.333 (10)
C2—H2A	0.9600	C32—F10	1.346 (11)
C2—H2B	0.9600	C37—O5	1.256 (8)
C2—H2C	0.9600	C37—C38	1.422 (10)
C3—N1	1.358 (12)	C38—C39	1.360 (10)
C3—C4	1.403 (14)	C38—H38	0.9300
C3—C8	1.419 (14)	C39—O6	1.260 (8)
C4—C5	1.394 (15)	C39—C40	1.541 (12)
C4—H4	0.9300	C40—F8	1.297 (13)
C5—C6	1.367 (14)	C40—F9	1.297 (12)
C5—H5	0.9300	C40—F7	1.306 (11)
C6—C7	1.382 (13)	C45—O3	1.249 (8)
C6—C9	1.491 (14)	C45—C46	1.400 (10)
C7—C8	1.360 (13)	C46—C47	1.384 (10)
C7—H7	0.9300	C46—H46	0.9300
C8—H8	0.9300	C47—O4	1.261 (8)
C9—C10	1.294 (13)	C47—C48	1.503 (11)

C9—H9	0.9300	C48—F4	1.269 (10)
C10—C11	1.464 (14)	C48—F6	1.269 (11)
C10—H10	0.9300	C48—F5	1.296 (11)
C11—C12	1.396 (14)	Gd1—O3	2.366 (5)
C11—C15	1.403 (12)	Gd1—O8	2.373 (5)
C12—C13	1.350 (14)	Gd1—O6	2.375 (4)
C12—H12	0.9300	Gd1—O5	2.375 (4)
C13—N2	1.351 (12)	Gd1—O1	2.382 (5)
C13—H13	0.9300	Gd1—O4	2.391 (5)
C14—C15	1.357 (13)	Gd1—O2	2.400 (5)
C14—N2	1.365 (12)	Gd1—O7	2.419 (4)

C44—S2—C41	94 (8)	O2—C21—C20	116.4 (7)
C42—C41—S2	113 (5)	C22—C21—C20	120.2 (6)
C42—C41—H41	123.3	C23—C22—C21	122.6 (7)
S2—C41—H41	123.3	C23—C22—H22	118.7
C41—C42—C43	109 (7)	C21—C22—H22	118.7
C41—C42—H42	125.6	O1—C23—C22	128.8 (7)
C43—C42—H42	125.6	O1—C23—C24	112.6 (7)
C44—C43—C42	111 (10)	C22—C23—C24	118.4 (7)
C44—C43—H43	124.6	F1—C24—F2	108.3 (8)
C42—C43—H43	124.6	F1—C24—F3	105.6 (9)
C43—C44—C45	128 (10)	F2—C24—F3	105.0 (8)
C43—C44—S2	113 (10)	F1—C24—C23	114.3 (8)
C45—C44—S2	119 (10)	F2—C24—C23	111.0 (8)
C41′—S2′—C44′	99 (10)	F3—C24—C23	112.0 (7)
C41′—C42′—C43′	110 (10)	C26—C25—S3	112.5 (7)
C41′—C42′—H42′	124.0	C26—C25—H25	123.7
C43′—C42′—H42′	125.1	S3—C25—H25	123.7
C42′—C41′—S2′	117 (10)	C25—C26—C27	116.1 (8)
C42′—C41′—H41′	121.5	C25—C26—H26	122.0
S2′—C41′—H41′	121.5	C27—C26—H26	122.0
C42′—C43′—C44′	105 (10)	C26—C27—C28	106.6 (8)
C42′—C43′—H43′	127.3	C26—C27—H27	126.7
C44′—C43′—H43′	130.0	C28—C27—H27	126.7
C43′—C44′—S2′	111 (10)	C27—C28—C29	128.3 (7)
C36—S4—C33	90 (4)	C27—C28—S3	113.2 (5)
C34—C33—S4	114 (5)	C29—C28—S3	118.4 (5)
C34—C33—H33	124.0	O8—C29—C30	123.2 (6)
S4—C33—H33	122.8	O8—C29—C28	116.8 (6)
C33—C34—C35	112 (6)	C30—C29—C28	119.9 (6)
C33—C34—H34	124.0	C31—C30—C29	121.2 (6)
C35—C34—H34	124.0	C31—C30—H30	119.4
C36—C35—C34	106 (7)	C29—C30—H30	119.4
C36—C35—H35	127.0	O7—C31—C30	130.6 (6)
C34—C35—H35	127.0	O7—C31—C32	111.5 (6)
C35—C36—C37	124 (9)	C30—C31—C32	117.8 (6)
C35—C36—S4	117 (7)	F12—C32—F11	107.9 (7)

