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Synthesis, crystal structures, photoluminescence, electrochemistry and DFT study of aluminium(III) and gallium(III) complexes containing a novel tetradentate Schiff base ligand

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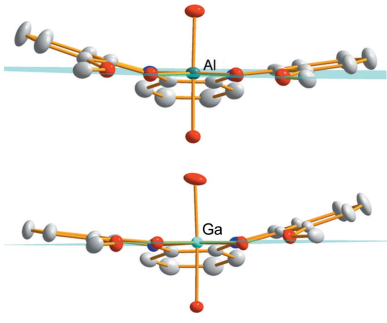
Single crystals of the aluminium and gallium complexes of 6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenol), namely diaqua(6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenolato)-$\kappa^4O^1,N,N',O^{1'}$)aluminium(III) nitrate ethanol monosolvate, $[Al(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3\cdot C_2H_5OH$, **1**, and diaqua(6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenolato)-$\kappa^4O^1,N,N',O^{1'}$)gallium(III) nitrate ethanol monosolvate, $[Ga(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3\cdot C_2H_5OH$, **2**, were obtained after successful synthesis in ethanol. Both complexes crystallized in the triclinic space group $P\overline{1}$, with two molecules in the asymmetric unit. In both structures, in one of the independent molecules the tetradentate ligand is almost planar while in the other independent molecule the ligand shows significant distortions from planarity, as illustrated by the largest distance from the plane constructed through the central metal atom and the *O*,*N*,*N*′,*O*′-coordinating atoms of the ligand in **1** of 1.155 (3) Å and a distance of 1.1707 (3) Å in **2**. The possible reason for this is that there are various strong π-interactions in the structures. This was confirmed by density functional theory (DFT) calculations, as were the other crystallographic data. DFT was also used to predict the outcome of cyclic voltammetry experiments. Ligand oxidation is more stabilized in the gallium complex. Solid-state photoluminescence gave an 80 nm red-shifted spectrum for the gallium complex, whereas the aluminium complex maintains the ligand curve with a smaller red shift of 40 nm.

1. Introduction

Aluminium is the most abundant metal on earth and has been used widely in many industrial fields, including motor vehicles and electronics. This of course has an impact on the environment and human health (Jeyanthi *et al.*, 2013; Flaten, 2001; Martyn *et al.*, 1989; Goswami *et al.*, 2013*b*; Gupta *et al.*, 2015).

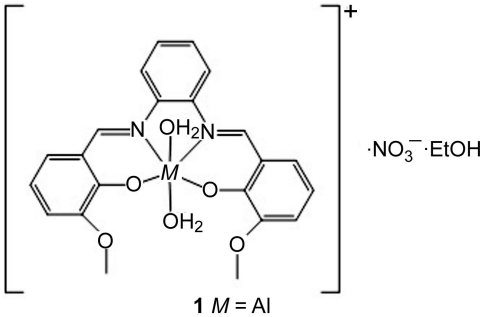
Complexes of aluminium and its third-row congener gallium with Schiff base ligands (Schiff, 1864) are currently of much interest for use as fluorescent probes and as organic light-emitting diodes (OLEDs) (Sivaraman *et al.*, 2012, 2014; Goswami *et al.*, 2013*a*; Han *et al.*, 2012). Gallium-containing OLEDs tend to exhibit higher electroluminescent yields than equivalent metal centres, such as aluminium (Burrows *et al.*, 1994; Wang *et al.*, 1999).

The photoluminescence properties of organometallic complexes are influenced by many factors, including the effects of trapped guest molecules, intermolecular interactions and, of course, the types of substituents (electronic and steric properties) on the ligands attached to the metal atom (Artizzu *et*



al., 2011; Goldman & Wehry, 1970; Forster & Rokos, 1976; Alexander *et al.*, 2017).

One of the many examples of Schiff bases which exhibit excellent results as chemosensors for aluminium is a combination of salicylic acid and phenylenediamines forming various tetradentate ligands. It is clear though, from this work, that there is uncertainty as to the nature of the aluminium complexes formed (Wang *et al.*, 2013; Gupta *et al.*, 2014; Dong *et al.*, 2010).



1 *M* = Al
2 *M* = Ga
Scheme 1

Our interest lies in the basic understanding of the synthesis and structural properties that influence the luminescence of these types of complexes. In this article, we present the synthesis, characterization and photoluminescence properties of the aluminium and gallium complexes of the novel Schiff based ligand 6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]-bis(methanylylidene)}bis(2-methoxyphenol) (H_2PAMM), namely [Al(PAMM)$(H_2O)_2$]$NO_3{\cdot}C_2H_5OH$, **1**, and [Ga(PAMM)-$(H_2O)_2$]$NO_3{\cdot}C_2H_5OH$, **2** (see Scheme 1).

2. Experimental

2.1. Materials and methods

Chemicals were of analytical grade, while all the solvents were purified and dried prior to use. IR spectra were recorded with a Hitachi 270-50 spectrophotometer, while the NMR spectra were obtained at 298 K on a Bruker Avance DPX 300 NMR spectrometer (300.130 MHz) and a Bruker Avance II 600 NMR spectrometer (600.130 MHz). The chemical shifts were reported relative to dimethyl sulfoxide (DMSO) (0.00 ppm) for the ^{1}H and ^{13}C NMR spectra.

Photoluminescence excitation and emission data were collected with a Cary Eclipse fluorescence spectrophotometer equipped with a Xenon flash lamp. The absorption spectra were collected on a PerkinElmer Lambda 950 UV–Vis spectrophotometer.

Electrochemical studies by means of cyclic voltammetry were performed at 25.0 °C on 5×10^{-4} mol dm^{-3} solutions of the complexes in CH_3CN/0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate, *i.e.* [(*n*-Bu_4)N][PF_6], electrolyte systems, under a blanket of purified argon, utilizing a BAS 100B/W electrochemical analyser. A three-electrode cell was used, with a glassy carbon (surface area 7.07×10^{-6} m^2) working electrode, a Pt auxiliary electrode and an Ag/Ag$^+$ (0.010 mol dm^{-3} $AgNO_3$ in CH_3CN) reference electrode (Sawyer & Roberts, 1974), mounted on a Luggin capillary (Evans *et al.*, 1983). All cited potentials are referenced against the FcH/FcH$^+$ couple, as suggested by the International Union of Pure and Applied Chemistry (IUPAC) (Gritzner & Kuta, 1984).

Density functional theory (DFT) calculations were carried out using the *ADF* (Amsterdam Density Functional) 2014 programme with the PW91 (Wang, 1991) GGA (Generalized Gradient Approximation) functional. The all-electron Slater-type TZP (triple-ζ polarized) basis set, with a fine mesh for numerical integration and tight convergence criteria, was used for minimum-energy searches. Numerical frequencies were computed to ensure that all optimized geometries were true minima on the energy surface.

2.2. Synthesis and crystallization

2.2.1. H_2PAMM. *o*-Vanillin (1.5235 g, 0.01 mol) was added to 1,2-phenylenediamine (0.5435 g, 0.005 mol) and placed in a ball mill at 25 Hz for 40 min. After completion, the product obtained was bright red. The reaction mixture was left to dry and needle-like crystals formed upon drying (yield 1.7005 g, 90.35%). ^{1}H NMR (300 MHz, DMSO): δ 13.00 (*s*, 1H), 8.92 (*s*, 1H), 7.43 (*d*, J = 8.6 Hz, 2H), 7.24 (*s*, 1H), 7.12 (*s*, 1H), 6.91 (*s*, 1H), 3.81 (*s*, 4H). ^{13}C NMR (75 MHz, DMSO): δ 164.83 (*s*), 151.08 (*s*), 148.35 (*s*), 142.57 (*s*), 128.29 (*s*), 124.25 (*s*), 120.28 (*s*), 119.80 (*s*), 119.03 (*s*), 115.89 (*s*), 56.13 (*s*). IR (cm^{-1}): ν(C═N) = 1567.9, ν(C—O) = 1246.0 and ν(C—N) = 1076.5. UV–Vis: λ_{max} = 270 nm, ε = 17320 M^{-1} cm^{-1}. Elemental analysis (C, H and N) calculated (%): C 70.2, H 5.36, N 7.44; found: C 70.34, H 5.20, N 7.49.

2.2.2. [Al(PAMM)$(H_2O)_2$]$NO_3{\cdot}C_2H_5OH$, 1. A solution of H_2PAMM (0.1564 g, 0.416 mmol) in chloroform (20 ml) was added slowly to a solution of aluminium nitrate nonahydrate (0.1558 g, 0.415 mmol) in methanol (10 ml), followed by a solution of sodium acetate (0.0399 g, 0.486 mmol) in methanol (10 ml). The reaction was stirred under reflux at 70 °C for 24 h. A precipitate formed upon cooling and was filtered off (yield 0.1632 g, 89.30%). ^{1}H NMR (600 MHz, DMSO): δ 9.31 (*s*, 1H), 8.17 (*dt*, J = 7.2, 3.6 Hz, 1H), 7.58 (*dd*, J = 6.2, 3.3 Hz, 1H), 7.34 (*d*, J = 7.5 Hz, 1H), 7.24 (*s*, 1H), 6.84 (*s*, 1H), 3.93 (*s*, 3H). IR (cm^{-1}): ν(O—H) = 3319.9, ν(C—O) = 1109.4 and ν(C—N) = 1134.8. UV–Vis: λ_{max} = 315 nm, ε = 19836 M^{-1} cm^{-1}. Elemental analysis (C, N and H) calculated (%): C 60.41, H 5.07, N 6.40; found: C 60.64, H 4.98, N 6.74.

2.2.3. [Ga(PAMM)$(H_2O)_2$]$NO_3{\cdot}C_2H_5OH$, 2. A solution of H_2PAMM (0.1518 g, 0.404 mmol) in chloroform (20 ml) was added slowly to a solution of gallium(III) nitrate hydrate (0.1011 g, 0.393 mmol) in methanol (10 ml), followed by a solution of sodium acetate (0.0400 g, 0.472 mmol) in methanol (10 ml). The reaction was stirred under reflux at 70 °C for 24 h. A precipitate formed upon cooling and was filtered off (yield 0.1657 g, 85.07%). ^{1}H NMR (300 MHz, DMSO): δ 9.29 (*s*, 1H), 7.95 (*s*, 1H), 7.24 (*d*, J = 7.4 Hz, 1H), 7.17 (*d*, J = 7.6 Hz, 1H), 6.79 (*t*, J = 7.6 Hz, 1H), 3.87 (*s*, 3H), 2.37 (*s*, 3H). IR (cm^{-1}): ν(O—H) = 3590.9, ν(C—O) = 1239.9 and ν(C—N) = 1077.2. UV–Vis: λ_{max} = 320 nm, ε = 34195 M^{-1} cm^{-1}. Elemental

Table 1
Experimental details.

