New polyethyleneglycol-functionalized texaphyrins: Synthesis and *in vitro* biological studies

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Contents of Supporting Information:

I: synthesis of 3,5-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-benzaldehyde.

A solution of 3,5-dihydroxybenzaldehyde (0.70 g, 5.07 mmol) in dried MeCN (10 ml), was added into a solution of 2-[2-(2-methoxyethoxy)ethoxy]ethoxyethyl *p*-toluenesulfonate (4.83 g, 15.2 mmol). Then K_2CO_3 (2.19 g, 15.8 mmol) was added and heated at reflux under argon overnight. The red suspension became yellow suspension, cooled and filtrated off yellow solid. The solid was washed with 50 ml of dichloromethane for 3 times. Combining solution was washed with H_2O for 3 times and dried with Na_2SO_4 overnight. Light yellow oil, compound 1 was obtained in 1.92 g, 88% after running column chromatography on silica (MeOH- CH_2Cl_2). CI-MS *m/z* 431 $[M+1]^+$; ^{1}H NMR (250 Hz, $CDCl_3$): 9.82 (s, 1H, CHO), 6.94 (s, 2H, Ar-H), 6.68 (s, 1H, Ar-H), 4.08 (t, *J* = 4.5 Hz, 4H, CH_2), 3.78 (t, *J* = 4.5 Hz, 4H, CH_2), 3.68-3.55 (m, 12H, CH_2), 3.46 (t, *J* = 4.3 Hz 4H, CH_2), 3.29 (s, 6H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): 190, 160.8, 138.6, 108.4, 72.3, 71.2, 70.9, 70.8, 69.8, 68.2, 59.3.

I: cyclic voltammograms of 1 MGd, 2, 3, 4 and 5

1) 1 MGd

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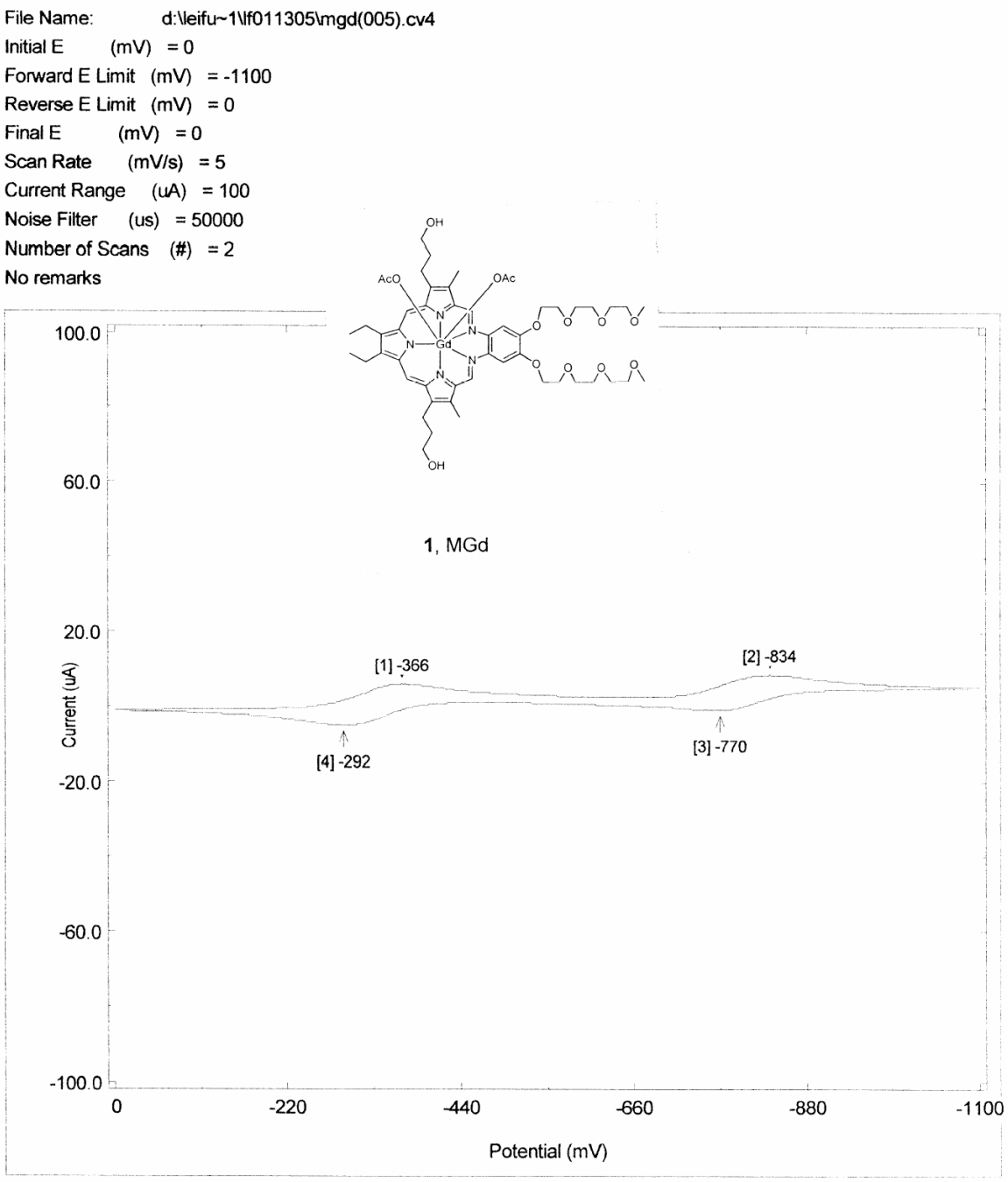

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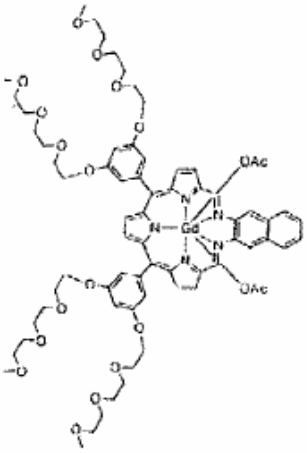

2

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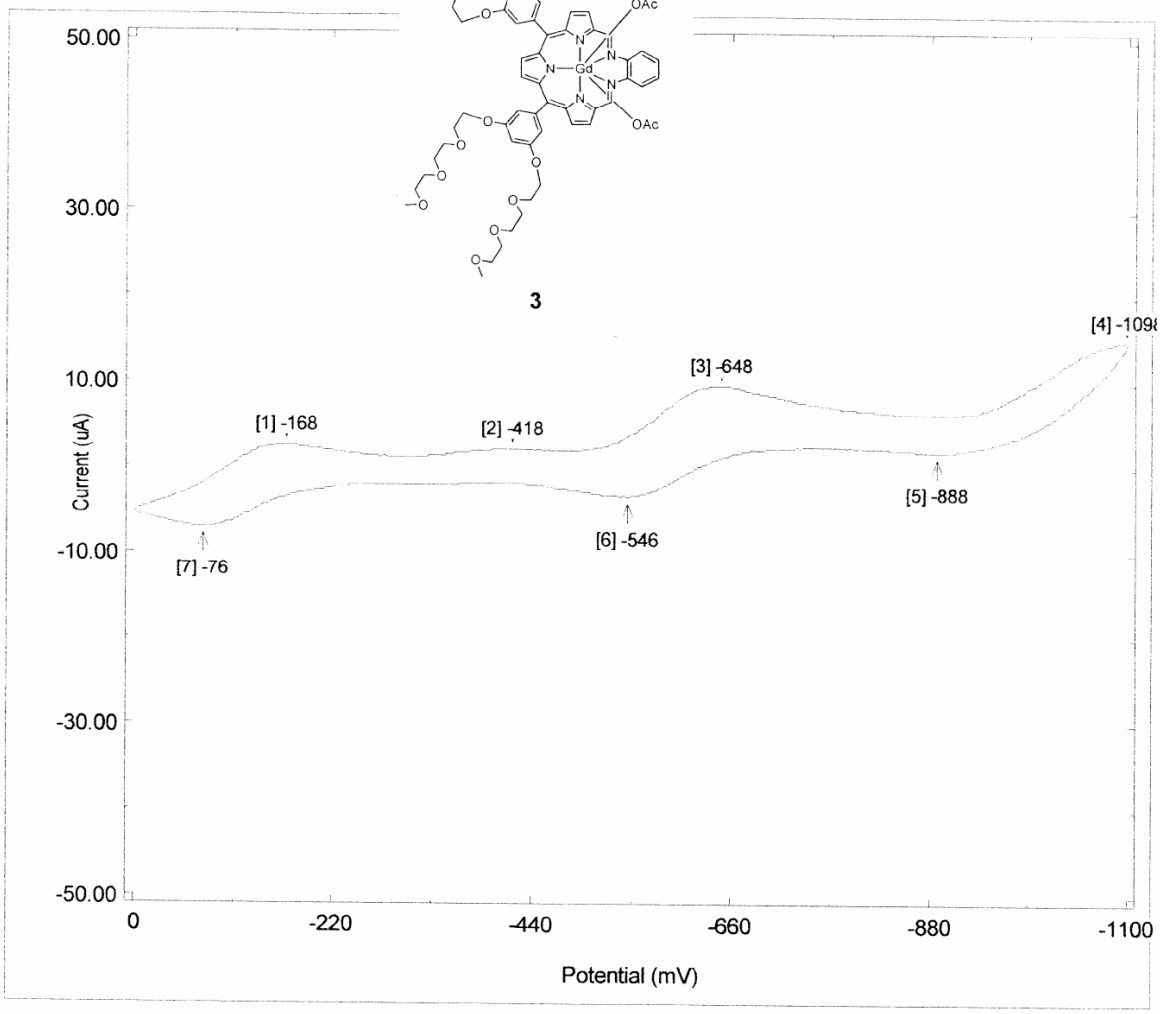