C37—C36—S4	118 (6)	F12—C32—F10	105.7 (8)
C33′—S4′—C36′	96 (9)	F11—C32—F10	105.5 (7)
C33′—C34′—C35′	97 (10)	F12—C32—C31	114.2 (7)
C33′—C34′—H34′	131.4	F11—C32—C31	111.3 (7)
C35′—C34′—H34′	131.5	F10—C32—C31	111.7 (7)
C34′—C33′—S4′	117 (10)	O5—C37—C38	123.2 (7)
C34′—C33′—H33′	121.3	O5—C37—C36′	116 (8)
S4′—C33′—H33′	121.3	C38—C37—C36′	121 (8)
C36′—C35′—C34′	125 (10)	O5—C37—C36	117 (4)
C36′—C35′—H35′	117.5	C38—C37—C36	120 (4)
C34′—C35′—H35′	117.5	C39—C38—C37	122.4 (7)
C35′—C36′—C37	125 (10)	C39—C38—H38	118.8
C35′—C36′—S4′	104 (10)	C37—C38—H38	118.8
C37—C36′—S4′	131 (10)	O6—C39—C38	129.1 (7)
N1—C1—H1A	109.5	O6—C39—C40	112.9 (7)
N1—C1—H1B	109.5	C38—C39—C40	117.8 (7)
H1A—C1—H1B	109.5	F8—C40—F9	108.2 (10)
N1—C1—H1C	109.5	F8—C40—F7	104.5 (11)
H1A—C1—H1C	109.5	F9—C40—F7	105.8 (9)
H1B—C1—H1C	109.5	F8—C40—C39	111.7 (9)
N1—C2—H2A	109.5	F9—C40—C39	113.9 (10)
N1—C2—H2B	109.5	F7—C40—C39	112.1 (8)
H2A—C2—H2B	109.5	O3—C45—C44′	118 (10)
N1—C2—H2C	109.5	O3—C45—C46	123.3 (7)
H2A—C2—H2C	109.5	C44′—C45—C46	119 (10)
H2B—C2—H2C	109.5	O3—C45—C44	113 (9)
N1—C3—C4	122.4 (10)	C46—C45—C44	123 (9)
N1—C3—C8	122.7 (9)	C47—C46—C45	122.7 (7)
C4—C3—C8	114.9 (10)	C47—C46—H46	118.6
C5—C4—C3	120.4 (10)	C45—C46—H46	118.6
C5—C4—H4	119.8	O4—C47—C46	128.0 (7)
C3—C4—H4	119.8	O4—C47—C48	114.9 (7)
C6—C5—C4	124.3 (10)	C46—C47—C48	117.1 (7)
C6—C5—H5	117.8	F4—C48—F6	106.4 (10)
C4—C5—H5	117.8	F4—C48—F5	106.6 (10)
C5—C6—C7	114.8 (10)	F6—C48—F5	100.1 (9)
C5—C6—C9	124.7 (10)	F4—C48—C47	116.6 (7)
C7—C6—C9	120.4 (10)	F6—C48—C47	112.3 (9)
C8—C7—C6	123.4 (10)	F5—C48—C47	113.4 (8)
C8—C7—H7	118.3	O3—Gd1—O8	145.78 (17)
C6—C7—H7	118.3	O3—Gd1—O6	113.47 (19)
C7—C8—C3	122.1 (10)	O8—Gd1—O6	78.58 (16)
C7—C8—H8	119.0	O3—Gd1—O5	72.66 (17)
C3—C8—H8	119.0	O8—Gd1—O5	139.85 (16)
C10—C9—C6	125.6 (10)	O6—Gd1—O5	71.39 (16)
C10—C9—H9	117.2	O3—Gd1—O1	76.16 (19)
C6—C9—H9	117.2	O8—Gd1—O1	111.65 (18)
C9—C10—C11	122.7 (10)	O6—Gd1—O1	147.37 (16)

C9—C10—H10	118.7	O5—Gd1—O1	83.11 (17)
C11—C10—H10	118.7	O3—Gd1—O4	70.91 (17)
C12—C11—C15	116.0 (10)	O8—Gd1—O4	81.99 (18)
C12—C11—C10	118.3 (9)	O6—Gd1—O4	76.49 (17)
C15—C11—C10	125.7 (10)	O5—Gd1—O4	114.97 (19)
C13—C12—C11	120.9 (9)	O1—Gd1—O4	134.31 (16)
C13—C12—H12	119.5	O3—Gd1—O2	83.09 (18)
C11—C12—H12	119.5	O8—Gd1—O2	69.56 (16)
C12—C13—N2	120.7 (10)	O6—Gd1—O2	139.31 (16)
C12—C13—H13	119.6	O5—Gd1—O2	147.91 (16)
N2—C13—H13	119.6	O1—Gd1—O2	70.68 (16)
C15—C14—N2	117.8 (9)	O4—Gd1—O2	74.64 (17)
C15—C14—H14	121.1	O3—Gd1—O7	142.07 (16)
N2—C14—H14	121.1	O8—Gd1—O7	70.05 (15)
C14—C15—C11	122.8 (10)	O6—Gd1—O7	78.17 (17)
C14—C15—H15	118.6	O5—Gd1—O7	78.07 (16)
C11—C15—H15	118.6	O1—Gd1—O7	76.86 (16)
N2—C16—H16A	109.5	O4—Gd1—O7	145.33 (15)
N2—C16—H16B	109.5	O2—Gd1—O7	112.17 (17)
H16A—C16—H16B	109.5	C3—N1—C2	121.7 (9)
N2—C16—H16C	109.5	C3—N1—C1	120.3 (9)
H16A—C16—H16C	109.5	C2—N1—C1	117.8 (10)
H16B—C16—H16C	109.5	C13—N2—C14	121.5 (9)
C18—C17—S1	111.9 (8)	C13—N2—C16	119.2 (9)
C18—C17—H17	124.1	C14—N2—C16	119.3 (8)
S1—C17—H17	124.1	C23—O1—Gd1	130.2 (4)
C17—C18—C19	116.2 (9)	C21—O2—Gd1	136.1 (5)
C17—C18—H18	121.9	C45—O3—Gd1	135.7 (5)
C19—C18—H18	121.9	C47—O4—Gd1	128.7 (4)
C18—C19—C20	108.7 (8)	C37—O5—Gd1	136.1 (5)
C18—C19—H19	125.7	C39—O6—Gd1	130.1 (5)
C20—C19—H19	125.7	C31—O7—Gd1	129.0 (4)
C19—C20—C21	130.3 (7)	C29—O8—Gd1	133.5 (4)
C19—C20—S1	111.4 (6)	C17—S1—C20	91.8 (5)
C21—C20—S1	118.3 (6)	C25—S3—C28	91.6 (5)
O2—C21—C22	123.4 (7)		