For both structures: triclinic, $P\overline{1}$, $Z = 4$. Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker APEXII CCD diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	1	**2**
Crystal data		
Chemical formula	$[Al(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3{\cdot}C_2H_6O$	$[Ga(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3{\cdot}C_2H_6O$
M_r	545.47	588.21
a, b, c (Å)	12.413 (5), 13.394 (5), 16.368 (5)	12.399 (5), 13.580 (5), 16.419 (5)
α, β, γ (°)	87.899 (5), 79.578 (5), 66.635 (5)	86.818 (5), 78.871 (5), 66.124 (5)
V (Å^3)	2455.1 (15)	2479.7 (16)
μ (mm^{-1})	0.15	1.17
Crystal size (mm)	0.30 × 0.27 × 0.13	0.58 × 0.24 × 0.23
Data collection		
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	64029, 11817, 7331	47407, 11972, 10426
R_{int}	0.062	0.027
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.661	0.661
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.163, 1.02	0.044, 0.114, 1.06
No. of reflections	11817	11886
No. of parameters	718	682
No. of restraints	19	20
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.80, −0.77	1.84, −2.07

Computer programs: *APEX2* (Bruker, 2010), *SAINT* (Bruker, 2010), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015) and *SHELXTL* (Bruker, 2010).

analysis (C, H and N) calculated (%): C 55.03, H 4.62, N 5.38; found: C 55.14, H 4.54, N 5.51.

2.3. Single-crystal X-ray crystallography

Crystal data, data collection and structure refinement details are summarized in Table 1. For **1** and **2**, all H atoms were positioned in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for sp^2 CH, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl groups. Disorder of the ethanol solvent species was observed for both complexes and during the refinement, distance and similarity restraints were applied to the chemically equivalent bond lengths and angles.

3. Results and discussion

3.1. Synthesis and crystal structures

H_2PAMM, $[Al(PAMM)(H_2O)_2]{\cdot}NO_3{\cdot}CH_3CH_2OH$ (**1**) and $[Ga(PAMM)(H_2O)_2]{\cdot}NO_3{\cdot}CH_3CH_2OH$ (**2**) were successfully synthesized and characterized by IR, UV–Vis, elemental analysis and ^{1}H NMR spectroscopy. The free ligand was prepared in the solid state with excellent yields, using a ball mill.

The aluminium and gallium complexes are isomorphous and crystallize in the triclinic space group $P\overline{1}$ with two independent molecules in the asymmetric unit. Each metal centre has an octahedral coordination geometry (Fig. 1). The central metal atoms are bound to the tetradentate ligands *via* two N and two O atoms. Two water molecules are also attached to the central metal atom in each case to complete the octahedral environments. Two nitrate counter-ions and two solvent molecules (ethanol) complete the asymmetric units in each case. Interestingly, both structures have one of the two solvent molecules disordered. Both **1** and **2** show 50/50 positional disorder for the ethanol molecule, the only difference being

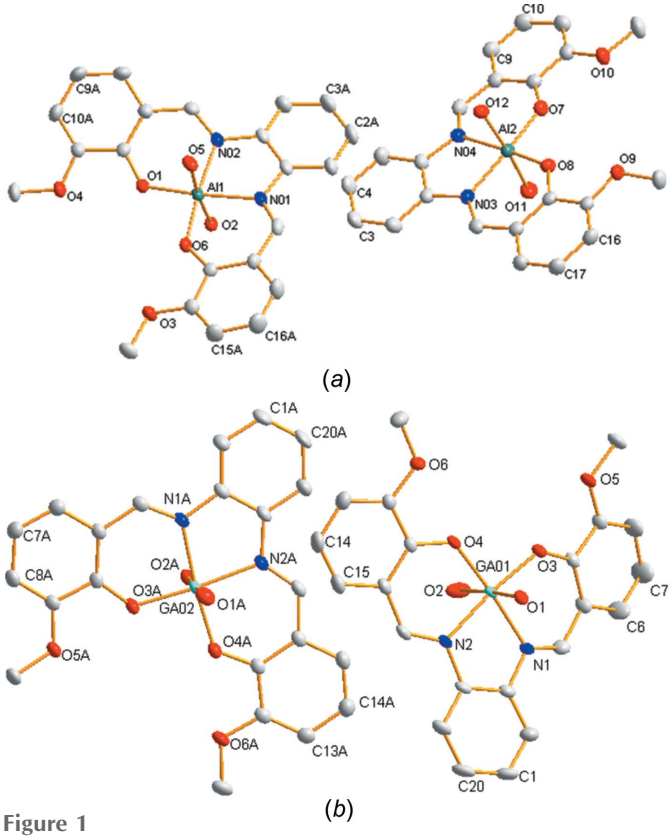


Figure 1
Structural representations of (*a*) **1** and (*b*) **2**. H atoms, solvent molecules and counter-ions have been omitted for clarity

Table 2
Selected geometric parameters (Å, °) for **1**.

N01—Al1	2.007 (2)	O1—Al1	1.8197 (19)
N02—Al1	1.988 (2)	O2—Al1	1.8066 (19)
N03—Al2	1.991 (2)	O7—Al2	1.812 (2)
N04—Al2	1.998 (2)	O8—Al2	1.809 (2)
O2—Al1—O1	93.64 (8)	O8—Al2—O7	92.64 (9)
O1—Al1—N02	92.09 (9)	O8—Al2—N03	93.18 (9)
O2—Al1—N01	93.08 (9)	O7—Al2—N04	92.57 (9)
N02—Al1—N01	81.16 (9)	N03—Al2—N04	81.73 (9)

Table 3
Selected geometric parameters (Å, °) for **2**.

Ga01—O4	1.8829 (18)	Ga02—O5*A*	1.887 (2)
Ga01—O3	1.8941 (18)	Ga02—O4*A*	1.8878 (18)
Ga01—N1	2.009 (2)	Ga02—N1*A*	2.005 (2)
Ga01—N2	2.022 (2)	Ga02—N2*A*	2.019 (2)
O4—Ga01—O3	91.95 (8)	O5*A*—Ga02—O4*A*	91.11 (8)
O3—Ga01—N1	92.60 (8)	O4*A*—Ga02—N1*A*	93.96 (8)
O4—Ga01—N2	93.84 (8)	O5*A*—Ga02—N2*A*	92.88 (8)
N1—Ga01—N2	81.59 (9)	N1*A*—Ga02—N2*A*	82.20 (9)

Table 4
Selected intramolecular hydrogen (bonds (Å, °) for **1** and **2**.

Complex **1**				
O5—H52···O16	0.87 (2)	1.83 (3)	2.684 (3)	169 (3)
O11—H11*B*···O1*A*	0.83 (3)	1.73 (3)	2.573 (4)	178 (7)
Complex **2**				
O2—H2*B*···O7	0.85 (3)	2.47 (4)	3.116 (3)	134 (5)
O2—H2*B*···O16	0.85 (3)	1.91 (4)	2.727 (3)	161 (6)

that the molecule in **1** seems to flip around the O atom while the disordered molecules are side-by-side in **2**. The Ga—N, Ga—O, Al—N and Al—O (Tables 2 and 3) bond lengths are considered to fall within the normal range (Knapp *et al.*, 2015; Obrey *et al.*, 2002). The deviations from perfect octahedral geometry of the complex molecules in **1** and **2** are best illustrated by the N02—Al1—N01 and N1*A*—Ga02—N2*A* angles of 81.16 (9) and 82.20 (9)°, respectively.

The tetradentate ligand reveals interesting characteristics in terms of its deviation from planarity in both **1** and **2**. When a plane is constructed through the central metal atom and the *N*,*N*′,*O*,*O*′-coordinating atoms of the ligand (Figs. 2*a* and 2*b*) for both molecules in the asymmetric units of **1** and **2**, a clear deviation from near planarity is observed for one of the complexes in each case. In **1**, atom C9*A* is 1.155 (3) Å from the plane through Al1/N01/N02/O1/O6, while atom C18 is only 0.257 (3) Å from the plane through Al2/N03/N04/O7/O8. In **2**, the longest distance from the plane through Ga01/N1/N2/O3/O4 is observed for atom C7 [1.1707 (3) Å], while the furthest atom (C6*A*) from the Ga02/N1*A*/N2*A*/O3A/O4*A* plane in the second molecule is only at a distance of 0.2925 (3) Å. Intramolecular O—H···O interactions are present in both **1** and **2** and are summarized in Table 4.

The more planar molecules in **2** (Ga02) pack above each other in a head-to-head fashion so that π–π interactions with a centroid-to-centroid distance of 3.9722 (5) Å can occur between the methoxyphenyl rings (Table 5). Another π–π interaction [distance 3.7031 (4) Å] is observed between the central arene rings (phenylenediamine building block) of the molecules containing atoms Ga01 and Ga02, which also pack in a head-to-head orientation (Yahsi, 2016).

The more planar molecules in **1** mimic the π–π interaction of **2**, with a centroid-to-centroid distance of 3.654 (3) Å between the two methoxyphenyl rings, but in this case no other interactions are observed.

C—H···π interactions (Table 6) in **1** and **2** are similar (Figs. 3 and 4) and occur between neighbouring molecules, from a methoxy substituent of one molecule towards an arene ring of another (Al2 and Ga02).

3.2. Photoluminescence

The emission spectra of the free ligand and complexes **1** and **2** were obtained in the solid state at room temperature (Fig. 5).

