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Crystal structure of aqua(2-{[2-({2-[bis(carboxylato-κO-methyl)amino-κN]ethyl}(carboxylato-κO-methyl)amino-κN)ethyl](carboxymethyl)azanium-yl}acetato)gallium(III) trihydrate

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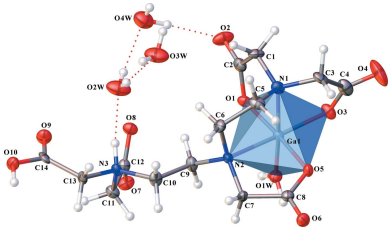
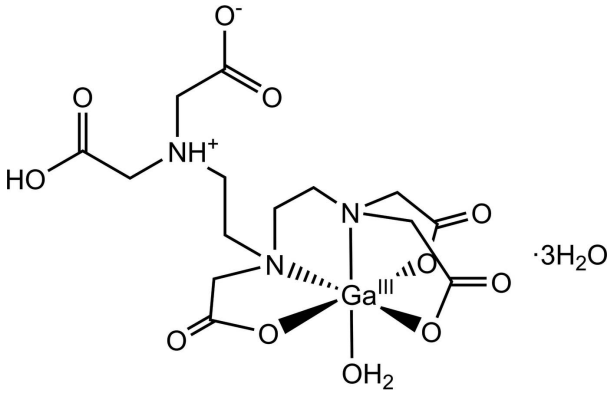
In the title Ga^{III} complex compound with pentetic acid, $[Ga(C_{14}H_{20}N_3O_{10})(H_2O)]\cdot 3H_2O$, the Ga^{III} centre is bound in a slightly distorted octahedral coordination sphere by two amine N atoms, three carboxylate O atoms and one water O atom. The complex molecule exists as a zwitterion. In the crystal, the complexes are linked to each other *via* O—H···O and C—H···O hydrogen bonds, forming layers parallel to (001). Three uncoordinating water molecules link the complex layers *via* O—H···O, N—H···O and C—H···O hydrogen bonds, forming a three-dimensional network.

1. Chemical context

The use of gallium-68 (^{68}Ga) for molecular imaging of diseases has become increasingly popular and the number of ^{68}Ga-related articles has increased drastically in the past 10 years, as pointed out by Velikyan (2014). The application span is wide and covers the diagnosis of cancer, cardiovascular disease, infection and inflammatory conditions (Brasse & Nonat, 2015; Jalilian & Akhlaghi, 2013; Banerjee & Pomper, 2013; Schultz *et al.*, 2013). The increase in popularity and use can be ascribed to several factors. On the one hand, ^{68}Ga produces high-quality PET images. On the other hand, it has a half-life of 68 min, which makes it suitable for use in patients as the radiation dose can be kept at a minimum (Hofman & Hicks, 2016). ^{68}Ga can be eluted from a ^{68}Ge/^{68}Ga generator multiple times a day, which makes it easy for hospitals to prepare gallium solutions for patients on demand. It is vital that gallium ions are complexed, as free ions may cause undesirable effects *in vivo*. First, free gallium can cause iron release from transferrin, which may cause free-radical toxicity. Second, gallium ions may cause an additional and unnecessary radiation dose. 2-(Bis{2-[bis(carboxymethyl)amino]ethyl}-amino)acetic acid (pentetic acid or DTPA) is an amino-polycarboxylic acid consisting of a diethylenetriamine backbone with five carboxy groups. A complex is easily formed between gallium and DTPA and it has a stability constant of $10^{23.32}$, which makes the complex stable against exchange with transferrin (Moerlein & Welch, 1981; Green & Welch, 1989). DTPA-peptides labelled with ^{68}Ga have been used for liver-function imaging, determination of low-density lipoprotein



metabolism, bone-marrow function and molecular identification of metastatic tumours (Haubner *et al.*, 2013; Moerlein *et al.*, 1991; Vera *et al.*, 2012; Pitalúa-Cortés *et al.*, 2017), but the molecular structure of our compound has not yet been reported. Here we present and describe the molecular structure of the title compound (Fig. 1).



2. Structural commentary

The complex molecule (abbreviated as Ga-DTPA) is a zwitterion and has a slightly distorted octahedral coordination geometry with one water and one amine in the axial positions, and three carboxylate groups and one amine in the equatorial positions. The complex consists of three five-membered Ga/N/C/C/O chelate rings and one five-membered Ga/N/C/C/N chelate ring. The Ga—N bonds [Ga1—N1 = 2.081 (4) Å and Ga1—N2 = 2.156 (3) Å] are significantly longer than the Ga—O bonds [Ga1—O1 = 1.933 (3) Å, Ga1—O3 = 1.925 (3) Å, Ga1—O5 = 1.964 (3) Å and Ga1—O1*W* = 1.916 (3) Å]. The C—O bond lengths coordinating to the Ga^{III} atom vary little, with the shortest and longest bonds differing by only 0.019 Å [C2—O1 = 1.286 (5) Å, C4—O3 = 1.305 (5) Å and C8—O5 = 1.293 (5) Å]. The three *trans* angles, N1—Ga1—O1*W*, O1—Ga1—O5 and O3—Ga1—N2, are 174.57 (16), 174.05 (12) and 164.97 (13)°, respectively. The O—Ga—O, O—Ga—N and N—Ga—N bite angles in the chelate rings deviate somewhat from 90°, ranging from 81.75 (12) to 95.91 (12)°.