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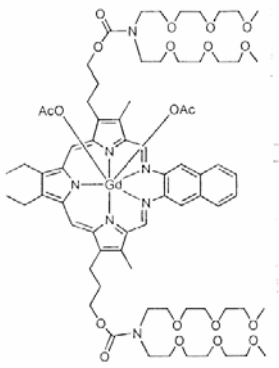

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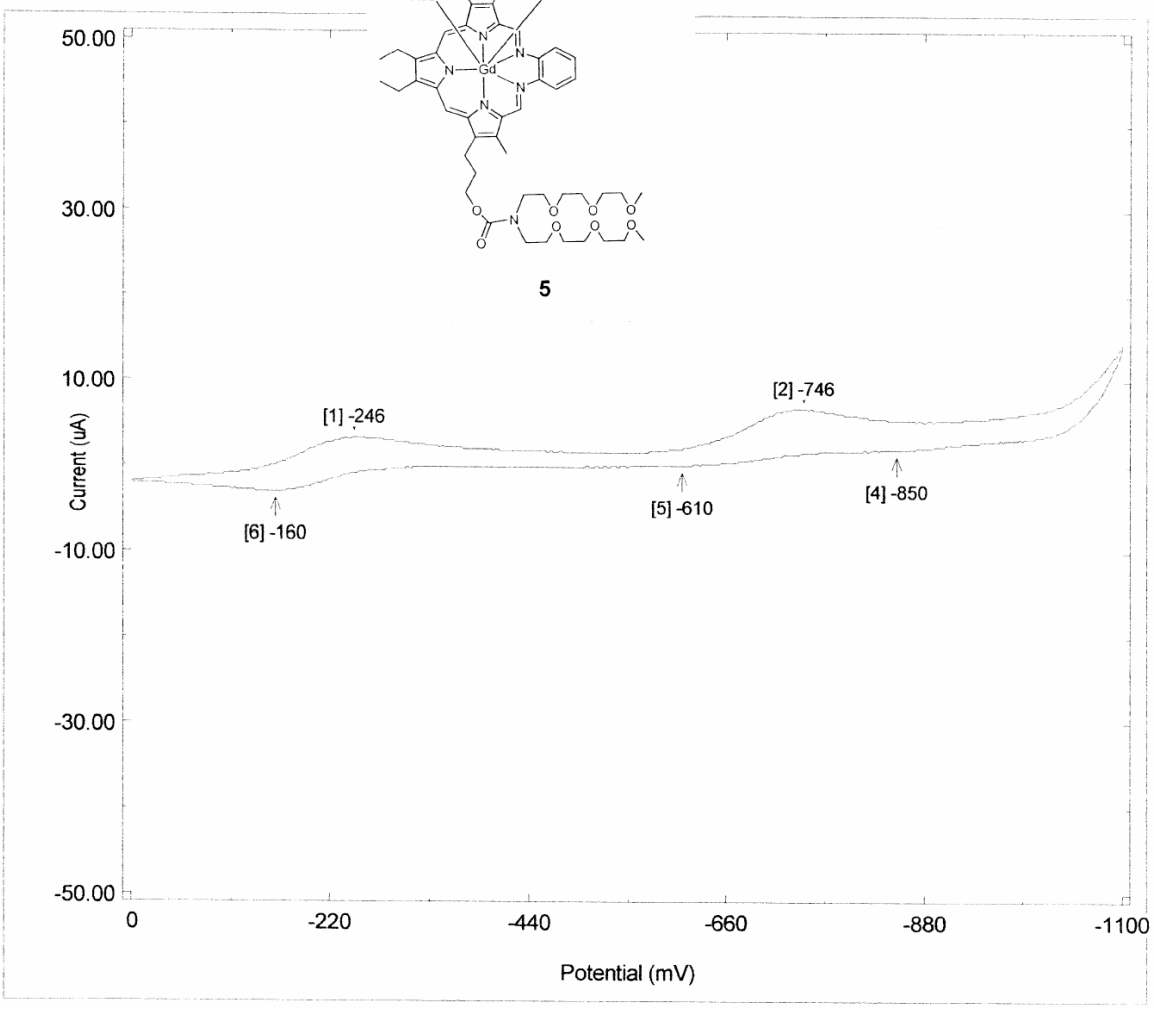

II: X-ray experimental for 14

X-ray Experimental for $(C_{36}H_{26}N_5O_2)Gd(NO_3)_2 - CH_3OH - ½\ C_6H_6$: Crystals grew as green prisms by slow evaporation from methanol-benzene. The data crystal was a prism that had approximate dimensions; 0.24 x 0.20 x 0.13 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 314 frames of data were collected using ω-scans with a scan range of 0.9° and a counting time of 49 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atom on the methanol oxygen atom was located in a ΔF map and refined with an isotropic displacement parameter. A molecule of benzene was found to be disordered around a crystallographic inversion center at 0, ½ , ½. The molecule was poorly resolved and its contribution to the scattering was removed using the utility, SQUEEZE.[4] The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0339*P)^2 + (1.0382*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0741, with R(F) equal to 0.0278 and a goodness of fit, S, = 1.145. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[5] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[6] All figures were generated using SHELXTL/PC.[7] Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through

7.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343-350.
3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
   $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
   $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
6) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
7) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Crystallographic Material for **1**.

X-ray Experimental.

Figure 1. View of **14** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Figure 2. Side view of **14**. Displacement ellipsoids are scaled to the 50% probability level. The Gd^{3+} ion is 0.698(1)Å out of the plane defined by the five nitrogen atoms of the texaphyrin macrocycle.

Figure 3. Unit cell packing diagram for **14**. The view is approximately down the **a** axis. The Gd-texaphyrin complex exists as H-bound dimers. The dimers are shown as ball-and-stick and wireframe pairs. The pairs are H-bound via the methanol hydroxyl group of one complex to a methoxy oxygen on an adjacent complex. The H-bonding geometry is: O1C-H1C···O34 (related by -x, -y, 1-z), O···O 2.791(3)Å, H···O 2.08(3)Å, O-H···O 155(3)°.

Table 1. Crystallographic Data for **14**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of **14**.

Table 3. Bond Lengths (Å) and Angles (°) for the non-hydrogen atoms of **14**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **14**.

Table 5. Fractional coordinates and isotropic thermal parameters (Å^2) for the hydrogen atoms of **14**.

Table 6. Torsion Angles (°) for the non-hydrogen atoms of **14**.

Figure 1. View of **14** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

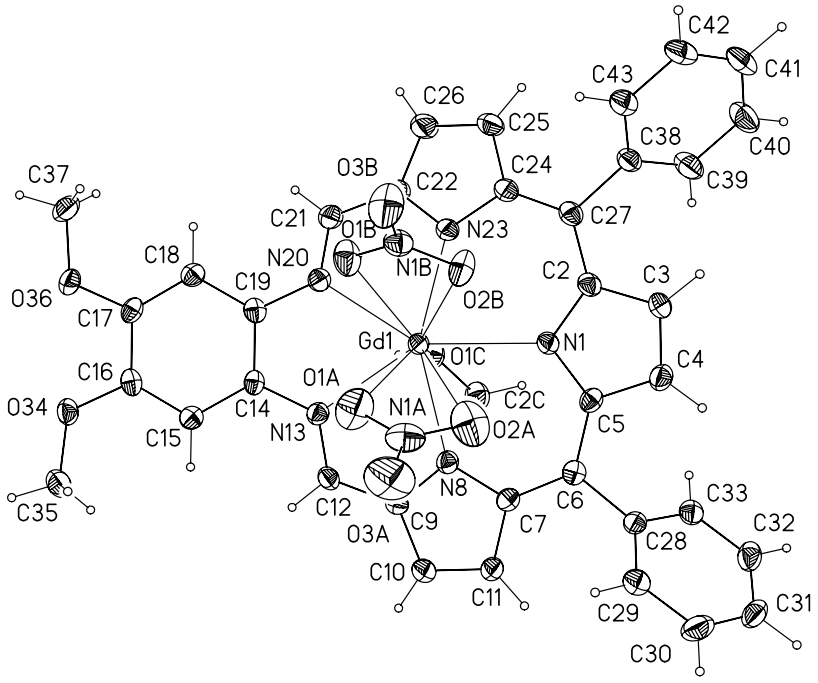

Figure 2. Side view of **14**. Displacement ellipsoids are scaled to the 50% probability level. The Gd^{3+} ion is 0.698(1)Å out of the plane defined by the five nitrogen atoms of the texaphyrin macrocycle.