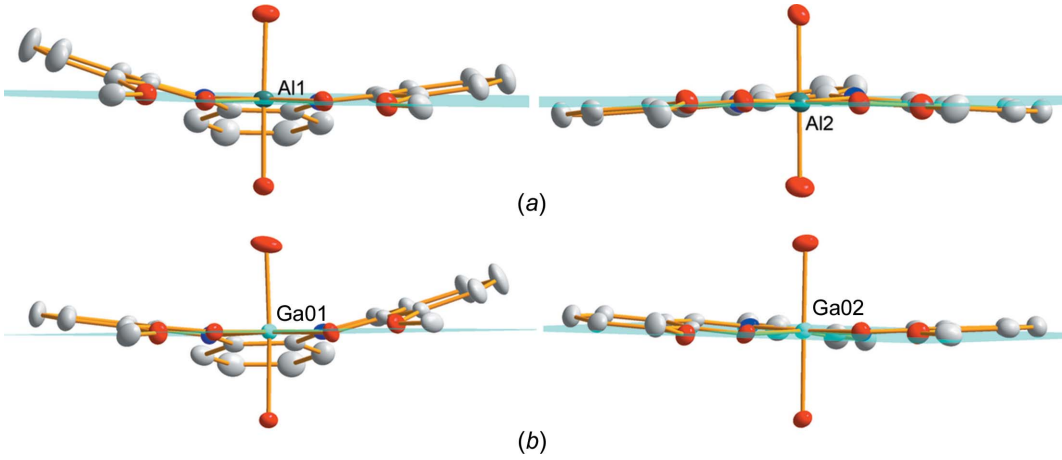


Figure 2
(*a*) Deviation from planarity through the Al—N—N—O—O planes of the tetradentate ligand in **1**. (*b*) Deviation from planarity through the Ga—N—N—O—O planes of the tetradentate ligand in **2**.

Table 5
Geometrical parameters (Å, °) for π–π stacking for **1** and **2**.

Complex	*Cgi*[a]	[Res]···*Cgj*[b]	Rc[c]	R1v[d]	R2v[e]	A[f]	B[g]	Γ[h]
1	*Cg*5	[2]···*Cg*6^{iii}	3.654 (3)	−3.3184 (10)	−3.3995 (12)	7.61 (15)	24.73	21.49
2	*Cg*1	[2]···*Cg*2^{i}	3.972 (5)	3.7819 (11)	3.1648 (11)	19.59 (18)	17.81	37.18
	*Cg*3	[2]···*Cg*4^{ii}	3.703 (4)	3.4169 (13)	3.3194 (18)	7.64 (13)	22.68	26.31

Symmetry codes (i) $-x, -y+1, -z$; (ii) $x, y-1, z-1$; (iii) $-x+1, -y, -z+1$. Notes: (*a*) for **1**, *Cg*5 and *Cg*6 are the centroids of the C8–C13 and C14–C19 rings, respectively. For **2**, *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the C1–C3/C18–C20, C1*A*–C3*A*/C18*A*–C20*A*, C5*A*–C10*A* and C11*A*–C16*A* rings, respectively; (*b*) [Res] = Residue; (*c*) Residue–centroid distance between ring *i* and ring *j*; (*d*) vertical distance from ring centroid *i* to ring *j*; (*e*) vertical distance from ring centroid *j* to ring *i*; (*f*) dihedral angle between the first ring mean plane and the second ring mean plane of the partner molecule; (*g*) angle between the centroid of the first ring and the second ring; (*h*) angle between the centroid of the first ring and the normal to the mean plane of the second ring of the partner molecule.

The ligand in the solid state was excited at 335 nm and emitted three peaks at 470, 492 and 511 nm, showing that it is luminescent. These excitations may be attributed to π–π^* transitions (Miles *et al.*, 1981).

The solid state of **2** emits green light at 545 nm upon excitation at 355 nm. The emission is due to a ligand-centred charge-transfer excited state, modulated by the presence of the Ga atom. It is indicated from this observation that the intraligand charge-transfer (ILCT) emitting state lies below any ligand–metal charge transfer (LMCT) excited states (Paul *et al.*, 2015). The red shift in the luminescence maxima of **2** was

Table 6
Geometrical parameters (Å, °) for X—H···π interactions.

Complex	X—H(I)	Res(I)→*Cg*(J)	H···*Cg*	X—H···*Cg*	Y···*Cg*
1	C021—H02*A*^{ii}	[1]→*Cg*2	2.86 (8)	170	3.817 (3)
2	C21—H21*B*^{i}	[1]→*Cg*11	2.80 (2)	162	3.729 (3)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, y, z-1$.

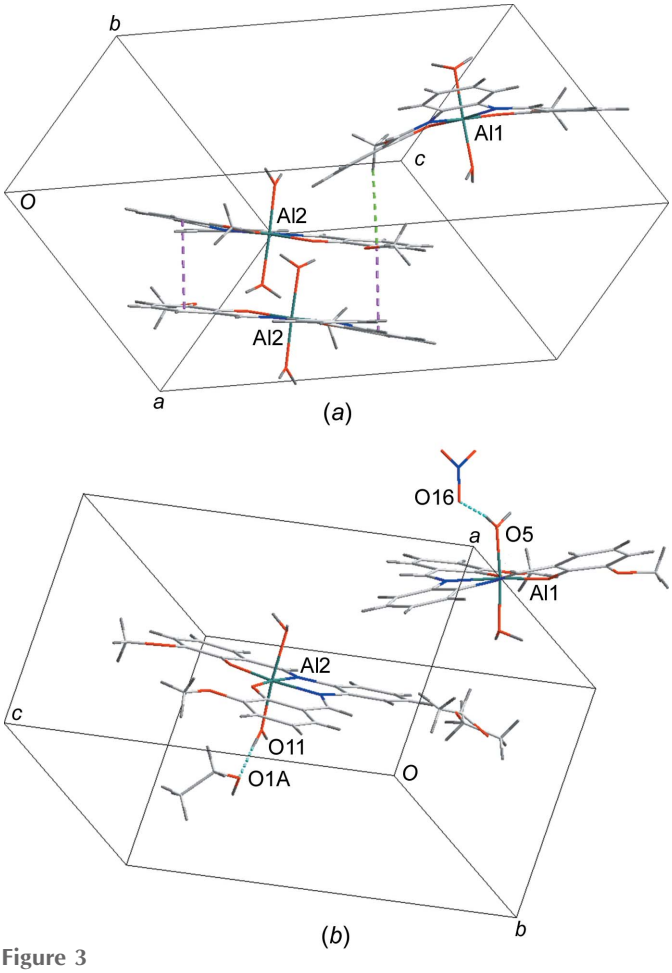


Figure 3
Illustration of (*a*) the π–π and C—H···π interactions, and (*b*) the hydrogen-bond interactions in **1**.

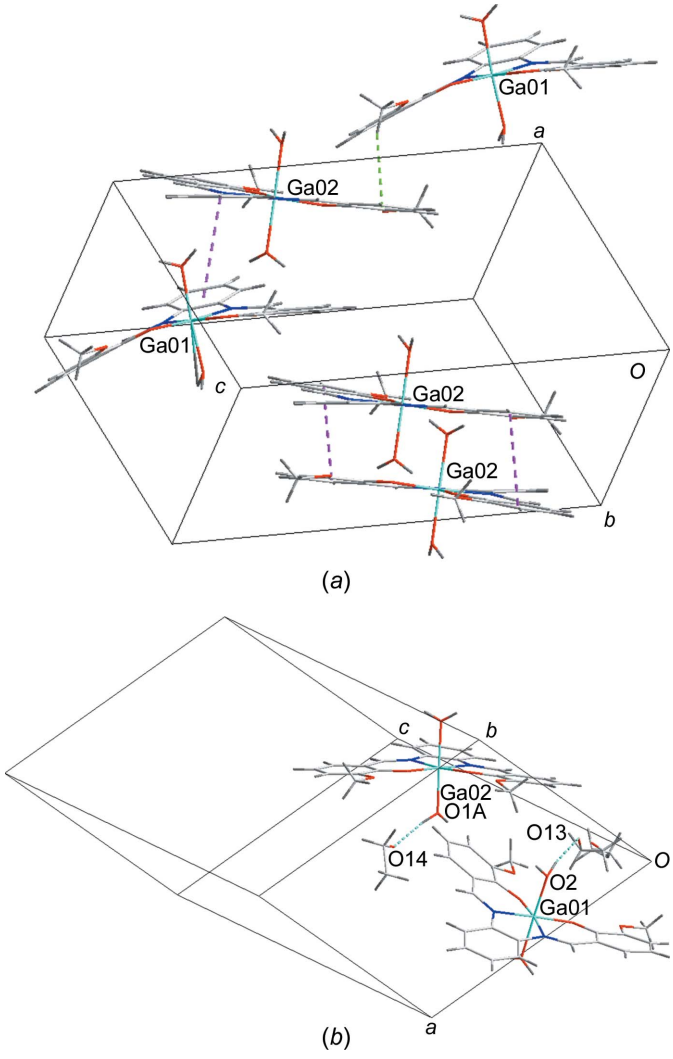


Figure 4
Illustration of (*a*) the π–π interactions and (*b*) the hydrogen-bond interactions in **2**.

Table 7
Selected experimental and DFT-calculated geometric parameters (Å, °) for the indicated complexes.

Complex	Bond	Bond length *via* XRD	Bond length *via* DFT	Angle	Bond angle *via* XRD	Bond angle *via* DFT
Complex **1**	N01—Al1	2.007 (2)	2.007	O2—Al1—O1	93.64 (8)	94.5
	N02—Al1	1.988 (2)	1.987	O2—Al1—N01	93.08 (9)	92.8
	O1—Al1	1.8197 (19)	1.820	N02—Al1—N01	81.16 (9)	81.6
	O2—Al1	1.8066 (19)	1.807	O1—Al1—N02	92.09 (9)	91.6
Complex **2**	O5*A*—Ga02	1.887 (2)	1.891	O4*A*—Ga02—O5*A*	91.11 (8)	91.5
	O4*A*—Ga02	1.8878 (18)	1.889	O5*A*—Ga02—N2*A*	92.88 (8)	93.1
	N2*A*—Ga02	2.019 (2)	2.022	N2*A*—Ga02—N1*A*	82.20 (9)	81.9
	N1*A*—Ga02	2.005 (2)	2.009	N1*A*—Ga02—O4*A*	93.96 (8)	94.2

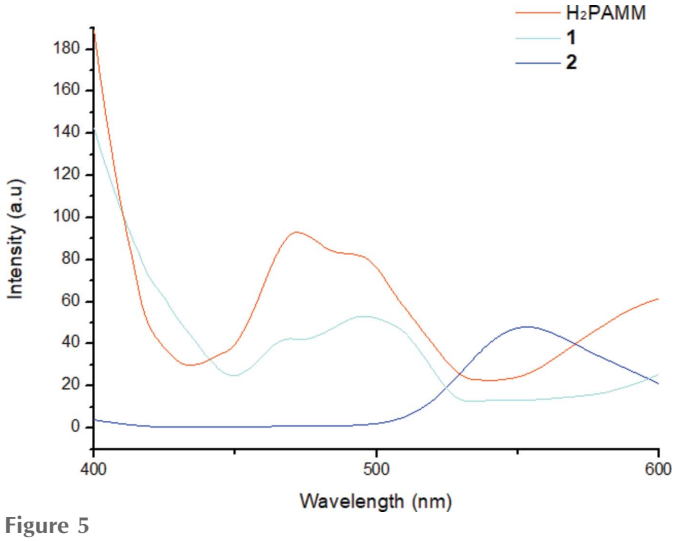


Figure 5
Comparison of the solid-state photoluminescence for H_2PAMM, **1** and **2**.

compared to that of the ligand. In elements with stable d^{10} configurations, the photoluminescence properties of the complexes are only determined by the organic ligand (Liuzzo *et al.*, 2010). The difference in emission properties between the ligand and the complex can therefore be attributed to the Ga atom. The ligand conformational rigidity is increased by the Ga atom and this is favourable for the formation of a more planar and conjugated structure. The reduction in the energy gap between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the ligand (2.139 eV) on coordination of the metal ions (1.752 and 1.694 eV for **1** and **2**, respectively) enhances the mobility of the electron transition due to back-coupling π-bonding between the metal and ligand, and this leads to a decrease in the electronic transition energy of the ILCT (Ali, 1987). Solvent molecules are incapable of forming π–π orbital overlaps with the ligands and simply act as spacer molecules, which reduces the intermolecular interactions involving the arene groups.