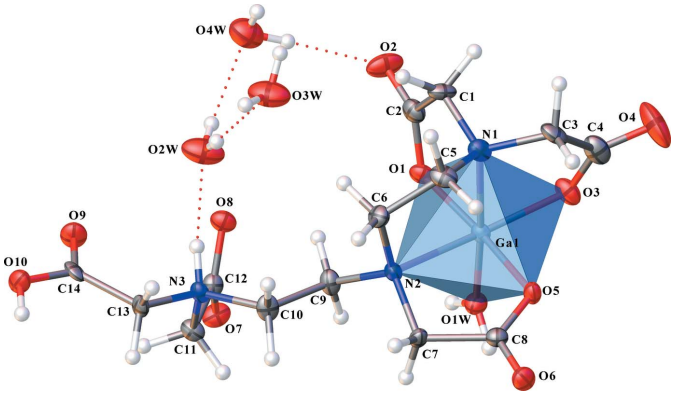


Figure 1
OLEX2 generated depiction of the title compound, with displacement ellipsoids drawn at the 75% probability level. Dashed lines show O—H···O and N—H···O hydrogen bonds.

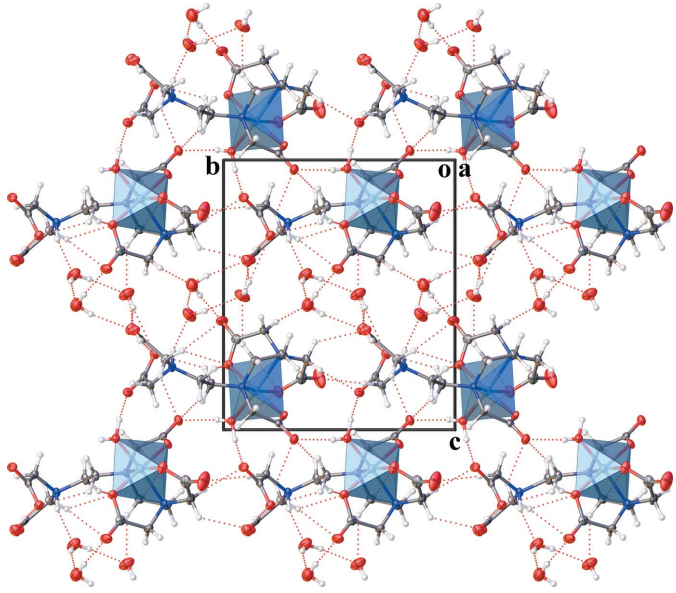


Figure 2
A packing diagram of the title compound, viewed along the *a* axis. Dashed lines show O—H···O, N—H···O and C—H···O hydrogen bonds.

3. Supramolecular features

Packing depictions viewed along the *a* and *b* axes provided in Figs. 2 and 3, respectively, show pairs of layers containing the complexes parallel to the (001) plane. In the layer, the complexes are linked to each other by O—H···O and C—H···O hydrogen bonds (Table 1). Three uncoordinating water