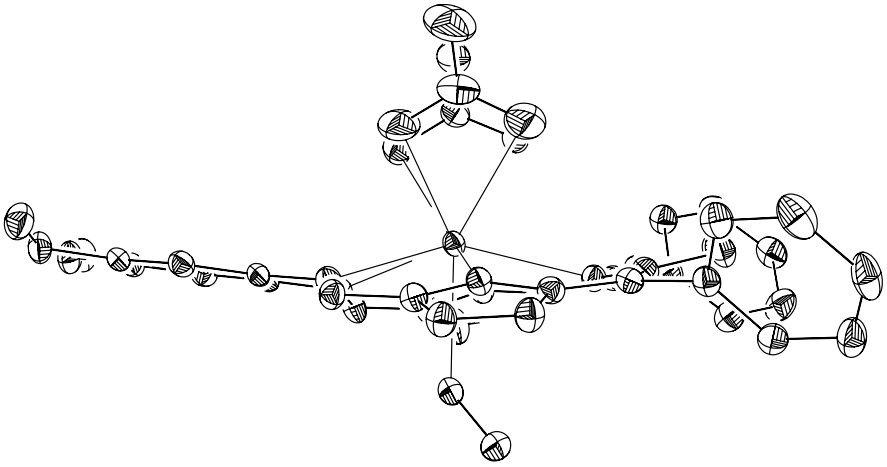

Figure 3. Unit cell packing diagram for **14**. The view is approximately down the **a** axis. The Gd-texaphyrin complex exists as H-bound dimers. The dimers are shown as ball-and-stick and wireframe pairs. The pairs are H-bound via the methanol hydroxyl group of one complex to a methoxy oxygen on an adjacent complex. The H-bonding geometry is: O1C-H1C···O34 (related by -x, -y, 1-z), O···O 2.791(3)Å, H···O 2.08(3)Å, O-H···O 155(3)°.

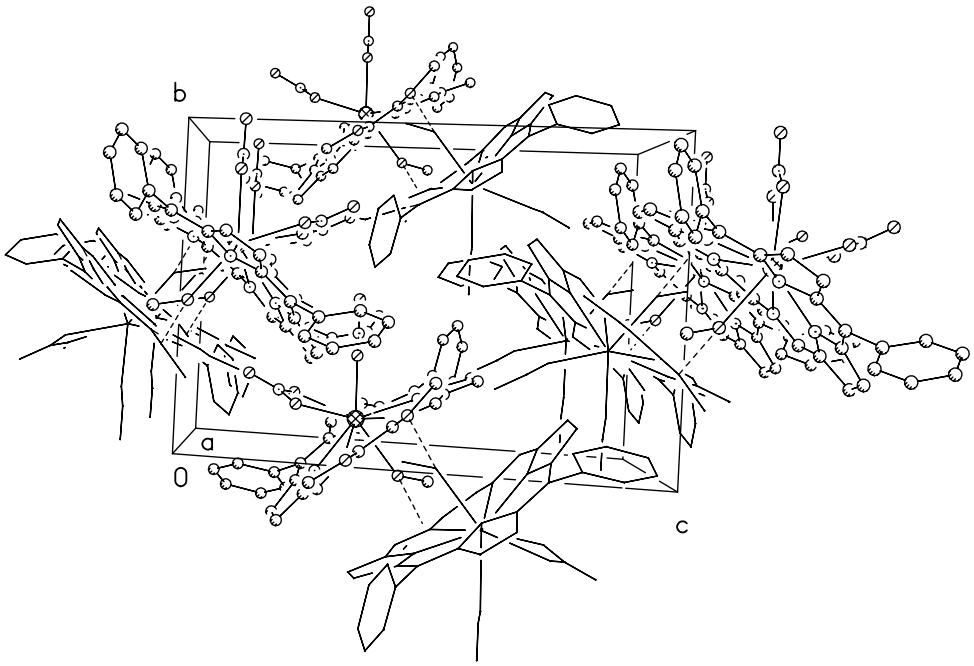

Table 1. Crystal data and structure refinement for 14.

Empirical formula	C40 H33 Gd N7 O9	
Formula weight	912.98	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 17.9235(2) Å	α= 90°.
	b = 11.9870(1) Å	β= 114.244(1)°.
	c = 18.7840(2) Å	γ = 90°.
Volume	3679.79(6) $Å^3$	
Z	4	
Density (calculated)	1.648 Mg/m^3	
Absorption coefficient	1.871 mm^{-1}	
F(000)	1832	
Crystal size	0.24 x 0.20 x 0.13 mm	
Theta range for data collection	2.92 to 27.50°.	
Index ranges	-23<=h<=23, -15<=k<=15, -24<=l<=23	
Reflections collected	14460	
Independent reflections	8372 [R(int) = 0.0171]	
Completeness to theta = 27.50°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8372 / 0 / 491	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0712	
R indices (all data)	R1 = 0.0362, wR2 = 0.0741	
Largest diff. peak and hole	1.38 and -1.05 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 14. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Gd1	1927(1)	1275(1)	3773(1)	18(1)

N1	3326(1)	911(2)	3857(1)	20(1)
C2	3468(2)	517(2)	3235(1)	22(1)
C3	4224(2)	965(2)	3266(2)	25(1)
C4	4555(2)	1587(2)	3924(2)	26(1)
C5	3999(2)	1551(2)	4294(1)	20(1)
C6	4171(2)	2091(2)	5028(1)	21(1)
C7	3636(2)	2216(2)	5391(1)	20(1)
N8	2824(1)	1941(2)	5053(1)	20(1)
C9	2514(2)	2145(2)	5581(1)	20(1)
C10	3135(2)	2566(2)	6294(1)	25(1)
C11	3833(2)	2615(2)	6183(1)	24(1)
C12	1670(2)	1905(2)	5389(1)	22(1)
N13	1244(1)	1448(2)	4715(1)	21(1)
C14	420(2)	1190(2)	4452(1)	19(1)
C15	-102(2)	1620(2)	4775(1)	21(1)
C16	-914(2)	1316(2)	4469(2)	21(1)
C17	-1234(1)	578(2)	3823(1)	21(1)
C18	-732(2)	153(2)	3495(1)	22(1)
C19	104(2)	444(2)	3812(1)	20(1)
N20	665(1)	64(2)	3528(1)	21(1)
C21	520(2)	-759(2)	3032(1)	26(1)
C22	1130(2)	-1000(2)	2748(2)	26(1)
N23	1798(1)	-351(2)	2963(1)	21(1)
C24	2245(2)	-728(2)	2568(1)	23(1)
C25	1828(2)	-1682(2)	2096(2)	31(1)
C26	1140(2)	-1850(2)	2212(2)	36(1)
C27	2988(2)	-271(2)	2654(1)	23(1)
C28	5010(2)	2565(2)	5432(1)	21(1)
C29	5118(2)	3698(2)	5615(2)	27(1)
C30	5900(2)	4146(3)	5949(2)	37(1)
C31	6580(2)	3475(3)	6105(2)	35(1)
C32	6479(2)	2352(3)	5946(2)	32(1)
C33	5700(2)	1893(2)	5616(1)	25(1)
O34	-1472(1)	1699(2)	4735(1)	25(1)
C35	-1247(2)	2641(2)	5259(2)	32(1)
O36	-2045(1)	375(2)	3566(1)	28(1)

C37	-2423(2)	-282(2)	2865(2)	32(1)
C38	3334(2)	-644(2)	2089(1)	24(1)
C39	4086(2)	-1172(2)	2337(2)	34(1)
C40	4412(2)	-1444(3)	1799(2)	38(1)
C41	3979(2)	-1199(2)	1018(2)	34(1)
C42	3225(2)	-686(2)	762(2)	32(1)
C43	2896(2)	-419(2)	1297(2)	29(1)
N1A	1937(2)	3832(2)	3747(1)	36(1)
O1A	1377(1)	3187(2)	3735(1)	47(1)
O2A	2563(2)	3390(2)	3753(1)	52(1)
O3A	1844(2)	4852(2)	3734(1)	61(1)
N1B	1076(1)	2054(2)	2138(1)	26(1)
O1B	682(1)	1686(2)	2509(1)	35(1)
O2B	1845(1)	1961(2)	2456(1)	33(1)
O3B	723(1)	2514(2)	1509(1)	47(1)
O1C	2399(1)	-374(2)	4710(1)	25(1)
C2C	3169(2)	-556(2)	5365(2)	30(1)

Table 3. Bond lengths [Å] and angles [°] for 14.

Gd1-N8	2.4142(19)	C3-H3	0.96
Gd1-N23	2.424(2)	C4-C5	1.431(4)
Gd1-O1A	2.484(2)	C4-H4	0.96
Gd1-N1	2.486(2)	C5-C6	1.438(3)
Gd1-N13	2.540(2)	C6-C7	1.394(3)
Gd1-O1C	2.5498(18)	C6-C28	1.492(3)
Gd1-O1B	2.5500(19)	C7-N8	1.368(3)
Gd1-O2B	2.5529(18)	C7-C11	1.461(3)
Gd1-N20	2.565(2)	N8-C9	1.343(3)
Gd1-O2A	2.786(3)	C9-C12	1.434(3)
N1-C2	1.377(3)	C9-C10	1.436(3)
N1-C5	1.380(3)	C10-C11	1.351(3)
C2-C27	1.432(3)	C10-H10	0.96
C2-C3	1.437(3)	C11-H11	0.96
C3-C4	1.354(4)	C12-N13	1.301(3)