When comparing the photoluminescence spectra of **1** and **2** with that of the ligand (Fig. 5), the gallium complex deviates from the ligand curve, resulting in a new curve (80 nm red shifted), whereas the aluminium complex maintains the ligand curve with a slight red shift (40 nm).

3.3. Computational chemistry

Selected bond lengths and angles of the optimized structures of **1** and **2** are given in Table 7. The optimized metal–ligand bond lengths compare well with the experimental single-crystal X-ray structure values; all calculated metal–oxygen and metal–nitrogen bonds are within 0.02 Å of the XRD data. The angles involving the metal atom are within 0.8° of the XRD data. Slightly larger DFT-calculated bond lengths than experimental bond lengths are generally observed for gas-phase DFT optimizations, and therefore differences between the experimentally measured metal–ligand bond lengths and the calculated bond lengths below a threshold of 0.02 Å are considered meaningless. Interestingly, the optimized structures also show deviations from planarity for the tetradentate ligands, with the largest distances of the C atoms from the metal—N—N—O—O plane being 0.63 and 0.92 Å for **1** and **2**, respectively.

The Ga-*d*-based molecular orbitals of **2** are shown in Fig. 6. It is interesting to note that the *d*-based orbitals point directly along the bonds in the direction of the ligands; namely d_z^2 (HOMO-72) and $d_{x^2-y^2}$ (HOMO-71) have lower energies than the orbitals pointing in between the bonds between Ga and the ligands, which are the $d\pi$ (HOMO-70 and HOMO-69) and

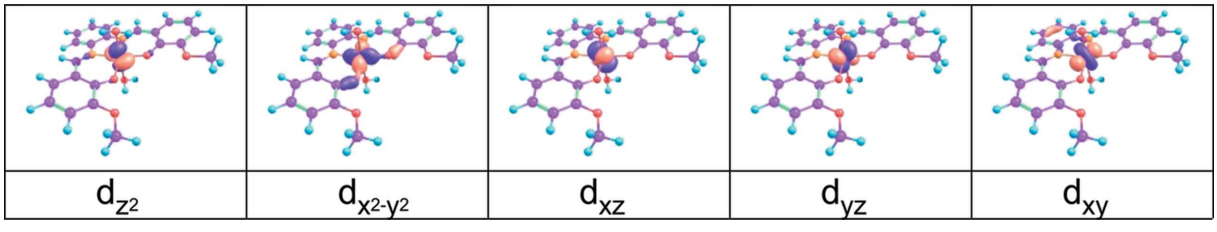


Figure 6
The Kohn–Sham Ga-*d*-based molecular orbitals of **2**, obtained from PW91/STO-TZP DFT calculation. The MO plots use a contour of 60 e nm^{-3}. Colour code of atoms: Ga green, C pink, O red, N orange and H sky blue.

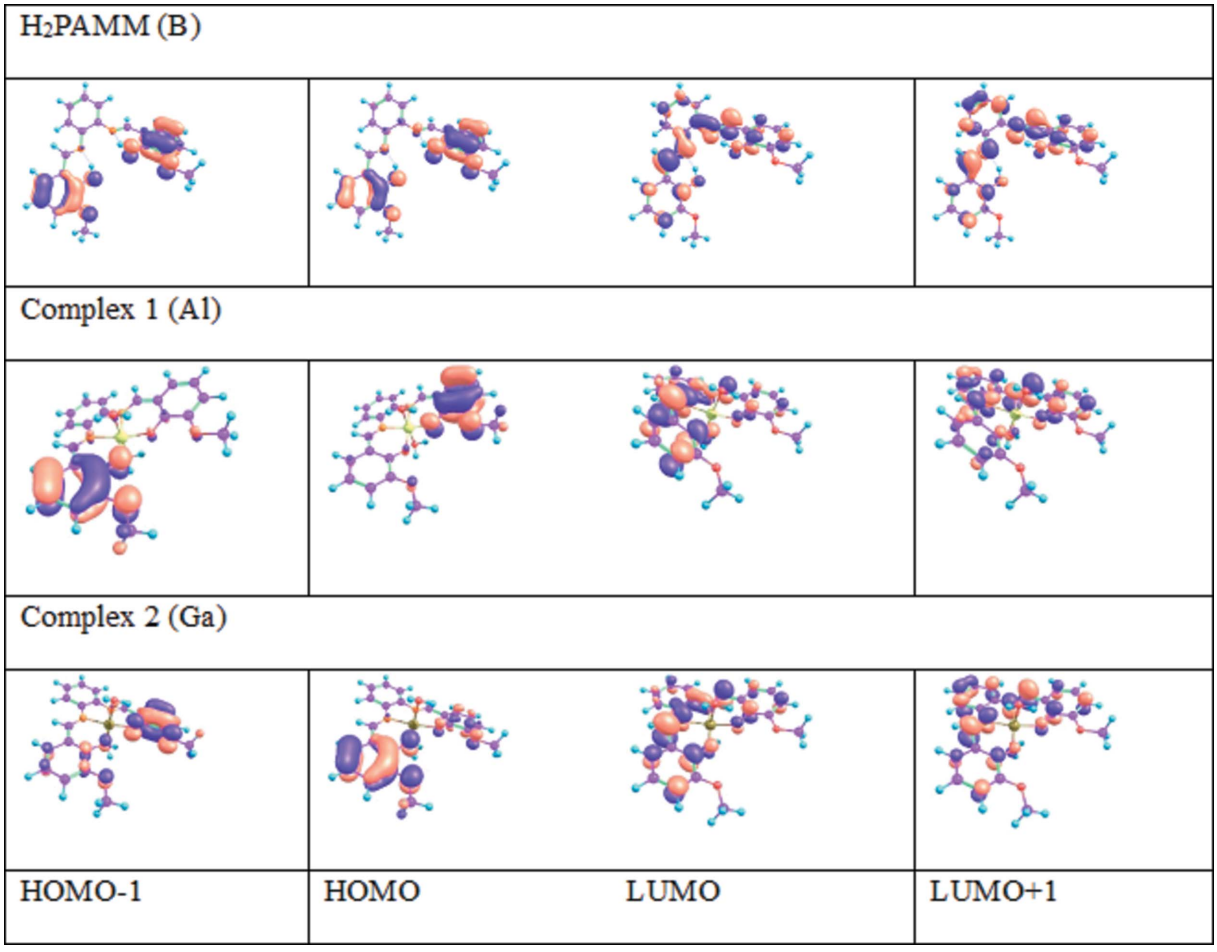


Figure 7
The Kohn–Sham frontier orbitals of H_2PAMM and **1** and **2**, obtained from PW91/STO-TZP DFT calculation. The MO plots use a contour of 60 e nm^{-3}. Colour code of atoms: Al yellow, Ga green, C pink, O red, N orange and H sky blue.

d_{xy} (HOMO-68) types of mainly *d*-based molecular orbitals.

Selected frontier molecular orbitals of H_2PAMM and **1** and **2** are compared in Fig. 7. They have similar features and are all ligand based. The HOMOs are mainly on the arene rings of the methoxyphenyl rings, while the LUMOs are spread over the ligand backbone showing effective communication through π-orbitals throughout the ligand.

The oxidation and reduction of a complex generally involve the removal of an electron from the HOMO, or the addition of an electron to the LUMO of the complex (Conradie, 2015). Since the HOMO and LUMO of H_2PAMM and complexes **1** and **2** are ligand based, the first oxidation and first reduction of these complexes will involve the ligand and is not expected to be metal based. Due to the low-lying *d* orbitals of **2**, Ga-metal-based oxidation and reduction are not expected. The electrochemical oxidation and reduction of H_2PAMM and complexes **1** and **2** will be discussed in the next section.

3.4. Cyclic voltammetry

The cyclic voltammograms (CVs) of H_2PAMM, **1** and **2**, at a scan rate of 0.100 V$_s^{-1}$, are given in Fig. 8. The ligand, **1** and **2** show several irreversible oxidation and reduction peaks

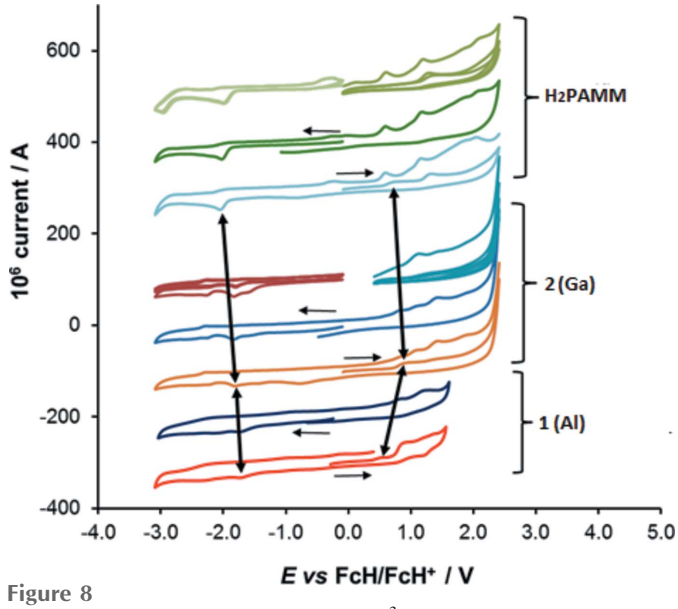


Figure 8
Cyclic voltammograms of 0.0005 mol dm^{-3} solutions of H_2PAMM (top), **2** (middle) and **1** (bottom) in acetonitrile, with supporting electrolyte tetrabutylammonium hexafluorophosphate and a glassy carbon working electrode, at a scan rate of 0.100 V s^{-1}, with potential *versus* FcH/FcH$^+$. Scans are initiated in the direction indicated by the arrows.