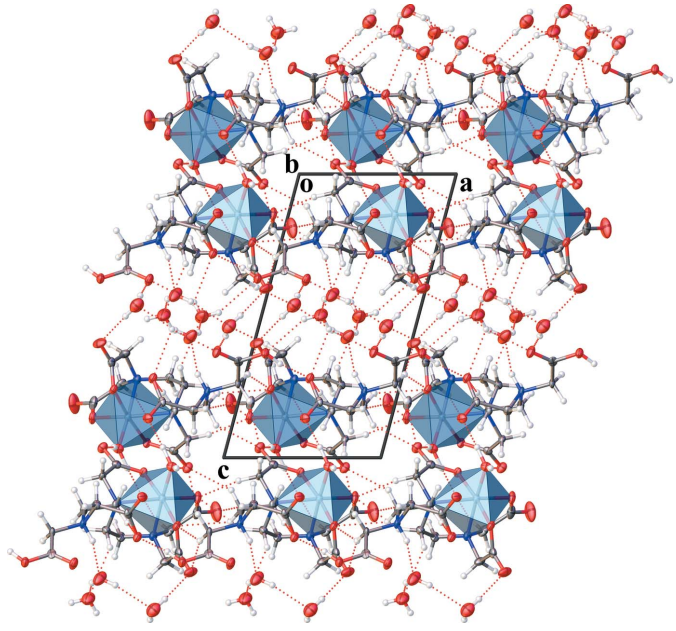


Figure 3
A packing diagram of the title compound, viewed along the *b* axis. Dashed lines show O—H···O, N—H···O and C—H···O hydrogen bonds.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*O*···O8^{i}	0.87 (6)	1.67 (6)	2.525 (4)	169 (6)
O1*W*—H1*WA*···O6^{ii}	0.71 (5)	1.93 (5)	2.636 (5)	174 (6)
O1*W*—H1*WB*···O7^{iii}	0.99 (6)	1.54 (6)	2.524 (5)	174 (5)
O2*W*—H2*WA*···O3*W*	0.84 (7)	1.94 (7)	2.741 (5)	158 (6)
O2*W*—H2*WB*···O4*W*	0.77 (6)	2.09 (6)	2.828 (5)	160 (6)
O3*W*—H3*WA*···O2^{i}	0.79 (10)	2.47 (10)	2.934 (5)	119 (9)
O3*W*—H3*WA*···O10^{iv}	0.79 (10)	2.37 (10)	3.096 (5)	153 (9)
O3*W*—H3*WB*···O8^{v}	0.81 (7)	2.60 (6)	3.215 (5)	134 (5)
O3*W*—H3*WB*···O9^{v}	0.81 (7)	2.28 (6)	2.934 (5)	138 (6)
O4*W*—H4*WA*···O2	0.80 (6)	2.00 (6)	2.806 (5)	175 (6)
O4*W*—H4*WB*···O9^{v}	0.83 (7)	2.09 (7)	2.911 (5)	168 (7)
N3—H3*N*···O2*W*	0.90 (5)	1.91 (5)	2.737 (5)	152 (4)
C1—H1*A*···O4*W*^{vi}	0.99	2.43	3.417 (6)	173
C3—H3*A*···O7^{vii}	0.99	2.25	3.197 (5)	159
C3—H3*B*···O10^{viii}	0.99	2.52	3.225 (5)	128
C6—H6*B*···O3*W*	0.99	2.53	3.254 (5)	130
C7—H7*B*···O3^{i}	0.99	2.28	3.227 (5)	161
C9—H9*B*···O8	0.99	2.53	3.207 (5)	126
C10—H10*A*···O6^{ix}	0.99	2.46	3.271 (5)	139
C10—H10*B*···O1^{i}	0.99	2.53	3.300 (5)	134
C11—H11*A*···O4^{x}	0.99	2.45	3.438 (5)	176
C13—H13*A*···O1^{i}	0.99	2.54	3.367 (5)	140
C13—H13*A*···O2^{i}	0.99	2.41	3.368 (5)	162
C13—H13*B*···O6^{ix}	0.99	2.34	3.150 (5)	139

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

molecules link the complex layers *via* O—H···O, N—H···O and C—H···O hydrogen bonds, forming a three-dimensional network.

4. Database survey

In our survey of the Cambridge Structural Database (CSD version 5.39, update November 2017; Groom *et al.*, 2016), we found 64 crystal structures of metal complexes with DTPA. In another search, we found 72 crystal structures of gallium complexes hexa-coordinated by two N and four O atoms.

5. Synthesis and crystallization

DTPA (50 mg) in acetate buffer (2 mL) adjusted to pH = 4.2 was heated with stirring for dissolution. Gallium nitrate (39.9 mg) was then added to the DTPA solution and the mixture was stirred for at least 10 min at 353 K. The solution was concentrated under ambient pressure at room temperature. When almost all of the solvent had evaporated, methanol was added dropwise to precipitate Ga-DTPA. The precipitate was collected on a 0.22 µm polyamide filter and dried at room temperature. The obtained Ga-DTPA (1.30 mg) was re-dissolved in ultra-pure water (1 mL) and single crystals suitable for X-ray diffraction were obtained after four weeks by slow diffusion of tetrahydrofuran into the aqueous solution, as illustrated in Fig. 4.

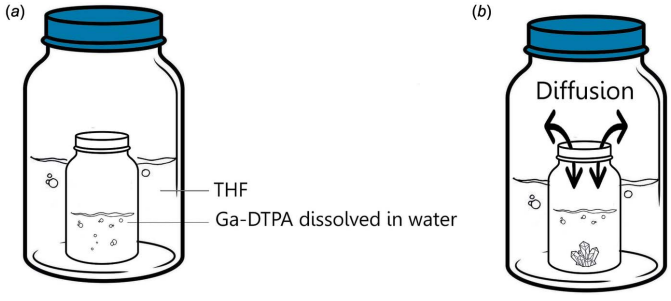


Figure 4
Vapor liquid diffusion technique illustration. (*a*) a HPLC vial containing Ga-DTPA dissolved in water was placed inside a bigger vial. The closed bigger vial contained THF. (*b*) THF diffused slowly into the small vial. After four weeks, visible Ga-DTPA crystals were formed.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ga(C_{14}H_{20}N_3O_{10})(H_2O)]\cdot 3H_2O$
M_r	532.11
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	7.1477 (2), 11.0616 (3), 13.3460 (4)
β (°)	104.929 (3)
V (Å^3)	1019.58 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.43
Crystal size (mm)	0.13 × 0.06 × 0.03
Data collection	
Diffractometer	Oxford Diffraction SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.915, 1.00
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23585, 6213, 5124
R_{int}	0.073
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.073, 1.05
No. of reflections	6213
No. of parameters	329
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.44
Absolute structure	Flack x determined using 2002 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.009 (7)