C12-H12	0.96	C32-C33	1.388(4)
N13-C14	1.387(3)	C32-H32	0.96
C14-C15	1.404(3)	C33-H33	0.96
C14-C19	1.417(3)	O34-C35	1.443(3)
C15-C16	1.377(3)	C35-H35A	0.96
C15-H15	0.96	C35-H35B	0.96
C16-O34	1.367(3)	C35-H35C	0.96
C16-C17	1.419(4)	O36-C37	1.442(3)
C17-O36	1.353(3)	C37-H37A	0.96
C17-C18	1.380(3)	C37-H37B	0.96
C18-C19	1.411(3)	C37-H37C	0.96
C18-H18	0.96	C38-C39	1.387(4)
C19-N20	1.394(3)	C38-C43	1.393(4)
N20-C21	1.307(3)	C39-C40	1.397(4)
C21-C22	1.430(4)	C39-H39	0.96
C21-H21	0.96	C40-C41	1.381(4)
C22-N23	1.344(3)	C40-H40	0.96
C22-C26	1.437(4)	C41-C42	1.379(4)
N23-C24	1.372(3)	C41-H41	0.96
C24-C27	1.387(4)	C42-C43	1.395(4)
C24-C25	1.453(4)	C42-H42	0.96
C25-C26	1.353(4)	C43-H43	0.96
C25-H25	0.96	N1A-O3A	1.233(3)
C26-H26	0.96	N1A-O2A	1.236(3)
C27-C38	1.501(3)	N1A-O1A	1.260(3)
C28-C33	1.394(4)	N1B-O3B	1.220(3)
C28-C29	1.396(3)	N1B-O1B	1.257(3)
C29-C30	1.387(4)	N1B-O2B	1.263(3)
C29-H29	0.96	O1C-C2C	1.439(3)
C30-C31	1.388(4)	O1C-H1C	0.76(3)
C30-H30	0.96	C2C-H2CC	0.96
C31-C32	1.374(4)	C2C-H2CA	0.96
C31-H31	0.96	C2C-H2CB	0.96

N8-Gd1-N23	138.00(7)	N23-Gd1-O1A	142.16(7)
N8-Gd1-O1A	79.48(7)	N8-Gd1-N1	75.68(6)

N23-Gd1-N1	74.46(7)	N13-Gd1-O2A	104.60(7)
O1A-Gd1-N1	122.79(7)	O1C-Gd1-O2A	133.85(6)
N8-Gd1-N13	66.02(7)	O1B-Gd1-O2A	91.07(7)
N23-Gd1-N13	123.63(7)	O2B-Gd1-O2A	63.59(7)
O1A-Gd1-N13	69.26(7)	N20-Gd1-O2A	148.02(7)
N1-Gd1-N13	137.06(6)	C2-N1-C5	106.0(2)
N8-Gd1-O1C	70.85(6)	C2-N1-Gd1	122.64(15)
N23-Gd1-O1C	74.26(6)	C5-N1-Gd1	123.56(16)
O1A-Gd1-O1C	138.61(7)	N1-C2-C27	127.6(2)
N1-Gd1-O1C	77.29(6)	N1-C2-C3	109.7(2)
N13-Gd1-O1C	72.54(6)	C27-C2-C3	122.6(2)
N8-Gd1-O1B	146.48(7)	C4-C3-C2	107.1(2)
N23-Gd1-O1B	75.51(7)	C4-C3-H3	126.6
O1A-Gd1-O1B	67.09(7)	C2-C3-H3	126.3
N1-Gd1-O1B	124.52(6)	C3-C4-C5	107.2(2)
N13-Gd1-O1B	98.38(6)	C3-C4-H4	126.7
O1C-Gd1-O1B	135.06(6)	C5-C4-H4	126.1
N8-Gd1-O2B	127.45(6)	N1-C5-C4	109.9(2)
N23-Gd1-O2B	72.44(6)	N1-C5-C6	127.7(2)
O1A-Gd1-O2B	79.12(7)	C4-C5-C6	122.4(2)
N1-Gd1-O2B	76.86(6)	C7-C6-C5	126.7(2)
N13-Gd1-O2B	142.83(6)	C7-C6-C28	117.6(2)
O1C-Gd1-O2B	142.13(6)	C5-C6-C28	115.6(2)
O1B-Gd1-O2B	49.90(6)	N8-C7-C6	124.1(2)
N8-Gd1-N20	122.94(6)	N8-C7-C11	108.6(2)
N23-Gd1-N20	65.33(6)	C6-C7-C11	127.3(2)
O1A-Gd1-N20	101.96(7)	C9-N8-C7	107.23(19)
N1-Gd1-N20	134.76(7)	C9-N8-Gd1	119.16(15)
N13-Gd1-N20	61.96(6)	C7-N8-Gd1	133.57(15)
O1C-Gd1-N20	72.74(6)	N8-C9-C12	119.5(2)
O1B-Gd1-N20	64.69(6)	N8-C9-C10	110.8(2)
O2B-Gd1-N20	108.23(6)	C12-C9-C10	129.7(2)
N8-Gd1-O2A	66.63(7)	C11-C10-C9	106.5(2)
N23-Gd1-O2A	131.09(7)	C11-C10-H10	126.9
O1A-Gd1-O2A	47.15(8)	C9-C10-H10	126.6
N1-Gd1-O2A	75.68(7)	C10-C11-C7	106.9(2)

C10-C11-H11	126.6	C22-N23-Gd1	119.85(16)
C7-C11-H11	126.5	C24-N23-Gd1	132.70(16)
N13-C12-C9	117.7(2)	N23-C24-C27	123.5(2)
N13-C12-H12	120.9	N23-C24-C25	108.8(2)
C9-C12-H12	121.3	C27-C24-C25	127.6(2)
C12-N13-C14	123.6(2)	C26-C25-C24	107.0(2)
C12-N13-Gd1	117.05(16)	C26-C25-H25	125.8
C14-N13-Gd1	118.77(15)	C24-C25-H25	127.2
N13-C14-C15	124.4(2)	C25-C26-C22	106.4(2)
N13-C14-C19	116.0(2)	C25-C26-H26	127.2
C15-C14-C19	119.6(2)	C22-C26-H26	126.4
C16-C15-C14	120.0(2)	C24-C27-C2	126.7(2)
C16-C15-H15	120.2	C24-C27-C38	117.1(2)
C14-C15-H15	119.8	C2-C27-C38	116.2(2)
O34-C16-C15	124.5(2)	C33-C28-C29	118.8(2)
O34-C16-C17	115.0(2)	C33-C28-C6	120.9(2)
C15-C16-C17	120.5(2)	C29-C28-C6	120.3(2)
O36-C17-C18	125.1(2)	C30-C29-C28	120.0(3)
O36-C17-C16	114.5(2)	C30-C29-H29	120.4
C18-C17-C16	120.3(2)	C28-C29-H29	119.6
C17-C18-C19	119.6(2)	C29-C30-C31	120.5(3)
C17-C18-H18	120.2	C29-C30-H30	119.8
C19-C18-H18	120.1	C31-C30-H30	119.6
N20-C19-C18	124.4(2)	C32-C31-C30	119.7(3)
N20-C19-C14	115.6(2)	C32-C31-H31	120.3
C18-C19-C14	119.9(2)	C30-C31-H31	120.0
C21-N20-C19	123.8(2)	C31-C32-C33	120.3(3)
C21-N20-Gd1	117.26(16)	C31-C32-H32	119.9
C19-N20-Gd1	117.86(15)	C33-C32-H32	119.8
N20-C21-C22	117.4(2)	C32-C33-C28	120.6(3)
N20-C21-H21	121.0	C32-C33-H33	120.1
C22-C21-H21	121.6	C28-C33-H33	119.3
N23-C22-C21	119.6(2)	C16-O34-C35	118.1(2)
N23-C22-C26	110.8(2)	O34-C35-H35A	109.0
C21-C22-C26	129.5(2)	O34-C35-H35B	109.5
C22-N23-C24	107.0(2)	H35A-C35-H35B	109.5

O34-C35-H35C	109.9	C38-C43-C42	120.4(3)
H35A-C35-H35C	109.5	C38-C43-H43	119.7
H35B-C35-H35C	109.5	C42-C43-H43	119.9
C17-O36-C37	117.3(2)	O3A-N1A-O2A	122.7(3)
O36-C37-H37A	109.4	O3A-N1A-O1A	120.5(3)
O36-C37-H37B	109.6	O2A-N1A-O1A	116.8(3)
H37A-C37-H37B	109.5	N1A-O1A-Gd1	105.19(18)
O36-C37-H37C	109.5	N1A-O2A-Gd1	90.85(18)
H37A-C37-H37C	109.5	O3B-N1B-O1B	120.7(2)
H37B-C37-H37C	109.5	O3B-N1B-O2B	121.9(2)
C39-C38-C43	119.4(2)	O1B-N1B-O2B	117.3(2)
C39-C38-C27	121.7(2)	O3B-N1B-Gd1	171.19(19)
C43-C38-C27	118.9(2)	O1B-N1B-Gd1	58.83(12)
C38-C39-C40	120.1(3)	O2B-N1B-Gd1	58.99(12)
C38-C39-H39	119.7	N1B-O1B-Gd1	96.22(14)
C40-C39-H39	120.1	N1B-O2B-Gd1	95.92(14)
C41-C40-C39	120.0(3)	C2C-O1C-Gd1	129.60(16)
C41-C40-H40	120.1	C2C-O1C-H1C	109(3)
C39-C40-H40	119.9	Gd1-O1C-H1C	111(3)
C42-C41-C40	120.5(3)	O1C-C2C-H2CC	109.6
C42-C41-H41	119.8	O1C-C2C-H2CA	109.8
C40-C41-H41	119.8	H2CC-C2C-H2CA	109.7
C41-C42-C43	119.7(3)	O1C-C2C-H2CB	109.8
C41-C42-H42	119.9	H2CC-C2C-H2CB	109.7
C43-C42-H42	120.4	H2CA-C2C-H2CB	108.2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Gd1	17(1)	21(1)	15(1)	0(1)	8(1)	-2(1)
N1	19(1)	24(1)	17(1)	0(1)	8(1)	0(1)
C2	23(1)	26(1)	17(1)	1(1)	10(1)	1(1)
C3	25(1)	33(1)	22(1)	-2(1)	14(1)	-4(1)
C4	21(1)	33(1)	23(1)	1(1)	10(1)	-5(1)