(Elgrishi *et al.*, 2018). The first oxidation peak of the ligand at 0.74 V *versus* FcH/FcH^+ shifts to a higher more positive potential, *i.e.* 0.93 V *versus* FcH/FcH^+, when complexed to **2**, but to a lower less positive potential, *i.e.* 0.53 V *versus* FcH/FcH^+, when complexed to **1**. The first oxidation peaks of the ligand and complexes **1** and **2** are assigned to ligand oxidation, based on the character of their HOMOs. Ligand oxidation is thus stabilized when complexed to Ga, and occur at a higher more positive potential for **2** than for the free ligand. The first reduction peak of the ligand at −2.04 V *versus* FcH/FcH^+ shifts to a higher less negative potential, *i.e.* −1.71 and −1.79 V *versus* FcH/FcH^+, when complexed to **1** and **2**, respectively. The first reduction peaks of the ligand and the complexes are assigned to ligand reduction, based on the character of their LUMOs. Upon reduction, a radical anion is formed with the π-electron density spread over the aromatic backbone of the ligand. This ligand reduction is easier at a less negative potential when complexed to Ga or Al.

4. Conclusions

This study reports some coordination-chemistry aspects of the novel Schiff base ligand 6,6′-{(1*E*,1′*E*)-[1,2-phenylene-bis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenol) (H_2PAMM) complexed to aluminium (**1**) and gallium (**2**). The crystal structures and packing of both **1** and **2** are very similar, even to the point of having one of the complex molecules in the asymmetric unit being almost planar, whereas the other deviates substantially from planarity. Planarity is attributed to strong π–π interactions. DFT calculations indicate that the ideal geometry would not be planar, but rather twisted.

Acknowledgements

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supporting information

Acta Cryst. (2019). C**75** [https://doi.org/10.1107/S2053229619008805]

Synthesis, crystal structures, photoluminescence, electrochemistry and DFT study of aluminium(III) and gallium(III) complexes containing a novel tetradentate Schiff base ligand

James Charles Truscott, Jeanet Conradie, Hendrik C. Swart, Mart-Marie Duvenhage and Hendrik Gideon Visser

Computing details

For both structures, data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Bruker, 2010); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2015).

Diaqua(6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenolato)-$\kappa^4O^1,N,N',O^{1'}$)aluminium(III) nitrate ethanol monosolvate (shelx)

Crystal data

$[Al(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3\cdot C_2H_6O$
M_r = 545.47
Triclinic, $P\overline{1}$
a = 12.413 (5) Å
b = 13.394 (5) Å
c = 16.368 (5) Å
α = 87.899 (5)°
β = 79.578 (5)°
γ = 66.635 (5)°
V = 2455.1 (15) Å^3
Z = 4
$F(000)$ = 1144
D_x = 1.476 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 9867 reflections
θ = 1.0–1.0°
μ = 0.15 mm^{-1}
T = 100 K
Cuboid, yellow
0.30 × 0.27 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
64029 measured reflections
11817 independent reflections
7331 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 28.0°, θ_{min} = 1.7°
h = −16→12
k = −17→17
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.163
S = 1.02
11817 reflections
718 parameters
19 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 2.3877P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.5080 (2)	0.3196 (2)	0.35492 (16)	0.0242 (6)	
C5A	0.9140 (2)	0.1954 (2)	0.08411 (17)	0.0224 (6)	
C1T	0.0336 (4)	0.2269 (4)	0.5388 (3)	0.0752 (14)	
H1T1	0.1042	0.1691	0.5528	0.090*	
H1T2	0.0057	0.1971	0.4979	0.090*	
C4A	0.8417 (3)	0.1404 (2)	0.07802 (19)	0.0297 (6)	
H4A	0.8370	0.1180	0.0262	0.036*	
C2	0.5570 (3)	0.3951 (2)	0.32735 (18)	0.0309 (7)	
H2	0.5862	0.4250	0.3640	0.037*	
C2T	−0.0622 (4)	0.2631 (4)	0.6162 (3)	0.0695 (12)	
H2TA	−0.0398	0.3009	0.6544	0.104*	
H2TB	−0.0709	0.2005	0.6420	0.104*	
H2TC	−0.1366	0.3107	0.6013	0.104*	
C3	0.5619 (3)	0.4253 (2)	0.24553 (19)	0.0345 (7)	
H3	0.5935	0.4763	0.2276	0.041*	
C3A	0.7767 (3)	0.1189 (2)	0.1491 (2)	0.0351 (7)	
H3A	0.7283	0.0818	0.1451	0.042*	
C4	0.5199 (3)	0.3800 (2)	0.18989 (18)	0.0343 (7)	
H4	0.5256	0.3993	0.1346	0.041*	
C2A	0.7835 (3)	0.1526 (2)	0.2262 (2)	0.0349 (7)	
H2A	0.7404	0.1369	0.2738	0.042*	
C1A	0.8534 (3)	0.2090 (2)	0.23351 (18)	0.0282 (6)	
H1A	0.8564	0.2322	0.2856	0.034*	
C5	0.4696 (3)	0.3064 (2)	0.21672 (18)	0.0319 (7)	
H5	0.4420	0.2758	0.1794	0.038*	
C20A	0.9197 (2)	0.2309 (2)	0.16182 (17)	0.0226 (6)	
C6	0.4603 (2)	0.2781 (2)	0.29950 (17)	0.0255 (6)	
C7	0.3410 (3)	0.1778 (2)	0.29453 (17)	0.0265 (6)	
H7	0.3340	0.2031	0.2413	0.032*	
C19A	1.0190 (2)	0.3174 (2)	0.22613 (16)	0.0228 (6)	
H19A	0.9933	0.2917	0.2762	0.027*	
C18A	1.0854 (2)	0.3842 (2)	0.22816 (16)	0.0223 (6)	
C8	0.2809 (2)	0.1087 (2)	0.32543 (17)	0.0243 (6)	
C17A	1.1076 (3)	0.4048 (2)	0.30642 (18)	0.0320 (7)	
H17A	1.0837	0.3719	0.3531	0.038*	
C9	0.2189 (3)	0.0800 (2)	0.27187 (18)	0.0280 (6)	

H9	0.2180	0.1070	0.2187	0.034*
C16A	1.1634 (3)	0.4719 (3)	0.31399 (19)	0.0375 (7)
H16A	1.1795	0.4831	0.3654	0.045*
C10	0.1608 (3)	0.0138 (2)	0.29680 (19)	0.0319 (7)
H10	0.1201	−0.0039	0.2611	0.038*
C11	0.1625 (3)	−0.0279 (2)	0.37686 (18)	0.0304 (6)
H11	0.1226	−0.0730	0.3941	0.036*
C15A	1.1970 (3)	0.5246 (2)	0.24454 (18)	0.0312 (7)
H15A	1.2340	0.5716	0.2503	0.037*
C14A	1.1755 (2)	0.5069 (2)	0.16792 (16)	0.0232 (6)
C12	0.2228 (2)	−0.0021 (2)	0.42984 (17)	0.0264 (6)
C13A	1.1224 (2)	0.4335 (2)	0.15751 (15)	0.0189 (5)
C13	0.2825 (2)	0.0675 (2)	0.40557 (16)	0.0226 (6)
C14	0.4968 (2)	0.1922 (2)	0.60431 (16)	0.0224 (6)
C12A	1.1073 (2)	0.2922 (2)	−0.13148 (16)	0.0206 (5)
C11A	1.1604 (2)	0.3190 (2)	−0.20851 (16)	0.0230 (6)
C15	0.5028 (2)	0.1578 (2)	0.68710 (16)	0.0227 (6)
C10A	1.1856 (3)	0.2562 (2)	−0.27980 (18)	0.0341 (7)
H10A	1.2233	0.2734	−0.3294	0.041*
C16	0.5523 (3)	0.1992 (2)	0.73854 (17)	0.0276 (6)
H16	0.5559	0.1753	0.7924	0.033*
C9A	1.1544 (3)	0.1664 (3)	−0.2774 (2)	0.0429 (8)
H9A	1.1738	0.1227	−0.3251	0.051*
C17	0.5973 (3)	0.2776 (2)	0.70969 (18)	0.0307 (6)
H17	0.6306	0.3057	0.7446	0.037*
C8A	1.0957 (3)	0.1423 (2)	−0.20543 (19)	0.0370 (7)
H8A	1.0715	0.0848	−0.2053	0.044*
C18	0.5923 (3)	0.3129 (2)	0.63031 (17)	0.0279 (6)
H18	0.6225	0.3648	0.6118	0.034*
C7A	1.0715 (2)	0.2045 (2)	−0.13123 (17)	0.0254 (6)
C19	0.5422 (2)	0.2716 (2)	0.57628 (16)	0.0229 (6)
C6A	1.0075 (2)	0.1765 (2)	−0.05780 (17)	0.0236 (6)
H6A	0.9814	0.1212	−0.0630	0.028*
C20	0.5427 (2)	0.3105 (2)	0.49339 (17)	0.0242 (6)
H20	0.5748	0.3623	0.4796	0.029*
C021	1.2292 (3)	0.4467 (2)	−0.28041 (17)	0.0296 (6)
H02A	1.3074	0.3945	−0.3033	0.044*
H02B	1.2332	0.5154	−0.2708	0.044*
H02C	1.1764	0.4554	−0.3188	0.044*
C21	0.1731 (3)	−0.1105 (3)	0.5381 (2)	0.0380 (7)
H21A	0.0886	−0.0724	0.5411	0.057*
H21B	0.1892	−0.1341	0.5923	0.057*
H21C	0.2023	−0.1726	0.5004	0.057*
C22	0.4375 (3)	0.0573 (3)	0.79402 (17)	0.0331 (7)
H22A	0.5126	0.0259	0.8127	0.050*
H22B	0.3993	0.0069	0.8015	0.050*
H22C	0.3874	0.1235	0.8257	0.050*
C022	1.2547 (3)	0.6319 (2)	0.10115 (19)	0.0314 (7)