Computer programs: *CrysAlis PRO* (Rigaku OOD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *WinGX* (Farrugia, 2012).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. N- and O-bound H atoms were located in difference-Fourier maps and freely refined. C-bound H atoms were positioned geometrically (C—H = 0.99 Å) and refined using a riding model with U_{iso}(H) = 1.2U_{eq}(C).

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Crystal structure of aqua(2-{[2-({2-[bis(carboxylato-κ*O*-methyl)amino-κ*N*]ethyl}(carboxylato-κ*O*-methyl)amino-κ*N*)ethyl](carboxymethyl)azaniumyl}acetato)-gallium(III) trihydrate

Martin Wallin, Peter Turner, Andrew Katsifis, Mingshi Yang and Hak-Kim Chan

Computing details

Data collection: *CrysAlis PRO* (Rigaku OOD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OOD, 2015); data reduction: *CrysAlis PRO* (Rigaku OOD, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Aqua(2-{[2-({2-[bis(carboxylato-κ*O*-methyl)amino-κ*N*]ethyl}(carboxylato-κ*O*-methyl)amino-κ*N*)ethyl](carboxymethyl)azaniumyl}acetato)gallium(III) trihydrate

Crystal data

$[Ga(C_{14}H_{20}N_3O_{10})(H_2O)]\cdot 3H_2O$
$M_r = 532.11$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 7.1477$ (2) Å
$b = 11.0616$ (3) Å
$c = 13.3460$ (4) Å
$\beta = 104.929$ (3)°
$V = 1019.58$ (5) Å^3
$Z = 2$
$F(000) = 552$
$D_x = 1.733$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5696 reflections
$\theta = 3.7$–$28.0°$
$\mu = 1.43$ mm^{-1}
$T = 100$ K
Blade, colourless
0.13 × 0.06 × 0.03 mm

Data collection

Oxford Diffraction SuperNova Dual Source diffractometer with an Atlas detector
Radiation source: micro-focus sealed X-ray tube
Mirror monochromator
Detector resolution: 10.5861 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
$T_{min} = 0.915$, $T_{max} = 1.00$
23585 measured reflections
6213 independent reflections
5124 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 30.5°$, $\theta_{min} = 3.2°$
$h = -10\rightarrow10$
$k = -15\rightarrow15$
$l = -19\rightarrow19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.073$
$S = 1.05$
6213 reflections
329 parameters
1 restraint
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Absolute structure: Flack *x* determined using 2002 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.009 (7)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ga1	0.67818 (6)	0.35920 (4)	0.14406 (3)	0.00910 (10)
C1	0.8057 (6)	0.3244 (4)	0.3657 (3)	0.0126 (9)
H1A	0.919556	0.274628	0.399527	0.015*
H1B	0.729278	0.337981	0.416943	0.015*
O1	0.8169 (4)	0.4789 (3)	0.2405 (2)	0.0112 (6)
O2	0.9839 (4)	0.5070 (3)	0.4037 (2)	0.0192 (7)
C2	0.8752 (6)	0.4454 (4)	0.3358 (3)	0.0119 (9)
O3	0.9021 (4)	0.2641 (3)	0.1407 (2)	0.0143 (7)
C3	0.7772 (6)	0.1419 (4)	0.2575 (3)	0.0143 (9)
H3A	0.676921	0.084101	0.220995	0.017*
H3B	0.844674	0.105973	0.325046	0.017*
O4	1.0435 (5)	0.0862 (3)	0.1905 (3)	0.0312 (9)
C4	0.9226 (6)	0.1631 (4)	0.1929 (4)	0.0164 (10)
O5	0.5143 (4)	0.2406 (3)	0.0522 (2)	0.0101 (6)
C5	0.4793 (6)	0.2422 (4)	0.2793 (3)	0.0120 (9)
H5A	0.474766	0.213062	0.348815	0.014*
H5B	0.413340	0.181905	0.227326	0.014*
O6	0.2129 (4)	0.1952 (3)	−0.0352 (2)	0.0132 (6)
C6	0.3768 (5)	0.3630 (5)	0.2572 (3)	0.0113 (7)
H6A	0.237081	0.351202	0.251339	0.014*
H6B	0.428383	0.418161	0.316320	0.014*
O7	0.5490 (4)	0.9137 (3)	0.1386 (2)	0.0133 (6)
C7	0.2595 (5)	0.3761 (4)	0.0650 (3)	0.0086 (9)
H7A	0.237373	0.439360	0.010694	0.010*
H7B	0.134525	0.359646	0.081351	0.010*
O8	0.5857 (4)	0.7981 (3)	0.2800 (2)	0.0120 (6)
C8	0.3304 (6)	0.2617 (4)	0.0239 (3)	0.0098 (8)
O9	0.2242 (4)	0.9005 (3)	0.3733 (2)	0.0154 (7)
O10	−0.0876 (4)	0.8862 (3)	0.3686 (2)	0.0134 (7)
H10O	−0.199 (8)	0.861 (7)	0.331 (4)	0.054 (18)*
O1W	0.6862 (5)	0.4657 (3)	0.0320 (3)	0.0124 (7)
C14	0.0674 (5)	0.8541 (5)	0.3389 (3)	0.0106 (7)
C13	0.0341 (6)	0.7512 (4)	0.2622 (3)	0.0100 (8)