C5	20(1)	22(1)	19(1)	2(1)	7(1)	-2(1)
C6	21(1)	20(1)	21(1)	3(1)	9(1)	0(1)
C7	20(1)	20(1)	20(1)	0(1)	8(1)	-1(1)
N8	20(1)	23(1)	20(1)	0(1)	9(1)	-1(1)
C9	21(1)	21(1)	19(1)	-2(1)	9(1)	-1(1)
C10	25(1)	29(2)	22(1)	-4(1)	11(1)	0(1)
C11	20(1)	30(1)	21(1)	-4(1)	7(1)	-2(1)
C12	22(1)	26(1)	22(1)	-1(1)	12(1)	2(1)
N13	19(1)	22(1)	20(1)	0(1)	8(1)	-1(1)
C14	17(1)	22(1)	19(1)	5(1)	9(1)	0(1)
C15	22(1)	23(1)	19(1)	2(1)	9(1)	-1(1)
C16	21(1)	23(1)	23(1)	7(1)	13(1)	3(1)
C17	17(1)	24(1)	21(1)	5(1)	7(1)	-2(1)
C18	22(1)	23(1)	20(1)	2(1)	7(1)	-1(1)
C19	22(1)	23(1)	18(1)	6(1)	11(1)	2(1)
N20	21(1)	23(1)	20(1)	0(1)	9(1)	-2(1)
C21	25(1)	29(1)	27(1)	-5(1)	14(1)	-9(1)
C22	27(1)	28(1)	26(1)	-6(1)	14(1)	-8(1)
N23	21(1)	24(1)	19(1)	-1(1)	9(1)	-1(1)
C24	25(1)	27(1)	19(1)	0(1)	10(1)	-1(1)
C25	34(2)	32(1)	31(2)	-13(1)	19(1)	-7(1)
C26	38(2)	35(2)	41(2)	-16(1)	22(1)	-14(1)
C27	25(1)	25(1)	19(1)	2(1)	11(1)	2(1)
C28	21(1)	28(1)	15(1)	0(1)	7(1)	-2(1)
C29	28(1)	30(2)	26(1)	-3(1)	13(1)	-2(1)
C30	41(2)	38(2)	33(2)	-10(1)	15(1)	-18(1)
C31	25(1)	57(2)	23(1)	-7(1)	9(1)	-17(1)
C32	21(1)	51(2)	22(1)	2(1)	8(1)	-2(1)
C33	24(1)	33(2)	18(1)	2(1)	8(1)	1(1)
O34	21(1)	28(1)	30(1)	-1(1)	15(1)	-1(1)
C35	31(2)	30(1)	41(2)	-5(1)	20(1)	1(1)
O36	17(1)	37(1)	29(1)	-2(1)	9(1)	-3(1)
C37	22(1)	46(2)	25(1)	-2(1)	5(1)	-5(1)
C38	29(1)	25(1)	23(1)	-5(1)	16(1)	-5(1)
C39	37(2)	43(2)	25(2)	0(1)	16(1)	9(1)
C40	39(2)	46(2)	34(2)	-1(1)	21(1)	15(1)
C41	48(2)	36(2)	30(2)	-5(1)	27(1)	0(1)

C42	43(2)	36(2)	21(1)	-3(1)	16(1)	-1(1)
C43	31(1)	33(2)	25(1)	-2(1)	13(1)	0(1)
N1A	49(2)	27(1)	27(2)	2(1)	11(1)	0(1)
O1A	46(1)	24(1)	68(2)	8(1)	19(1)	-2(1)
O2A	59(2)	57(1)	48(1)	19(1)	29(1)	13(1)
O3A	87(2)	25(1)	78(2)	0(1)	42(2)	-7(1)
N1B	30(1)	29(1)	21(1)	2(1)	11(1)	0(1)
O1B	31(1)	50(1)	29(1)	14(1)	17(1)	6(1)
O2B	21(1)	40(1)	35(1)	11(1)	10(1)	0(1)
O3B	36(1)	72(2)	30(1)	28(1)	11(1)	11(1)
O1C	22(1)	29(1)	27(1)	5(1)	12(1)	0(1)
C2C	27(1)	34(2)	30(1)	6(1)	12(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 14.

	x	y	z	U(eq)
H3	4451	845	2889	30
H4	5065	1981	4109	31
H10	3067	2765	6758	30
H11	4358	2868	6553	29
H12	1425	2077	5744	27
H15	109	2129	5207	25
H18	-949	-344	3056	26
H21	20	-1178	2863	31
H25	2001	-2119	1762	37
H26	735	-2420	1984	43
H29	4649	4162	5513	33
H30	5972	4927	6070	45
H31	7119	3795	6323	42
H32	6949	1882	6065	38
H33	5631	1108	5508	30
H35A	-1692	2812	5401	48
H35B	-769	2460	5720	48
H35C	-1134	3276	5008	48
H37A	-2995	-366	2742	49

H37B	-2357	86	2441	49
H37C	-2170	-1004	2946	49
H39	4389	-1333	2881	41
H40	4930	-1819	1972	46
H41	4209	-1374	651	41
H42	2927	-522	217	39
H43	2366	-78	1120	35
H2CC	3584	-104	5309	45
H2CA	3318	-1329	5390	45
H2CB	3121	-366	5841	45
H1C	2050(20)	-570(30)	4818(19)	45(11)

Table 6. Torsion angles [°] for the macrocycle in 14.

C5-N1-C2-C27	173.5(2)	N8-C9-C10-C11	0.1(3)
C5-N1-C2-C3	-2.9(3)	C12-C9-C10-C11	178.3(3)
N1-C2-C3-C4	2.7(3)	C9-C10-C11-C7	-0.1(3)
C27-C2-C3-C4	-173.9(2)	N8-C7-C11-C10	0.0(3)
C2-C3-C4-C5	-1.3(3)	C6-C7-C11-C10	-178.2(2)
C2-N1-C5-C4	2.1(3)	N8-C9-C12-N13	3.0(3)
C2-N1-C5-C6	-175.9(2)	C10-C9-C12-N13	-175.0(2)
C3-C4-C5-N1	-0.4(3)	C9-C12-N13-C14	-178.9(2)
C3-C4-C5-C6	177.7(2)	C12-N13-C14-C15	16.3(4)
N1-C5-C6-C7	-10.2(4)	C12-N13-C14-C19	-164.0(2)
C4-C5-C6-C7	172.0(2)	N13-C14-C15-C16	179.7(2)
N1-C5-C6-C28	170.0(2)	C19-C14-C15-C16	0.1(3)
C4-C5-C6-C28	-7.8(3)	C14-C15-C16-O34	-179.2(2)
C5-C6-C7-N8	-7.6(4)	C14-C15-C16-C17	-0.7(4)
C28-C6-C7-N8	172.2(2)	O34-C16-C17-O36	0.6(3)
C5-C6-C7-C11	170.4(2)	C15-C16-C17-O36	-178.1(2)
C28-C6-C7-C11	-9.8(4)	O34-C16-C17-C18	178.8(2)
C6-C7-N8-C9	178.3(2)	C15-C16-C17-C18	0.2(4)
C11-C7-N8-C9	0.0(3)	O36-C17-C18-C19	179.0(2)
C7-N8-C9-C12	-178.5(2)	C16-C17-C18-C19	0.9(4)
C7-N8-C9-C10	-0.1(3)	C17-C18-C19-N20	180.0(2)