H02D	1.2020	0.6898	0.1403	0.047*	
H02E	1.2669	0.6611	0.0475	0.047*	
H02F	1.3299	0.5966	0.1192	0.047*	
N01	0.99260 (19)	0.29061 (16)	0.15943 (13)	0.0201 (5)	
N02	0.98374 (19)	0.22294 (16)	0.01499 (13)	0.0201 (5)	
N03	0.5016 (2)	0.27866 (17)	0.43608 (13)	0.0225 (5)	
N04	0.4048 (2)	0.20796 (17)	0.33505 (14)	0.0242 (5)	
N07	1.2872 (2)	−0.06382 (18)	0.07667 (15)	0.0290 (5)	
N08	0.7856 (2)	0.43557 (19)	0.45715 (14)	0.0286 (5)	
O1	1.09202 (16)	0.35187 (13)	−0.06456 (11)	0.0204 (4)	
O1A	0.0628 (2)	0.3039 (3)	0.5058 (2)	0.0765 (9)	
H1AA	0.0025	0.3565	0.4995	0.115*	
O2	1.10899 (16)	0.41676 (14)	0.08147 (10)	0.0203 (4)	
O3	1.20306 (17)	0.55492 (14)	0.09594 (11)	0.0249 (4)	
O4	1.18555 (16)	0.40955 (14)	−0.20349 (11)	0.0238 (4)	
O5	1.20062 (17)	0.20279 (15)	0.04417 (13)	0.0256 (4)	
O6	0.89451 (16)	0.44340 (14)	0.05168 (11)	0.0199 (4)	
O7	0.33834 (17)	0.08916 (14)	0.46022 (11)	0.0245 (4)	
O8	0.44928 (17)	0.14838 (14)	0.55821 (11)	0.0248 (4)	
O9	0.45715 (17)	0.08044 (15)	0.70789 (11)	0.0259 (4)	
O10	0.23163 (18)	−0.03909 (15)	0.50890 (12)	0.0295 (4)	
O11	0.2739 (2)	0.30139 (17)	0.48967 (13)	0.0324 (5)	
O12	0.57291 (18)	0.05570 (15)	0.40929 (12)	0.0251 (4)	
O13	0.6790 (2)	0.49714 (18)	0.47098 (16)	0.0496 (6)	
O14	0.8200 (2)	0.34409 (16)	0.42420 (13)	0.0372 (5)	
O15	0.8595 (2)	0.4692 (2)	0.47657 (15)	0.0478 (6)	
O16	1.18516 (17)	0.01059 (15)	0.07687 (13)	0.0325 (5)	
O18	1.2986 (2)	−0.15766 (16)	0.09207 (15)	0.0413 (6)	
Al1	1.05248 (7)	0.32514 (6)	0.04415 (5)	0.01802 (17)	
Al2	0.41964 (7)	0.17640 (6)	0.45372 (5)	0.02215 (19)	
C4R	1.4110 (4)	0.3722 (3)	−0.0676 (2)	0.0651 (12)	
H4R1	1.4261	0.4338	−0.0534	0.098*	
H4R2	1.3324	0.3968	−0.0806	0.098*	
H4R3	1.4689	0.3330	−0.1149	0.098*	
O4T	1.4043 (5)	0.2113 (3)	−0.0212 (3)	0.0478 (6)	0.5
H4T	1.4649	0.1696	−0.0512	0.072*	0.5
C4T	1.4190 (11)	0.3067 (5)	−0.0030 (6)	0.0478 (6)	0.5
H4T1	1.3585	0.3460	0.0440	0.057*	0.5
H4T2	1.4964	0.2868	0.0127	0.057*	0.5
O4U	1.4144 (5)	0.2145 (3)	0.0158 (3)	0.0496 (6)	0.5
H4U	1.4471	0.1796	−0.0283	0.074*	0.5
C4U	1.4270 (10)	0.3121 (6)	0.0117 (6)	0.0496 (6)	0.5
H4U1	1.5061	0.2989	0.0219	0.059*	0.5
H4U2	1.3700	0.3598	0.0568	0.059*	0.5
O17	1.37647 (19)	−0.04004 (17)	0.06044 (16)	0.0444 (6)	
H52	1.203 (3)	0.1372 (18)	0.049 (2)	0.048 (10)*	
H51	1.269 (2)	0.200 (4)	0.021 (3)	0.097 (18)*	
H61	0.879 (3)	0.461 (3)	0.0022 (14)	0.056 (12)*	

H62	0.891 (3)	0.500 (2)	0.077 (2)	0.049 (11)*
H11B	0.205 (2)	0.301 (3)	0.494 (2)	0.061 (13)*
H11A	0.269 (4)	0.364 (2)	0.496 (3)	0.071 (14)*
H12B	0.563 (3)	0.003 (2)	0.389 (2)	0.045 (10)*
H12A	0.620 (3)	0.028 (3)	0.443 (2)	0.081 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0277 (14)	0.0180 (13)	0.0214 (14)	−0.0039 (11)	−0.0039 (11)	0.0037 (10)
C5A	0.0218 (13)	0.0152 (12)	0.0275 (14)	−0.0058 (10)	−0.0028 (11)	0.0080 (10)
C1T	0.057 (3)	0.085 (3)	0.057 (3)	0.001 (3)	−0.009 (2)	−0.007 (3)
C4A	0.0304 (16)	0.0283 (15)	0.0336 (16)	−0.0148 (13)	−0.0068 (12)	0.0061 (12)
C2	0.0418 (18)	0.0234 (14)	0.0290 (15)	−0.0134 (13)	−0.0101 (13)	0.0061 (12)
C2T	0.065 (3)	0.061 (3)	0.075 (3)	−0.020 (2)	−0.006 (2)	0.003 (2)
C3	0.0456 (19)	0.0253 (15)	0.0347 (17)	−0.0170 (14)	−0.0075 (14)	0.0119 (13)
C3A	0.0359 (17)	0.0332 (16)	0.0422 (18)	−0.0223 (14)	−0.0028 (14)	0.0085 (14)
C4	0.0455 (19)	0.0335 (16)	0.0252 (15)	−0.0163 (14)	−0.0107 (13)	0.0143 (13)
C2A	0.0341 (17)	0.0338 (16)	0.0363 (17)	−0.0180 (14)	0.0033 (13)	0.0104 (13)
C1A	0.0313 (16)	0.0252 (14)	0.0271 (15)	−0.0125 (12)	−0.0011 (12)	0.0086 (12)
C5	0.0401 (17)	0.0335 (16)	0.0250 (15)	−0.0161 (14)	−0.0110 (13)	0.0091 (12)
C20A	0.0211 (13)	0.0165 (12)	0.0266 (14)	−0.0048 (10)	−0.0030 (11)	0.0084 (11)
C6	0.0301 (15)	0.0207 (13)	0.0232 (14)	−0.0075 (11)	−0.0056 (11)	0.0063 (11)
C7	0.0319 (15)	0.0221 (13)	0.0203 (14)	−0.0049 (12)	−0.0068 (11)	0.0060 (11)
C19A	0.0203 (13)	0.0210 (13)	0.0200 (13)	−0.0019 (11)	−0.0023 (10)	0.0086 (10)
C18A	0.0242 (14)	0.0213 (13)	0.0185 (13)	−0.0056 (11)	−0.0059 (10)	0.0055 (10)
C8	0.0256 (14)	0.0208 (13)	0.0224 (14)	−0.0046 (11)	−0.0050 (11)	0.0014 (11)
C17A	0.0365 (17)	0.0397 (17)	0.0225 (15)	−0.0173 (14)	−0.0087 (12)	0.0107 (13)
C9	0.0314 (16)	0.0261 (14)	0.0238 (14)	−0.0067 (12)	−0.0094 (12)	0.0026 (11)
C16A	0.0474 (19)	0.0491 (19)	0.0236 (15)	−0.0240 (16)	−0.0143 (14)	0.0062 (14)
C10	0.0317 (16)	0.0328 (16)	0.0325 (16)	−0.0114 (13)	−0.0125 (13)	0.0018 (13)
C11	0.0281 (15)	0.0285 (15)	0.0339 (16)	−0.0114 (12)	−0.0040 (12)	0.0022 (12)
C15A	0.0342 (16)	0.0380 (17)	0.0287 (16)	−0.0192 (14)	−0.0121 (13)	0.0024 (13)
C14A	0.0200 (13)	0.0227 (13)	0.0239 (14)	−0.0053 (11)	−0.0043 (11)	0.0035 (11)
C12	0.0283 (15)	0.0221 (13)	0.0235 (14)	−0.0055 (12)	−0.0030 (11)	0.0023 (11)
C13A	0.0162 (12)	0.0159 (12)	0.0200 (13)	−0.0011 (10)	−0.0047 (10)	0.0026 (10)
C13	0.0228 (14)	0.0187 (13)	0.0220 (14)	−0.0033 (11)	−0.0050 (11)	0.0008 (10)
C14	0.0231 (14)	0.0173 (12)	0.0203 (13)	−0.0017 (11)	−0.0026 (10)	−0.0024 (10)
C12A	0.0189 (13)	0.0167 (12)	0.0206 (13)	−0.0014 (10)	−0.0034 (10)	0.0018 (10)
C11A	0.0236 (14)	0.0193 (13)	0.0232 (14)	−0.0059 (11)	−0.0040 (11)	0.0036 (11)
C15	0.0252 (14)	0.0177 (12)	0.0196 (13)	−0.0035 (11)	−0.0021 (11)	0.0000 (10)
C10A	0.0394 (18)	0.0361 (17)	0.0220 (15)	−0.0144 (14)	0.0055 (13)	−0.0032 (12)
C16	0.0302 (15)	0.0302 (15)	0.0192 (14)	−0.0085 (12)	−0.0047 (11)	−0.0008 (11)
C9A	0.063 (2)	0.0401 (18)	0.0267 (16)	−0.0267 (17)	0.0068 (15)	−0.0143 (14)
C17	0.0367 (17)	0.0340 (16)	0.0249 (15)	−0.0166 (13)	−0.0075 (12)	−0.0011 (12)
C8A	0.051 (2)	0.0291 (16)	0.0327 (17)	−0.0210 (15)	0.0010 (14)	−0.0082 (13)
C18	0.0316 (16)	0.0280 (14)	0.0250 (15)	−0.0136 (12)	−0.0027 (12)	0.0006 (12)
C7A	0.0295 (15)	0.0187 (13)	0.0252 (14)	−0.0080 (11)	−0.0021 (11)	0.0012 (11)