H13A	−0.010336	0.678992	0.293384	0.012*
H13B	−0.068191	0.773773	0.199606	0.012*
H1WA	0.717 (7)	0.527 (5)	0.037 (4)	0.013 (15)*
H1WB	0.596 (8)	0.451 (5)	−0.036 (5)	0.039 (17)*
N1	0.6840 (5)	0.2560 (3)	0.2752 (3)	0.0108 (8)
N2	0.4008 (5)	0.4211 (3)	0.1594 (3)	0.0084 (7)
N3	0.2166 (5)	0.7221 (3)	0.2324 (3)	0.0091 (7)
H3N	0.306 (7)	0.719 (4)	0.293 (4)	0.017 (13)*
C9	0.3931 (6)	0.5548 (4)	0.1691 (3)	0.0108 (8)
H9A	0.416736	0.592496	0.106217	0.013*
H9B	0.497536	0.581169	0.229345	0.013*
C10	0.1989 (6)	0.5987 (4)	0.1829 (3)	0.0115 (9)
H10A	0.103663	0.602054	0.114376	0.014*
H10B	0.150619	0.540629	0.226776	0.014*
C12	0.4880 (5)	0.8448 (4)	0.1976 (3)	0.0098 (8)
C11	0.2714 (6)	0.8182 (4)	0.1662 (3)	0.0110 (9)
H11A	0.199397	0.893211	0.171991	0.013*
H11B	0.233493	0.791951	0.092846	0.013*
O2W	0.4169 (6)	0.6478 (4)	0.4259 (3)	0.0250 (9)
H2WA	0.373 (9)	0.581 (6)	0.441 (5)	0.05 (2)*
H2WB	0.526 (9)	0.660 (6)	0.449 (5)	0.04 (2)*
O3W	0.3776 (6)	0.4191 (4)	0.4967 (3)	0.0260 (9)
H3WA	0.278 (14)	0.409 (10)	0.511 (8)	0.15 (5)*
H3WB	0.452 (9)	0.390 (6)	0.547 (5)	0.06 (2)*
O4W	0.8110 (5)	0.6367 (3)	0.5369 (3)	0.0239 (8)
H4WA	0.865 (8)	0.603 (6)	0.499 (5)	0.04 (2)*
H4WB	0.806 (9)	0.574 (7)	0.571 (5)	0.06 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.00710 (17)	0.00922 (19)	0.01104 (19)	0.0001 (2)	0.00244 (14)	−0.0001 (2)
C1	0.014 (2)	0.013 (2)	0.009 (2)	−0.0019 (17)	−0.0004 (17)	0.0032 (16)
O1	0.0069 (14)	0.0131 (16)	0.0119 (15)	−0.0001 (12)	−0.0005 (12)	0.0006 (12)
O2	0.0205 (17)	0.0209 (18)	0.0129 (16)	−0.0102 (14)	−0.0018 (14)	−0.0009 (14)
C2	0.0083 (19)	0.014 (2)	0.014 (2)	0.0032 (17)	0.0043 (18)	0.0001 (18)
O3	0.0074 (14)	0.0141 (16)	0.0213 (17)	0.0017 (13)	0.0038 (13)	0.0035 (13)
C3	0.012 (2)	0.011 (2)	0.018 (2)	0.0029 (17)	−0.0011 (18)	0.0037 (18)
O4	0.0219 (18)	0.023 (2)	0.054 (3)	0.0120 (16)	0.0190 (18)	0.0114 (18)
C4	0.0086 (19)	0.016 (2)	0.024 (3)	−0.0025 (18)	0.0021 (19)	−0.0013 (19)
O5	0.0080 (13)	0.0093 (15)	0.0128 (15)	0.0013 (12)	0.0022 (12)	−0.0041 (12)
C5	0.0103 (19)	0.012 (2)	0.013 (2)	−0.0014 (17)	0.0031 (17)	0.0054 (17)
O6	0.0120 (14)	0.0107 (15)	0.0154 (16)	−0.0012 (12)	0.0007 (13)	−0.0020 (12)
C6	0.0110 (16)	0.0127 (18)	0.0110 (17)	0.001 (2)	0.0044 (14)	0.000 (2)
O7	0.0138 (14)	0.0143 (15)	0.0121 (15)	−0.0054 (13)	0.0039 (13)	0.0009 (12)
C7	0.0068 (16)	0.010 (2)	0.0087 (17)	−0.0003 (16)	0.0006 (14)	−0.0033 (16)
O8	0.0088 (14)	0.0130 (15)	0.0131 (15)	−0.0006 (12)	0.0009 (12)	0.0017 (12)
C8	0.0118 (19)	0.009 (2)	0.009 (2)	−0.0005 (17)	0.0037 (17)	0.0019 (16)