C17-C18-C19-C14	-1.5(3)	C31-C32-C33-C28	0.8(4)
N13-C14-C19-N20	0.0(3)	C29-C28-C33-C32	-2.6(4)
C15-C14-C19-N20	179.7(2)	C6-C28-C33-C32	175.8(2)
N13-C14-C19-C18	-178.6(2)	C15-C16-O34-C35	13.0(3)
C15-C14-C19-C18	1.0(3)	C17-C16-O34-C35	-165.6(2)
C18-C19-N20-C21	-13.2(4)	C18-C17-O36-C37	-4.0(3)
C14-C19-N20-C21	168.2(2)	C16-C17-O36-C37	174.2(2)
C19-N20-C21-C22	175.4(2)	C24-C27-C38-C39	-119.6(3)
N20-C21-C22-N23	-3.3(4)	C2-C27-C38-C39	59.7(3)
N20-C21-C22-C26	179.4(3)	C24-C27-C38-C43	62.5(3)
C21-C22-N23-C24	-176.2(2)	C2-C27-C38-C43	-118.2(3)
C26-C22-N23-C24	1.6(3)	C43-C38-C39-C40	2.0(4)
C22-N23-C24-C27	-178.8(2)	C27-C38-C39-C40	-175.9(3)
C22-N23-C24-C25	-1.3(3)	C38-C39-C40-C41	-0.8(5)
N23-C24-C25-C26	0.5(3)	C39-C40-C41-C42	0.0(5)
C27-C24-C25-C26	177.9(3)	C40-C41-C42-C43	-0.3(4)
C24-C25-C26-C22	0.4(3)	C39-C38-C43-C42	-2.3(4)
N23-C22-C26-C25	-1.3(3)	C27-C38-C43-C42	175.7(2)
C21-C22-C26-C25	176.3(3)	C41-C42-C43-C38	1.5(4)
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C25-C24-C27-C2	-166.4(3)		
N23-C24-C27-C38	-170.1(2)		
C25-C24-C27-C38	12.8(4)		
N1-C2-C27-C24	5.5(4)		
C3-C2-C27-C24	-178.5(2)		
N1-C2-C27-C38	-173.8(2)		
C3-C2-C27-C38	2.2(4)		
C7-C6-C28-C33	123.5(3)		
C5-C6-C28-C33	-56.6(3)		
C7-C6-C28-C29	-58.0(3)		
C5-C6-C28-C29	121.8(3)		
C33-C28-C29-C30	2.2(4)		
C6-C28-C29-C30	-176.2(2)		
C28-C29-C30-C31	0.0(4)		
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_diffrn_reflns_theta_min          2.92
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_reflns_number_total              8372
_reflns_number_gt                 6989
_reflns_threshold_expression      >2sigma(I)
_computing_structure_solution     'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
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_refine_special_details
;
 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^ > 2sigma(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.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0339P)^2^+1.0382P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          8372
_refine_ls_number_parameters      491
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_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0362
_refine_ls_R_factor_gt            0.0278
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_refine_ls_wR_factor_gt           0.0712
_refine_ls_goodness_of_fit_ref    1.145
_refine_ls_restrained_S_all       1.145
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Gd1 Gd 0.192661(7) 0.127545(9) 0.377274(6) 0.01767(5) Uani 1 1 d . . .
N1 N 0.33259(12) 0.09114(18) 0.38567(11) 0.0200(4) Uani 1 1 d . . .
C2 C 0.34678(15) 0.0517(2) 0.32347(13) 0.0215(5) Uani 1 1 d . . .
C3 C 0.42240(16) 0.0965(2) 0.32655(15) 0.0254(5) Uani 1 1 d . . .
H3 H 0.4451 0.0845 0.2889 0.030 Uiso 1 1 d R . .
C4 C 0.45545(16) 0.1587(2) 0.39236(15) 0.0256(6) Uani 1 1 d . . .
H4 H 0.5065 0.1981 0.4109 0.031 Uiso 1 1 d R . .
C5 C 0.39989(15) 0.1551(2) 0.42941(14) 0.0204(5) Uani 1 1 d . . .
C6 C 0.41706(15) 0.2091(2) 0.50282(13) 0.0207(5) Uani 1 1 d . . .
C7 C 0.36359(15) 0.2216(2) 0.53912(13) 0.0200(5) Uani 1 1 d . . .
N8 N 0.28241(12) 0.19411(16) 0.50527(11) 0.0203(4) Uani 1 1 d . . .
C9 C 0.25144(15) 0.2145(2) 0.55806(13) 0.0201(5) Uani 1 1 d . . .
C10 C 0.31353(15) 0.2566(2) 0.62935(14) 0.0247(6) Uani 1 1 d . . .
H10 H 0.3067 0.2765 0.6758 0.030 Uiso 1 1 d R . .
C11 C 0.38332(16) 0.2615(2) 0.61831(14) 0.0241(5) Uani 1 1 d . . .
H11 H 0.4358 0.2868 0.6553 0.029 Uiso 1 1 d R . .
C12 C 0.16700(15) 0.1905(2) 0.53892(14) 0.0221(5) Uani 1 1 d . . .
H12 H 0.1425 0.2077 0.5744 0.027 Uiso 1 1 d R . .
N13 N 0.12443(13) 0.14479(16) 0.47152(12) 0.0205(4) Uani 1 1 d . . .
C14 C 0.04198(15) 0.11898(19) 0.44524(14) 0.0188(5) Uani 1 1 d . . .
C15 C -0.01019(15) 0.1620(2) 0.47748(14) 0.0209(5) Uani 1 1 d . . .
H15 H 0.0109 0.2129 0.5207 0.025 Uiso 1 1 d R . .
C16 C -0.09141(15) 0.13164(19) 0.44693(15) 0.0208(5) Uani 1 1 d . . .
C17 C -0.12335(14) 0.0578(2) 0.38231(13) 0.0211(5) Uani 1 1 d . . .
C18 C -0.07318(15) 0.0153(2) 0.34948(14) 0.0219(5) Uani 1 1 d . . .
H18 H -0.0949 -0.0344 0.3056 0.026 Uiso 1 1 d R . .
C19 C 0.01044(15) 0.0444(2) 0.38120(13) 0.0203(5) Uani 1 1 d . . .
N20 N 0.06648(12) 0.00642(17) 0.35275(11) 0.0211(4) Uani 1 1 d . . .
C21 C 0.05200(16) -0.0759(2) 0.30324(14) 0.0262(6) Uani 1 1 d . . .
H21 H 0.0020 -0.1178 0.2863 0.031 Uiso 1 1 d R . .
C22 C 0.11296(16) -0.1000(2) 0.27476(15) 0.0260(6) Uani 1 1 d . . .
N23 N 0.17984(12) -0.03507(17) 0.29634(11) 0.0208(4) Uani 1 1 d . . .
C24 C 0.22446(15) -0.0728(2) 0.25684(14) 0.0228(5) Uani 1 1 d . . .
C25 C 0.18277(17) -0.1682(2) 0.20957(16) 0.0306(6) Uani 1 1 d . . .
H25 H 0.2001 -0.2119 0.1762 0.037 Uiso 1 1 d R . .
C26 C 0.11395(18) -0.1850(2) 0.22121(17) 0.0359(7) Uani 1 1 d . . .
```

```
H26 H 0.0735 -0.2420 0.1984 0.043 Uiso 1 1 d R . .
C27 C 0.29877(15) -0.0271(2) 0.26541(14) 0.0226(5) Uani 1 1 d . . .
C28 C 0.50104(15) 0.2565(2) 0.54319(13) 0.0210(5) Uani 1 1 d . . .
C29 C 0.51180(18) 0.3698(2) 0.56150(16) 0.0274(6) Uani 1 1 d . . .
H29 H 0.4649 0.4162 0.5513 0.033 Uiso 1 1 d R . .
C30 C 0.58998(19) 0.4146(3) 0.59491(17) 0.0374(7) Uani 1 1 d . . .
H30 H 0.5972 0.4927 0.6070 0.045 Uiso 1 1 d R . .
C31 C 0.65804(17) 0.3475(3) 0.61048(16) 0.0349(7) Uani 1 1 d . . .
H31 H 0.7119 0.3795 0.6323 0.042 Uiso 1 1 d R . .
C32 C 0.64791(17) 0.2352(3) 0.59461(15) 0.0317(6) Uani 1 1 d . . .
H32 H 0.6949 0.1882 0.6065 0.038 Uiso 1 1 d R . .
C33 C 0.56998(15) 0.1893(2) 0.56160(13) 0.0248(5) Uani 1 1 d . . .
H33 H 0.5631 0.1108 0.5508 0.030 Uiso 1 1 d R . .
O34 O -0.14718(10) 0.16988(15) 0.47352(10) 0.0249(4) Uani 1 1 d . . .
C35 C -0.12470(17) 0.2641(2) 0.52592(17) 0.0320(6) Uani 1 1 d . . .
H35A H -0.1692 0.2812 0.5401 0.048 Uiso 1 1 d R . .
H35B H -0.0769 0.2460 0.5720 0.048 Uiso 1 1 d R . .
H35C H -0.1134 0.3276 0.5008 0.048 Uiso 1 1 d R . .
O36 O -0.20448(10) 0.03748(15) 0.35656(10) 0.0275(4) Uani 1 1 d . . .
C37 C -0.24229(16) -0.0282(2) 0.28650(15) 0.0323(6) Uani 1 1 d . . .
H37A H -0.2995 -0.0366 0.2742 0.049 Uiso 1 1 d R . .
H37B H -0.2357 0.0086 0.2441 0.049 Uiso 1 1 d R . .
H37C H -0.2170 -0.1004 0.2946 0.049 Uiso 1 1 d R . .
C38 C 0.33337(16) -0.0644(2) 0.20888(14) 0.0242(5) Uani 1 1 d . . .
C39 C 0.40864(19) -0.1172(2) 0.23368(17) 0.0338(7) Uani 1 1 d . . .
H39 H 0.4389 -0.1333 0.2881 0.041 Uiso 1 1 d R . .
C40 C 0.4412(2) -0.1444(3) 0.17992(18) 0.0381(7) Uani 1 1 d . . .
H40 H 0.4930 -0.1819 0.1972 0.046 Uiso 1 1 d R . .
C41 C 0.3979(2) -0.1199(2) 0.10176(17) 0.0342(7) Uani 1 1 d . . .
H41 H 0.4209 -0.1374 0.0651 0.041 Uiso 1 1 d R . .
C42 C 0.32251(18) -0.0686(2) 0.07621(16) 0.0322(6) Uani 1 1 d . . .
H42 H 0.2927 -0.0522 0.0217 0.039 Uiso 1 1 d R . .
C43 C 0.28962(17) -0.0419(2) 0.12971(15) 0.0291(6) Uani 1 1 d . . .
H43 H 0.2366 -0.0078 0.1120 0.035 Uiso 1 1 d R . .
N1A N 0.19374(16) 0.3832(2) 0.37472(13) 0.0356(7) Uani 1 1 d . . .
O1A O 0.13774(14) 0.31871(17) 0.37354(14) 0.0474(6) Uani 1 1 d . . .
O2A O 0.25633(16) 0.3390(2) 0.37534(14) 0.0524(6) Uani 1 1 d . . .
O3A O 0.18440(16) 0.4852(2) 0.37344(14) 0.0607(7) Uani 1 1 d . . .
N1B N 0.10757(14) 0.20536(18) 0.21382(12) 0.0262(5) Uani 1 1 d . . .
O1B O 0.06824(12) 0.16857(18) 0.25090(11) 0.0354(5) Uani 1 1 d . . .
O2B O 0.18453(11) 0.19611(16) 0.24561(11) 0.0325(4) Uani 1 1 d . . .
O3B O 0.07229(13) 0.2514(2) 0.15087(12) 0.0470(6) Uani 1 1 d . . .
O1C O 0.23988(12) -0.03738(15) 0.47102(10) 0.0252(4) Uani 1 1 d . . .
C2C C 0.31692(16) -0.0556(2) 0.53647(15) 0.0300(6) Uani 1 1 d . . .
H2CC H 0.3584 -0.0104 0.5309 0.045 Uiso 1 1 d R . .
H2CA H 0.3318 -0.1329 0.5390 0.045 Uiso 1 1 d R . .
H2CB H 0.3121 -0.0366 0.5841 0.045 Uiso 1 1 d R . .
H1C H 0.205(2) -0.057(3) 0.4818(19) 0.045(11) Uiso 1 1 d . . .