C19	0.0227 (14)	0.0188 (13)	0.0224 (14)	−0.0042 (11)	−0.0016 (11)	−0.0005 (10)
C6A	0.0268 (14)	0.0149 (12)	0.0271 (15)	−0.0066 (11)	−0.0041 (11)	0.0029 (11)
C20	0.0231 (14)	0.0186 (13)	0.0260 (14)	−0.0041 (11)	−0.0022 (11)	0.0009 (11)
C021	0.0285 (15)	0.0305 (15)	0.0244 (15)	−0.0102 (12)	0.0033 (11)	0.0082 (12)
C21	0.0372 (18)	0.0424 (18)	0.0384 (18)	−0.0217 (15)	−0.0055 (14)	0.0159 (15)
C22	0.0419 (18)	0.0403 (17)	0.0208 (14)	−0.0205 (15)	−0.0063 (13)	0.0084 (13)
C022	0.0359 (17)	0.0281 (15)	0.0387 (17)	−0.0190 (13)	−0.0145 (13)	0.0076 (13)
N01	0.0203 (11)	0.0157 (10)	0.0215 (11)	−0.0047 (9)	−0.0038 (9)	0.0078 (9)
N02	0.0206 (11)	0.0158 (10)	0.0219 (11)	−0.0055 (9)	−0.0037 (9)	0.0055 (9)
N03	0.0255 (12)	0.0188 (11)	0.0177 (11)	−0.0036 (9)	−0.0033 (9)	0.0038 (9)
N04	0.0294 (13)	0.0185 (11)	0.0226 (12)	−0.0069 (10)	−0.0065 (10)	0.0045 (9)
N07	0.0304 (13)	0.0187 (12)	0.0391 (14)	−0.0074 (10)	−0.0150 (11)	0.0034 (10)
N08	0.0384 (15)	0.0236 (12)	0.0237 (12)	−0.0130 (11)	−0.0049 (10)	0.0067 (10)
O1	0.0237 (9)	0.0173 (9)	0.0188 (9)	−0.0069 (7)	−0.0034 (7)	0.0028 (7)
O1A	0.0380 (16)	0.099 (3)	0.084 (2)	−0.0208 (16)	−0.0100 (15)	0.024 (2)
O2	0.0246 (10)	0.0196 (9)	0.0167 (9)	−0.0086 (8)	−0.0054 (7)	0.0059 (7)
O3	0.0308 (11)	0.0233 (9)	0.0254 (10)	−0.0155 (8)	−0.0068 (8)	0.0058 (8)
O4	0.0267 (10)	0.0231 (9)	0.0206 (10)	−0.0103 (8)	−0.0013 (8)	0.0059 (7)
O5	0.0206 (10)	0.0169 (9)	0.0363 (11)	−0.0057 (8)	−0.0033 (8)	0.0077 (8)
O6	0.0209 (9)	0.0172 (9)	0.0189 (10)	−0.0052 (7)	−0.0030 (7)	0.0040 (8)
O7	0.0310 (10)	0.0226 (9)	0.0201 (10)	−0.0097 (8)	−0.0082 (8)	0.0055 (7)
O8	0.0340 (11)	0.0217 (9)	0.0194 (9)	−0.0107 (8)	−0.0078 (8)	0.0024 (7)
O9	0.0349 (11)	0.0256 (10)	0.0179 (9)	−0.0131 (9)	−0.0043 (8)	0.0037 (8)
O10	0.0362 (11)	0.0295 (10)	0.0247 (10)	−0.0154 (9)	−0.0061 (8)	0.0084 (8)
O11	0.0342 (13)	0.0217 (11)	0.0334 (12)	−0.0043 (10)	−0.0028 (9)	0.0033 (9)
O12	0.0319 (11)	0.0190 (10)	0.0229 (10)	−0.0078 (8)	−0.0066 (9)	0.0017 (8)
O13	0.0346 (11)	0.0331 (10)	0.0604 (15)	0.0043 (9)	0.0002 (10)	0.0015 (10)
O14	0.0487 (14)	0.0199 (10)	0.0402 (13)	−0.0102 (9)	−0.0085 (10)	−0.0024 (9)
O15	0.0620 (14)	0.0528 (13)	0.0459 (13)	−0.0404 (11)	−0.0113 (11)	0.0024 (10)
O16	0.0244 (11)	0.0204 (10)	0.0500 (13)	−0.0040 (8)	−0.0126 (9)	0.0052 (9)
O18	0.0480 (14)	0.0181 (10)	0.0614 (15)	−0.0122 (10)	−0.0224 (11)	0.0103 (10)
Al1	0.0185 (4)	0.0146 (4)	0.0191 (4)	−0.0051 (3)	−0.0031 (3)	0.0054 (3)
Al2	0.0274 (4)	0.0183 (4)	0.0188 (4)	−0.0069 (3)	−0.0051 (3)	0.0040 (3)
C4R	0.052 (2)	0.065 (3)	0.045 (2)	0.006 (2)	0.0040 (18)	−0.0008 (19)
O4T	0.0620 (14)	0.0528 (13)	0.0459 (13)	−0.0404 (11)	−0.0113 (11)	0.0024 (10)
C4T	0.0620 (14)	0.0528 (13)	0.0459 (13)	−0.0404 (11)	−0.0113 (11)	0.0024 (10)
O4U	0.0346 (11)	0.0331 (10)	0.0604 (15)	0.0043 (9)	0.0002 (10)	0.0015 (10)
C4U	0.0346 (11)	0.0331 (10)	0.0604 (15)	0.0043 (9)	0.0002 (10)	0.0015 (10)
O17	0.0264 (12)	0.0281 (11)	0.0793 (18)	−0.0105 (9)	−0.0118 (11)	0.0024 (11)

Geometric parameters (Å, º)

C1—C2	1.396 (4)	C16—H16	0.9300
C1—C6	1.405 (4)	C9A—C8A	1.367 (4)
C1—N03	1.419 (3)	C9A—H9A	0.9300
C5A—C4A	1.385 (4)	C17—C18	1.370 (4)
C5A—C20A	1.398 (4)	C17—H17	0.9300
C5A—N02	1.426 (3)	C8A—C7A	1.415 (4)

C1T—O1A	1.293 (6)	C8A—H8A	0.9300
C1T—C2T	1.517 (6)	C18—C19	1.409 (4)
C1T—H1T1	0.9700	C18—H18	0.9300
C1T—H1T2	0.9700	C7A—C6A	1.441 (4)
C4A—C3A	1.381 (4)	C19—C20	1.435 (4)
C4A—H4A	0.9300	C6A—N02	1.294 (3)
C2—C3	1.382 (4)	C6A—H6A	0.9300
C2—H2	0.9300	C20—N03	1.303 (4)
C2T—H2TA	0.9600	C20—H20	0.9300
C2T—H2TB	0.9600	C021—O4	1.431 (3)
C2T—H2TC	0.9600	C021—H02A	0.9600
C3—C4	1.390 (4)	C021—H02B	0.9600
C3—H3	0.9300	C021—H02C	0.9600
C3A—C2A	1.384 (5)	C21—O10	1.436 (3)
C3A—H3A	0.9300	C21—H21A	0.9600
C4—C5	1.383 (4)	C21—H21B	0.9600
C4—H4	0.9300	C21—H21C	0.9600
C2A—C1A	1.379 (4)	C22—O9	1.431 (3)
C2A—H2A	0.9300	C22—H22A	0.9600
C1A—C20A	1.399 (4)	C22—H22B	0.9600
C1A—H1A	0.9300	C22—H22C	0.9600
C5—C6	1.390 (4)	C022—O3	1.425 (3)
C5—H5	0.9300	C022—H02D	0.9600
C20A—N01	1.420 (3)	C022—H02E	0.9600
C6—N04	1.423 (3)	C022—H02F	0.9600
C7—N04	1.301 (4)	N01—Al1	2.007 (2)
C7—C8	1.430 (4)	N02—Al1	1.988 (2)
C7—H7	0.9300	N03—Al2	1.991 (2)
C19A—N01	1.296 (3)	N04—Al2	1.998 (2)
C19A—C18A	1.442 (4)	N07—O18	1.229 (3)
C19A—H19A	0.9300	N07—O17	1.252 (3)
C18A—C13A	1.406 (4)	N07—O16	1.263 (3)
C18A—C17A	1.417 (4)	N08—O13	1.233 (3)
C8—C13	1.405 (4)	N08—O14	1.235 (3)
C8—C9	1.418 (4)	N08—O15	1.261 (3)
C17A—C16A	1.354 (4)	O1—Al1	1.8197 (19)
C17A—H17A	0.9300	O1A—H1AA	0.8200
C9—C10	1.360 (4)	O2—Al1	1.8066 (19)
C9—H9	0.9300	O5—Al1	1.918 (2)
C16A—C15A	1.403 (4)	O5—H52	0.870 (18)
C16A—H16A	0.9300	O5—H51	0.845 (19)
C10—C11	1.406 (4)	O6—Al1	1.958 (2)
C10—H10	0.9300	O6—H61	0.871 (18)
C11—C12	1.376 (4)	O6—H62	0.860 (18)
C11—H11	0.9300	O7—Al2	1.812 (2)
C15A—C14A	1.376 (4)	O8—Al2	1.809 (2)
C15A—H15A	0.9300	O11—Al2	1.925 (2)
C14A—O3	1.376 (3)	O11—H11B	0.852 (19)

C14A—C13A	1.413 (4)	O11—H11A	0.826 (19)
C12—O10	1.376 (3)	O12—Al2	1.977 (2)
C12—C13	1.411 (4)	O12—H12B	0.852 (18)
C13A—O2	1.324 (3)	O12—H12A	0.848 (19)
C13—O7	1.330 (3)	C4R—C4T	1.340 (7)
C14—O8	1.316 (3)	C4R—C4U	1.504 (9)
C14—C19	1.415 (4)	C4R—H4R1	0.9600
C14—C15	1.421 (4)	C4R—H4R2	0.9600
C12A—O1	1.321 (3)	C4R—H4R3	0.9600
C12A—C7A	1.410 (4)	O4T—C4T	1.410 (4)
C12A—C11A	1.417 (4)	O4T—H4T	0.8200
C11A—O4	1.375 (3)	C4T—H4T1	0.9700
C11A—C10A	1.378 (4)	C4T—H4T2	0.9700
C15—O9	1.372 (3)	O4U—C4U	1.376 (9)
C15—C16	1.372 (4)	O4U—H4U	1.2082
C10A—C9A	1.400 (4)	C4U—H4U1	0.9700
C10A—H10A	0.9300	C4U—H4U2	0.9700
C16—C17	1.404 (4)		