O9	0.0086 (13)	0.0172 (16)	0.0187 (16)	−0.0016 (12)	0.0006 (12)	−0.0037 (13)
O10	0.0080 (13)	0.018 (2)	0.0136 (15)	0.0008 (12)	0.0023 (12)	−0.0027 (12)
O1W	0.0157 (16)	0.0096 (17)	0.0120 (17)	0.0001 (14)	0.0041 (13)	0.0004 (13)
C14	0.0104 (16)	0.0093 (17)	0.0118 (17)	0.004 (2)	0.0025 (14)	0.007 (2)
C13	0.0051 (18)	0.012 (2)	0.013 (2)	0.0008 (17)	0.0033 (16)	−0.0022 (17)
N1	0.0086 (17)	0.0101 (18)	0.0131 (19)	−0.0016 (15)	0.0018 (15)	0.0001 (15)
N2	0.0074 (16)	0.0080 (17)	0.0097 (17)	0.0015 (14)	0.0021 (14)	−0.0005 (14)
N3	0.0052 (16)	0.0086 (17)	0.0129 (19)	−0.0008 (14)	0.0013 (15)	−0.0005 (14)
C9	0.0082 (19)	0.009 (2)	0.016 (2)	−0.0019 (16)	0.0042 (17)	−0.0022 (17)
C10	0.0079 (19)	0.009 (2)	0.018 (2)	−0.0036 (16)	0.0033 (17)	−0.0022 (17)
C12	0.0094 (16)	0.008 (2)	0.0131 (18)	−0.0030 (18)	0.0046 (15)	−0.0025 (18)
C11	0.0099 (19)	0.0107 (19)	0.012 (2)	0.0005 (16)	0.0029 (17)	0.0030 (16)
O2W	0.0194 (19)	0.026 (2)	0.026 (2)	−0.0052 (17)	−0.0019 (17)	0.0104 (17)
O3W	0.0217 (19)	0.033 (2)	0.021 (2)	−0.0020 (17)	0.0021 (17)	0.0110 (17)
O4W	0.0231 (19)	0.020 (2)	0.026 (2)	0.0017 (16)	0.0015 (17)	0.0028 (17)

Geometric parameters (Å, º)

Ga1—O1W	1.916 (3)	C7—H7A	0.9900
Ga1—O3	1.925 (3)	C7—H7B	0.9900
Ga1—O1	1.933 (3)	O8—C12	1.251 (5)
Ga1—O5	1.964 (3)	O9—C14	1.211 (5)
Ga1—N1	2.081 (4)	O10—C14	1.318 (4)
Ga1—N2	2.156 (3)	O10—H10O	0.87 (6)
C1—N1	1.499 (5)	O1W—H1WA	0.71 (5)
C1—C2	1.517 (6)	O1W—H1WB	0.99 (6)
C1—H1A	0.9900	C14—C13	1.508 (6)
C1—H1B	0.9900	C13—N3	1.493 (5)
O1—C2	1.286 (5)	C13—H13A	0.9900
O2—C2	1.236 (5)	C13—H13B	0.9900
O3—C4	1.305 (5)	N2—C9	1.486 (5)
C3—N1	1.474 (5)	N3—C11	1.497 (5)
C3—C4	1.530 (6)	N3—C10	1.507 (5)
C3—H3A	0.9900	N3—H3N	0.90 (5)
C3—H3B	0.9900	C9—C10	1.526 (5)
O4—C4	1.219 (5)	C9—H9A	0.9900
O5—C8	1.293 (5)	C9—H9B	0.9900
C5—N1	1.486 (5)	C10—H10A	0.9900
C5—C6	1.516 (6)	C10—H10B	0.9900
C5—H5A	0.9900	C12—C11	1.525 (5)
C5—H5B	0.9900	C11—H11A	0.9900
O6—C8	1.236 (5)	C11—H11B	0.9900
C6—N2	1.505 (5)	O2W—H2WA	0.84 (7)
C6—H6A	0.9900	O2W—H2WB	0.77 (6)
C6—H6B	0.9900	O3W—H3WA	0.79 (10)
O7—C12	1.252 (5)	O3W—H3WB	0.81 (7)
C7—N2	1.483 (5)	O4W—H4WA	0.80 (6)
C7—C8	1.517 (6)	O4W—H4WB	0.83 (7)