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Gd1 0.01700(8) 0.02149(8) 0.01543(8) -0.00011(4) 0.00758(5) -0.00174(4)
N1 0.0190(10) 0.0244(11) 0.0171(10) -0.0001(8) 0.0081(8) 0.0002(9)
C2 0.0225(12) 0.0259(13) 0.0174(12) 0.0011(10) 0.0095(10) 0.0009(10)
```

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C3 0.0252(13) 0.0331(14) 0.0223(13) -0.0020(11) 0.0144(11) -0.0039(11)
C4 0.0209(13) 0.0332(14) 0.0232(13) 0.0007(11) 0.0097(11) -0.0048(11)
C5 0.0195(12) 0.0215(12) 0.0193(12) 0.0020(10) 0.0072(10) -0.0024(10)
C6 0.0212(12) 0.0199(12) 0.0211(12) 0.0031(10) 0.0089(10) -0.0002(10)
C7 0.0200(12) 0.0196(12) 0.0201(12) 0.0002(10) 0.0079(10) -0.0010(10)
N8 0.0195(10) 0.0229(11) 0.0195(10) -0.0002(8) 0.0090(8) -0.0014(8)
C9 0.0213(12) 0.0209(12) 0.0186(12) -0.0018(10) 0.0086(10) -0.0006(10)
C10 0.0246(14) 0.0294(15) 0.0216(14) -0.0038(10) 0.0109(11) -0.0003(10)
C11 0.0201(13) 0.0301(14) 0.0205(12) -0.0037(10) 0.0068(10) -0.0022(10)
C12 0.0217(13) 0.0257(13) 0.0216(12) -0.0008(10) 0.0116(10) 0.0019(10)
N13 0.0191(11) 0.0224(11) 0.0203(11) 0.0000(8) 0.0083(9) -0.0013(8)
C14 0.0170(12) 0.0218(12) 0.0188(12) 0.0053(9) 0.0086(10) 0.0004(9)
C15 0.0216(13) 0.0232(12) 0.0186(12) 0.0022(10) 0.0088(10) -0.0006(10)
C16 0.0211(13) 0.0225(13) 0.0228(13) 0.0071(9) 0.0130(10) 0.0029(10)
C17 0.0171(12) 0.0241(12) 0.0212(12) 0.0049(10) 0.0071(10) -0.0017(10)
C18 0.0223(12) 0.0226(12) 0.0196(12) 0.0021(10) 0.0074(10) -0.0009(10)
C19 0.0217(12) 0.0234(12) 0.0179(12) 0.0055(10) 0.0105(10) 0.0017(10)
N20 0.0211(11) 0.0233(11) 0.0198(10) 0.0002(8) 0.0094(9) -0.0021(9)
C21 0.0254(13) 0.0294(14) 0.0273(13) -0.0053(11) 0.0144(11) -0.0087(11)
C22 0.0273(14) 0.0283(13) 0.0257(14) -0.0061(11) 0.0142(11) -0.0079(11)
N23 0.0214(11) 0.0237(11) 0.0186(10) -0.0009(8) 0.0094(8) -0.0010(9)
C24 0.0248(13) 0.0266(13) 0.0185(12) -0.0004(10) 0.0104(10) -0.0006(11)
C25 0.0342(15) 0.0320(14) 0.0309(15) -0.0128(12) 0.0188(12) -0.0073(13)
C26 0.0378(17) 0.0352(16) 0.0405(16) -0.0162(13) 0.0219(14) -0.0143(13)
C27 0.0249(13) 0.0252(13) 0.0191(12) 0.0016(10) 0.0106(10) 0.0023(11)
C28 0.0206(13) 0.0277(13) 0.0147(12) -0.0002(9) 0.0073(10) -0.0018(10)
C29 0.0280(14) 0.0301(15) 0.0256(14) -0.0030(10) 0.0125(12) -0.0017(11)
C30 0.0414(18) 0.0384(16) 0.0326(16) -0.0098(13) 0.0153(13) -0.0176(14)
C31 0.0247(14) 0.0567(19) 0.0225(14) -0.0070(13) 0.0089(11) -0.0169(14)
C32 0.0211(13) 0.0511(18) 0.0223(13) 0.0017(12) 0.0083(11) -0.0015(13)
C33 0.0240(13) 0.0329(15) 0.0175(12) 0.0020(10) 0.0084(10) 0.0010(11)
O34 0.0207(9) 0.0279(9) 0.0303(10) -0.0012(8) 0.0148(8) -0.0012(8)
C35 0.0306(15) 0.0297(14) 0.0407(16) -0.0053(12) 0.0197(13) 0.0012(12)
O36 0.0169(9) 0.0366(11) 0.0290(9) -0.0022(8) 0.0092(7) -0.0034(8)
C37 0.0218(13) 0.0458(17) 0.0249(14) -0.0021(12) 0.0049(11) -0.0049(12)
C38 0.0289(14) 0.0252(13) 0.0234(13) -0.0045(10) 0.0157(11) -0.0049(11)
C39 0.0365(16) 0.0434(17) 0.0251(15) 0.0002(12) 0.0164(13) 0.0088(13)
C40 0.0392(17) 0.0464(18) 0.0341(17) -0.0006(13) 0.0205(14) 0.0151(14)
C41 0.0476(19) 0.0357(16) 0.0298(15) -0.0052(12) 0.0265(14) -0.0004(13)
C42 0.0425(17) 0.0356(16) 0.0213(13) -0.0028(12) 0.0160(12) -0.0008(13)
C43 0.0306(14) 0.0334(15) 0.0251(14) -0.0019(11) 0.0130(12) 0.0000(12)
N1A 0.0488(19) 0.0268(14) 0.0271(15) 0.0017(9) 0.0114(13) 0.0002(11)
O1A 0.0464(13) 0.0240(11) 0.0679(15) 0.0080(10) 0.0194(12) -0.0016(10)
O2A 0.0590(16) 0.0570(14) 0.0482(14) 0.0192(12) 0.0293(12) 0.0128(13)
O3A 0.087(2) 0.0250(12) 0.0784(19) 0.0003(11) 0.0421(16) -0.0069(11)
N1B 0.0296(12) 0.0288(12) 0.0206(11) 0.0019(9) 0.0105(10) -0.0002(10)
O1B 0.0314(11) 0.0503(12) 0.0287(10) 0.0137(9) 0.0167(9) 0.0062(10)
O2B 0.0212(10) 0.0400(11) 0.0349(10) 0.0113(9) 0.0099(8) -0.0002(8)
O3B 0.0360(12) 0.0724(16) 0.0298(11) 0.0283(11) 0.0107(10) 0.0105(11)
O1C 0.0222(9) 0.0289(10) 0.0266(10) 0.0050(8) 0.0124(8) -0.0002(8)
C2C 0.0266(14) 0.0337(15) 0.0297(14) 0.0062(12) 0.0115(11) 0.0047(12)

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;
 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.
;

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Gd1 N8 2.4142(19) . ?
Gd1 N23 2.424(2) . ?
Gd1 O1A 2.484(2) . ?
Gd1 N1 2.486(2) . ?
Gd1 N13 2.540(2) . ?
Gd1 O1C 2.5498(18) . ?
Gd1 O1B 2.5500(19) . ?
Gd1 O2B 2.5529(18) . ?
Gd1 N20 2.565(2) . ?
Gd1 O2A 2.786(3) . ?
Gd1 N1B 2.963(2) . ?
N1 C2 1.377(3) . ?
N1 C5 1.380(3) . ?
C2 C27 1.432(3) . ?
C2 C3 1.437(3) . ?
C3 C4 1.354(4) . ?
C3 H3 0.9600 . ?
C4 C5 1.431(4) . ?
C4 H4 0.9598 . ?
C5 C6 1.438(3) . ?
C6 C7 1.394(3) . ?
C6 C28 1.492(3) . ?
C7 N8 1.368(3) . ?
C7 C11 1.461(3) . ?
N8 C9 1.343(3) . ?
C9 C12 1.434(3) . ?
C9 C10 1.436(3) . ?
C10 C11 1.351(3) . ?
C10 H10 0.9600 . ?
C11 H11 0.9600 . ?
C12 N13 1.301(3) . ?
C12 H12 0.9600 . ?
N13 C14 1.387(3) . ?
C14 C15 1.404(3) . ?
C14 C19 1.417(3) . ?
C15 C16 1.377(3) . ?
C15 H15 0.9600 . ?
C16 O34 1.367(3) . ?
C16 C17 1.419(4) . ?
C17 O36 1.353(3) . ?
C17 C18 1.380(3) . ?
C18 C19 1.411(3) . ?
C18 H18 0.9600 . ?
C19 N20 1.394(3) . ?
N20 C21 1.307(3) . ?
C21 C22 1.430(4) . ?
C21 H21 0.9602 . ?