O1W—Ga1—O3	97.21 (13)	O5—C8—C7	117.1 (3)
O1W—Ga1—O1	89.15 (14)	C14—O10—H10O	117 (4)
O3—Ga1—O1	95.91 (12)	Ga1—O1W—H1WA	125 (4)
O1W—Ga1—O5	93.24 (14)	Ga1—O1W—H1WB	118 (3)
O3—Ga1—O5	89.19 (12)	H1WA—O1W—H1WB	111 (5)
O1—Ga1—O5	174.05 (12)	O9—C14—O10	122.6 (4)
O1W—Ga1—N1	174.57 (16)	O9—C14—C13	123.2 (4)
O3—Ga1—N1	83.30 (14)	O10—C14—C13	114.2 (3)
O1—Ga1—N1	85.42 (13)	N3—C13—C14	110.3 (3)
O5—Ga1—N1	92.17 (13)	N3—C13—H13A	109.6
O1W—Ga1—N2	95.26 (13)	C14—C13—H13A	109.6
O3—Ga1—N2	164.97 (13)	N3—C13—H13B	109.6
O1—Ga1—N2	92.62 (12)	C14—C13—H13B	109.6
O5—Ga1—N2	81.75 (12)	H13A—C13—H13B	108.1
N1—Ga1—N2	85.08 (13)	C3—N1—C5	114.1 (3)
N1—C1—C2	113.2 (3)	C3—N1—C1	111.7 (3)
N1—C1—H1A	108.9	C5—N1—C1	113.2 (3)
C2—C1—H1A	108.9	C3—N1—Ga1	104.3 (3)
N1—C1—H1B	108.9	C5—N1—Ga1	106.3 (2)
C2—C1—H1B	108.9	C1—N1—Ga1	106.4 (2)
H1A—C1—H1B	107.7	C7—N2—C9	112.0 (3)
C2—O1—Ga1	116.2 (3)	C7—N2—C6	112.9 (3)
O2—C2—O1	123.3 (4)	C9—N2—C6	109.5 (3)
O2—C2—C1	118.6 (4)	C7—N2—Ga1	104.7 (2)
O1—C2—C1	118.0 (4)	C9—N2—Ga1	112.3 (2)
C4—O3—Ga1	115.8 (3)	C6—N2—Ga1	105.1 (2)
N1—C3—C4	111.1 (4)	C13—N3—C11	112.6 (3)
N1—C3—H3A	109.4	C13—N3—C10	109.4 (3)
C4—C3—H3A	109.4	C11—N3—C10	112.9 (3)
N1—C3—H3B	109.4	C13—N3—H3N	104 (3)
C4—C3—H3B	109.4	C11—N3—H3N	109 (3)
H3A—C3—H3B	108.0	C10—N3—H3N	108 (3)
O4—C4—O3	124.5 (4)	N2—C9—C10	112.5 (3)
O4—C4—C3	119.8 (4)	N2—C9—H9A	109.1
O3—C4—C3	115.7 (4)	C10—C9—H9A	109.1
C8—O5—Ga1	117.3 (3)	N2—C9—H9B	109.1
N1—C5—C6	109.5 (3)	C10—C9—H9B	109.1
N1—C5—H5A	109.8	H9A—C9—H9B	107.8
C6—C5—H5A	109.8	N3—C10—C9	111.5 (3)
N1—C5—H5B	109.8	N3—C10—H10A	109.3
C6—C5—H5B	109.8	C9—C10—H10A	109.3
H5A—C5—H5B	108.2	N3—C10—H10B	109.3
N2—C6—C5	112.8 (3)	C9—C10—H10B	109.3
N2—C6—H6A	109.0	H10A—C10—H10B	108.0
C5—C6—H6A	109.0	O8—C12—O7	126.7 (3)
N2—C6—H6B	109.0	O8—C12—C11	117.3 (4)
C5—C6—H6B	109.0	O7—C12—C11	115.9 (3)

H6A—C6—H6B	107.8	N3—C11—C12	112.1 (3)
N2—C7—C8	111.7 (3)	N3—C11—H11A	109.2
N2—C7—H7A	109.3	C12—C11—H11A	109.2
C8—C7—H7A	109.3	N3—C11—H11B	109.2
N2—C7—H7B	109.3	C12—C11—H11B	109.2
C8—C7—H7B	109.3	H11A—C11—H11B	107.9
H7A—C7—H7B	107.9	H2WA—O2W—H2WB	117 (6)
O6—C8—O5	123.4 (4)	H3WA—O3W—H3WB	101 (8)
O6—C8—C7	119.5 (3)	H4WA—O4W—H4WB	93 (6)