C22 N23 1.344(3) . ?
C22 C26 1.437(4) . ?
N23 C24 1.372(3) . ?
C24 C27 1.387(4) . ?
C24 C25 1.453(4) . ?
C25 C26 1.353(4) . ?
C25 H25 0.9600 . ?
C26 H26 0.9601 . ?
C27 C38 1.501(3) . ?
C28 C33 1.394(4) . ?
C28 C29 1.396(3) . ?
C29 C30 1.387(4) . ?
C29 H29 0.9600 . ?
C30 C31 1.388(4) . ?
C30 H30 0.9600 . ?
C31 C32 1.374(4) . ?
C31 H31 0.9599 . ?
C32 C33 1.388(4) . ?
C32 H32 0.9600 . ?
C33 H33 0.9599 . ?
O34 C35 1.443(3) . ?
C35 H35A 0.9600 . ?
C35 H35B 0.9599 . ?
C35 H35C 0.9601 . ?
O36 C37 1.442(3) . ?
C37 H37A 0.9601 . ?
C37 H37B 0.9599 . ?
C37 H37C 0.9600 . ?
C38 C39 1.387(4) . ?
C38 C43 1.393(4) . ?
C39 C40 1.397(4) . ?
C39 H39 0.9599 . ?
C40 C41 1.381(4) . ?
C40 H40 0.9598 . ?
C41 C42 1.379(4) . ?
C41 H41 0.9600 . ?
C42 C43 1.395(4) . ?
C42 H42 0.9601 . ?
C43 H43 0.9601 . ?
N1A O3A 1.233(3) . ?
N1A O2A 1.236(3) . ?
N1A O1A 1.260(3) . ?
N1B O3B 1.220(3) . ?
N1B O1B 1.257(3) . ?
N1B O2B 1.263(3) . ?
O1C C2C 1.439(3) . ?
O1C H1C 0.76(3) . ?
C2C H2CC 0.9599 . ?
C2C H2CA 0.9600 . ?
C2C H2CB 0.9601 . ?
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C31 C32 C33 C28 0.8(4) . . . . ?
C29 C28 C33 C32 -2.6(4) . . . . ?
C6 C28 C33 C32 175.8(2) . . . . ?
C15 C16 O34 C35 13.0(3) . . . . ?
C17 C16 O34 C35 -165.6(2) .  . . ?
C18 C17 O36 C37 -4.0(3) . . . . ?
C16 C17 O36 C37 174.2(2) . . . . ?
C24 C27 C38 C39 -119.6(3) . .  . ?
C2 C27 C38 C39 59.7(3) . . . . ?
C24 C27 C38 C43 62.5(3) . . . . ?
C2 C27 C38 C43 -118.2(3) . . . . ?
C43 C38 C39 C40 2.0(4) . . . . ?
C27 C38 C39 C40 -175.9(3) . .  . ?
C38 C39 C40 C41 -0.8(5) . . . . ?
C39 C40 C41 C42 0.0(5) . . . . ?
C40 C41 C42 C43 -0.3(4) . . . . ?
C39 C38 C43 C42 -2.3(4) . . . . ?
C27 C38 C43 C42 175.7(2) . . . . ?
C41 C42 C43 C38 1.5(4) . . . . ?
O3A N1A O1A Gd1 -179.9(2) . .. . ?
O2A N1A O1A Gd1 1.7(3) . . . . ?
N8 Gd1 O1A N1A 66.87(17) . . . . ?
N23 Gd1 O1A N1A -106.41(18) .. . ?
N1 Gd1 O1A N1A 1.6(2) . . . . ?
N13 Gd1 O1A N1A 135.04(18) . . . ?
O1C Gd1 O1A N1A 111.21(17) . . . ?
O1B Gd1 O1A N1A -115.73(18) .. . ?
O2B Gd1 O1A N1A -64.84(17) . . . ?
N20 Gd1 O1A N1A -171.40(16) .  . ?
O2A Gd1 O1A N1A -0.92(14) . . .. ?
N1B Gd1 O1A N1A -88.99(17) . . . ?
O3A N1A O2A Gd1 -179.8(2) . . .  ?
O1A N1A O2A Gd1 -1.5(2) . . . . ?
N8 Gd1 O2A N1A -96.54(16) . . .  ?
N23 Gd1 O2A N1A 129.25(15) . . . ?
O1A Gd1 O2A N1A 0.90(14) . . . . ?
N1 Gd1 O2A N1A -176.88(17) . . . ?
N13 Gd1 O2A N1A -41.30(17) . . . ?
O1C Gd1 O2A N1A -120.95(16) . . .
O1B Gd1 O2A N1A 57.65(16) . . .  ?
O2B Gd1 O2A N1A 100.88(17) . . . ?
N20 Gd1 O2A N1A 18.7(2) . . . . ?
N1B Gd1 O2A N1A 76.85(16) . . .. ?
N8 Gd1 N1B O3B -29.6(12) . . . . ?
N23 Gd1 N1B O3B 179(100) . . . . ?
O1A Gd1 N1B O3B 10.1(12) . . . . ?
N1 Gd1 N1B O3B -110.8(12) . . .. ?
N13 Gd1 N1B O3B 59.1(12) . . . . ?
O1C Gd1 N1B O3B 165.0(11) . . .  ?
O1B Gd1 N1B O3B 89.5(12) . . . . ?
O2B Gd1 N1B O3B -98.6(12) . . .  ?
N20 Gd1 N1B O3B 114.0(12) . . .  ?
O2A Gd1 N1B O3B -39.2(12) . . .  ?
N8 Gd1 N1B O1B -119.12(16) . . . ?
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N23 Gd1 N1B O1B 89.59(16) . . .  ?
O1A Gd1 N1B O1B -79.41(16) . . . ?
N1 Gd1 N1B O1B 159.63(15) . . . .?
N13 Gd1 N1B O1B -30.49(17) . . . ?
O1C Gd1 N1B O1B 75.45(19) . . . .?
O2B Gd1 N1B O1B 171.9(2) . . . . ?
N20 Gd1 N1B O1B 24.45(15) . . .  ?
O2A Gd1 N1B O1B -128.78(16) . .. ?
N8 Gd1 N1B O2B 69.01(18) . . . . ?
N23 Gd1 N1B O2B -82.29(15) . . . ?
O1A Gd1 N1B O2B 108.72(15) . . . ?
N1 Gd1 N1B O2B -12.24(15) . . .  ?
N13 Gd1 N1B O2B 157.64(14) . . . ?
O1C Gd1 N1B O2B -96.43(17) . . . ?
O1B Gd1 N1B O2B -171.9(2) . . .  ?
N20 Gd1 N1B O2B -147.42(15) .  . ?
O2A Gd1 N1B O2B 59.35(15) . . . ?
O3B N1B O1B Gd1 -169.7(2) . . .. ?
O2B N1B O1B Gd1 7.8(2) . . . . ?
N8 Gd1 O1B N1B 95.19(17) . . . . ?
N23 Gd1 O1B N1B -83.55(15) . . . ?
O1A Gd1 O1B N1B 90.56(16) . . .  ?
N1 Gd1 O1B N1B -24.46(18) . . .  ?
N13 Gd1 O1B N1B 153.76(15) . . . ?
O1C Gd1 O1B N1B -132.60(14) .. . ?
O2B Gd1 O1B N1B -4.49(13) . . .. ?
N20 Gd1 O1B N1B -152.79(17) .. . ?
O2A Gd1 O1B N1B 48.83(16) . . . ?
O3B N1B O2B Gd1 169.7(2) . . . . ?
O1B N1B O2B Gd1 -7.8(2) . . . . ?
N8 Gd1 O2B N1B -132.24(14) . . . ?
N23 Gd1 O2B N1B 90.08(15) . . . .
O1A Gd1 O2B N1B -64.65(15) . . . ?
N1 Gd1 O2B N1B 167.68(15) . . . .
N13 Gd1 O2B N1B -32.88(19) . . . ?
O1C Gd1 O2B N1B 119.60(15) . . . ?
O1B Gd1 O2B N1B 4.47(13) . . . . ?
N20 Gd1 O2B N1B 34.49(16) . . .. ?
O2A Gd1 O2B N1B -111.98(16)  . . ?
N8 Gd1 O1C C2C -33.82(19) . . .. ?
N23 Gd1 O1C C2C 122.4(2) . . . . ?
O1A Gd1 O1C C2C -80.5(2) . . . . ?
N1 Gd1 O1C C2C 45.2(2) . . . . ?
N13 Gd1 O1C C2C -103.8(2) . . . ?
O1B Gd1 O1C C2C 171.83(18) . . . ?
O2B Gd1 O1C C2C 93.2(2) . . . . ?
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O2A Gd1 O1C C2C -10.2(2) . . . . ?
N1B Gd1 O1C C2C 136.53(19) .  . ?
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 _geom_hbond_distance_DA
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O1C H1C O34  0.76(3) 2.08(3)
2.791(3) 155(3) 3_556
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_diffrn_measured_fraction_theta_fu
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