Ga1—O1—C2—O2	171.5 (3)	C2—C1—N1—C3	116.1 (4)
Ga1—O1—C2—C1	−8.7 (4)	C2—C1—N1—C5	−113.6 (4)
N1—C1—C2—O2	−176.8 (4)	C2—C1—N1—Ga1	2.9 (4)
N1—C1—C2—O1	3.5 (5)	C8—C7—N2—C9	150.0 (3)
Ga1—O3—C4—O4	172.0 (4)	C8—C7—N2—C6	−85.8 (4)
Ga1—O3—C4—C3	−5.9 (5)	C8—C7—N2—Ga1	28.0 (4)
N1—C3—C4—O4	163.3 (4)	C5—C6—N2—C7	83.8 (4)
N1—C3—C4—O3	−18.7 (5)	C5—C6—N2—C9	−150.7 (3)
N1—C5—C6—N2	51.6 (4)	C5—C6—N2—Ga1	−29.8 (4)
Ga1—O5—C8—O6	178.6 (3)	C14—C13—N3—C11	−70.5 (4)
Ga1—O5—C8—C7	−0.2 (5)	C14—C13—N3—C10	163.1 (3)
N2—C7—C8—O6	160.4 (4)	C7—N2—C9—C10	63.9 (4)
N2—C7—C8—O5	−20.7 (5)	C6—N2—C9—C10	−62.1 (4)
O9—C14—C13—N3	−3.2 (6)	Ga1—N2—C9—C10	−178.5 (3)
O10—C14—C13—N3	179.4 (3)	C13—N3—C10—C9	−169.5 (3)
C4—C3—N1—C5	146.3 (4)	C11—N3—C10—C9	64.3 (4)
C4—C3—N1—C1	−83.8 (4)	N2—C9—C10—N3	158.1 (3)
C4—C3—N1—Ga1	30.7 (4)	C13—N3—C11—C12	138.0 (4)
C6—C5—N1—C3	−158.9 (3)	C10—N3—C11—C12	−97.6 (4)
C6—C5—N1—C1	72.0 (4)	O8—C12—C11—N3	−9.5 (6)
C6—C5—N1—Ga1	−44.5 (4)	O7—C12—C11—N3	171.9 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*O*···O8^{i}	0.87 (6)	1.67 (6)	2.525 (4)	169 (6)
O1*W*—H1*WA*···O6^{ii}	0.71 (5)	1.93 (5)	2.636 (5)	174 (6)
O1*W*—H1*WB*···O7^{iii}	0.99 (6)	1.54 (6)	2.524 (5)	174 (5)
O2*W*—H2*WA*···O3*W*	0.84 (7)	1.94 (7)	2.741 (5)	158 (6)
O2*W*—H2*WB*···O4*W*	0.77 (6)	2.09 (6)	2.828 (5)	160 (6)
O3*W*—H3*WA*···O2^{i}	0.79 (10)	2.47 (10)	2.934 (5)	119 (9)
O3*W*—H3*WA*···O10^{iv}	0.79 (10)	2.37 (10)	3.096 (5)	153 (9)
O3*W*—H3*WB*···O8^{v}	0.81 (7)	2.60 (6)	3.215 (5)	134 (5)
O3*W*—H3*WB*···O9^{v}	0.81 (7)	2.28 (6)	2.934 (5)	138 (6)
O4*W*—H4*WA*···O2	0.80 (6)	2.00 (6)	2.806 (5)	175 (6)
O4*W*—H4*WB*···O9^{v}	0.83 (7)	2.09 (7)	2.911 (5)	168 (7)
N3—H3*N*···O2*W*	0.90 (5)	1.91 (5)	2.737 (5)	152 (4)
C1—H1*A*···O4*W*^{vi}	0.99	2.43	3.417 (6)	173

C3—H3*A*···O7^{vii}	0.99	2.25	3.197 (5)	159
C3—H3*B*···O10^{viii}	0.99	2.52	3.225 (5)	128
C6—H6*B*···O3*W*	0.99	2.53	3.254 (5)	130
C7—H7*B*···O3^{i}	0.99	2.28	3.227 (5)	161
C9—H9*B*···O8	0.99	2.53	3.207 (5)	126
C10—H10*A*···O6^{ix}	0.99	2.46	3.271 (5)	139
C10—H10*B*···O1^{i}	0.99	2.53	3.300 (5)	134
C11—H11*A*···O4^{x}	0.99	2.45	3.438 (5)	176
C13—H13*A*···O1^{i}	0.99	2.54	3.367 (5)	140
C13—H13*A*···O2^{i}	0.99	2.41	3.368 (5)	162
C13—H13*B*···O6^{ix}	0.99	2.34	3.150 (5)	139

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+1, *y*+1/2, −*z*; (iii) −*x*+1, *y*−1/2, −*z*; (iv) −*x*, *y*−1/2, −*z*+1; (v) −*x*+1, *y*−1/2, −*z*+1; (vi) −*x*+2, *y*−1/2, −*z*+1; (vii) *x*, *y*−1, *z*; (viii) *x*+1, *y*−1, *z*; (ix) −*x*, *y*+1/2, −*z*; (x) *x*−1, *y*+1, *z*.