C2—C1—C6	119.3 (2)	C18—C19—C14	119.5 (2)
C2—C1—N03	125.6 (3)	C18—C19—C20	117.7 (2)
C6—C1—N03	115.1 (2)	C14—C19—C20	122.8 (2)
C4A—C5A—C20A	120.2 (2)	N02—C6A—C7A	124.5 (2)
C4A—C5A—N02	124.6 (3)	N02—C6A—H6A	117.8
C20A—C5A—N02	115.1 (2)	C7A—C6A—H6A	117.8
O1A—C1T—C2T	113.9 (4)	N03—C20—C19	124.8 (3)
O1A—C1T—H1T1	108.8	N03—C20—H20	117.6
C2T—C1T—H1T1	108.8	C19—C20—H20	117.6
O1A—C1T—H1T2	108.8	O4—C021—H02A	109.5
C2T—C1T—H1T2	108.8	O4—C021—H02B	109.5
H1T1—C1T—H1T2	107.7	H02A—C021—H02B	109.5
C3A—C4A—C5A	119.9 (3)	O4—C021—H02C	109.5
C3A—C4A—H4A	120.0	H02A—C021—H02C	109.5
C5A—C4A—H4A	120.0	H02B—C021—H02C	109.5
C3—C2—C1	119.9 (3)	O10—C21—H21A	109.5
C3—C2—H2	120.0	O10—C21—H21B	109.5
C1—C2—H2	120.0	H21A—C21—H21B	109.5
C1T—C2T—H2TA	109.5	O10—C21—H21C	109.5
C1T—C2T—H2TB	109.5	H21A—C21—H21C	109.5
H2TA—C2T—H2TB	109.5	H21B—C21—H21C	109.5
C1T—C2T—H2TC	109.5	O9—C22—H22A	109.5
H2TA—C2T—H2TC	109.5	O9—C22—H22B	109.5
H2TB—C2T—H2TC	109.5	H22A—C22—H22B	109.5
C2—C3—C4	120.6 (3)	O9—C22—H22C	109.5
C2—C3—H3	119.7	H22A—C22—H22C	109.5
C4—C3—H3	119.7	H22B—C22—H22C	109.5
C4A—C3A—C2A	120.0 (3)	O3—C022—H02D	109.5
C4A—C3A—H3A	120.0	O3—C022—H02E	109.5

C2A—C3A—H3A	120.0	H02D—C022—H02E	109.5
C5—C4—C3	120.0 (3)	O3—C022—H02F	109.5
C5—C4—H4	120.0	H02D—C022—H02F	109.5
C3—C4—H4	120.0	H02E—C022—H02F	109.5
C1A—C2A—C3A	121.0 (3)	C19A—N01—C20A	122.2 (2)
C1A—C2A—H2A	119.5	C19A—N01—Al1	124.05 (18)
C3A—C2A—H2A	119.5	C20A—N01—Al1	113.73 (17)
C2A—C1A—C20A	119.3 (3)	C6A—N02—C5A	121.5 (2)
C2A—C1A—H1A	120.3	C6A—N02—Al1	124.28 (18)
C20A—C1A—H1A	120.3	C5A—N02—Al1	113.89 (17)
C4—C5—C6	120.0 (3)	C20—N03—C1	121.2 (2)
C4—C5—H5	120.0	C20—N03—Al2	124.53 (19)
C6—C5—H5	120.0	C1—N03—Al2	114.18 (18)
C5A—C20A—C1A	119.5 (3)	C7—N04—C6	121.2 (2)
C5A—C20A—N01	114.8 (2)	C7—N04—Al2	124.68 (19)
C1A—C20A—N01	125.7 (3)	C6—N04—Al2	113.82 (18)
C5—C6—C1	120.0 (3)	O18—N07—O17	120.7 (2)
C5—C6—N04	125.0 (3)	O18—N07—O16	120.7 (2)
C1—C6—N04	115.0 (2)	O17—N07—O16	118.6 (2)
N04—C7—C8	125.1 (2)	O13—N08—O14	121.5 (3)
N04—C7—H7	117.4	O13—N08—O15	118.1 (3)
C8—C7—H7	117.4	O14—N08—O15	120.4 (3)
N01—C19A—C18A	124.6 (2)	C12A—O1—Al1	128.82 (16)
N01—C19A—H19A	117.7	C1T—O1A—H1AA	109.5
C18A—C19A—H19A	117.7	C13A—O2—Al1	129.86 (16)
C13A—C18A—C17A	119.5 (3)	C14A—O3—C022	117.7 (2)
C13A—C18A—C19A	123.0 (2)	C11A—O4—C021	116.4 (2)
C17A—C18A—C19A	117.4 (2)	Al1—O5—H52	121 (2)
C13—C8—C9	119.2 (3)	Al1—O5—H51	126 (3)
C13—C8—C7	122.7 (3)	H52—O5—H51	109 (4)
C9—C8—C7	118.0 (2)	Al1—O6—H61	110 (3)
C16A—C17A—C18A	120.8 (3)	Al1—O6—H62	111 (2)
C16A—C17A—H17A	119.6	H61—O6—H62	108 (3)
C18A—C17A—H17A	119.6	C13—O7—Al2	130.62 (17)
C10—C9—C8	121.2 (3)	C14—O8—Al2	130.45 (17)
C10—C9—H9	119.4	C15—O9—C22	117.1 (2)
C8—C9—H9	119.4	C12—O10—C21	117.0 (2)
C17A—C16A—C15A	120.3 (3)	Al2—O11—H11B	124 (3)
C17A—C16A—H16A	119.9	Al2—O11—H11A	125 (3)
C15A—C16A—H16A	119.9	H11B—O11—H11A	111 (4)
C9—C10—C11	119.7 (3)	Al2—O12—H12B	112 (2)
C9—C10—H10	120.2	Al2—O12—H12A	116 (3)
C11—C10—H10	120.2	H12B—O12—H12A	106 (4)
C12—C11—C10	120.3 (3)	O2—Al1—O1	93.64 (8)
C12—C11—H11	119.8	O2—Al1—O5	91.91 (9)
C10—C11—H11	119.8	O1—Al1—O5	93.74 (9)
C14A—C15A—C16A	120.2 (3)	O2—Al1—O6	90.49 (9)
C14A—C15A—H15A	119.9	O1—Al1—O6	90.72 (8)

C16A—C15A—H15A	119.9	O5—Al1—O6	174.80 (9)
O3—C14A—C15A	125.2 (3)	O2—Al1—N02	174.22 (9)
O3—C14A—C13A	114.0 (2)	O1—Al1—N02	92.09 (9)
C15A—C14A—C13A	120.7 (2)	O5—Al1—N02	88.49 (10)
C11—C12—O10	125.3 (3)	O6—Al1—N02	88.67 (9)
C11—C12—C13	120.9 (3)	O2—Al1—N01	93.08 (9)
O10—C12—C13	113.8 (2)	O1—Al1—N01	172.56 (10)
O2—C13A—C18A	124.0 (2)	O5—Al1—N01	89.23 (9)
O2—C13A—C14A	117.5 (2)	O6—Al1—N01	86.03 (8)
C18A—C13A—C14A	118.4 (2)	N02—Al1—N01	81.16 (9)
O7—C13—C8	123.8 (2)	O8—Al2—O7	92.64 (9)
O7—C13—C12	117.5 (2)	O8—Al2—O11	93.25 (9)
C8—C13—C12	118.6 (2)	O7—Al2—O11	90.98 (10)
O8—C14—C19	123.9 (2)	O8—Al2—O12	90.12 (9)
O8—C14—C15	118.0 (2)	O7—Al2—O12	92.38 (9)
C19—C14—C15	118.2 (2)	O11—Al2—O12	175.12 (10)
O1—C12A—C7A	123.9 (2)	O8—Al2—N03	93.18 (9)
O1—C12A—C11A	118.2 (2)	O7—Al2—N03	173.99 (9)
C7A—C12A—C11A	117.9 (2)	O11—Al2—N03	87.18 (10)
O4—C11A—C10A	125.1 (2)	O12—Al2—N03	89.12 (10)
O4—C11A—C12A	113.7 (2)	O8—Al2—N04	173.64 (10)
C10A—C11A—C12A	121.2 (3)	O7—Al2—N04	92.57 (9)
O9—C15—C16	125.2 (2)	O11—Al2—N04	90.32 (10)
O9—C15—C14	113.5 (2)	O12—Al2—N04	86.01 (9)
C16—C15—C14	121.2 (3)	N03—Al2—N04	81.73 (9)
C11A—C10A—C9A	119.8 (3)	C4T—C4R—H4R1	109.5
C11A—C10A—H10A	120.1	C4T—C4R—H4R2	109.5
C9A—C10A—H10A	120.1	H4R1—C4R—H4R2	109.5
C15—C16—C17	119.9 (3)	C4T—C4R—H4R3	109.5
C15—C16—H16	120.0	H4R1—C4R—H4R3	109.5
C17—C16—H16	120.0	H4R2—C4R—H4R3	109.5
C8A—C9A—C10A	120.6 (3)	C4T—O4T—H4T	109.5
C8A—C9A—H9A	119.7	C4R—C4T—O4T	112.5 (6)
C10A—C9A—H9A	119.7	C4R—C4T—H4T1	109.1
C18—C17—C16	120.3 (3)	O4T—C4T—H4T1	109.1
C18—C17—H17	119.8	C4R—C4T—H4T2	109.1
C16—C17—H17	119.8	O4T—C4T—H4T2	109.1
C9A—C8A—C7A	120.2 (3)	H4T1—C4T—H4T2	107.8
C9A—C8A—H8A	119.9	C4U—O4U—H4U	104.5
C7A—C8A—H8A	119.9	O4U—C4U—C4R	117.6 (7)
C17—C18—C19	120.9 (3)	O4U—C4U—H4U1	107.9
C17—C18—H18	119.6	C4R—C4U—H4U1	107.9
C19—C18—H18	119.6	O4U—C4U—H4U2	107.9
C12A—C7A—C8A	120.0 (2)	C4R—C4U—H4U2	107.9
C12A—C7A—C6A	122.3 (2)	H4U1—C4U—H4U2	107.2
C8A—C7A—C6A	117.7 (3)		

C20A—C5A—C4A—C3A	−1.1 (4)	O1—C12A—C7A—C6A	4.1 (4)

N02—C5A—C4A—C3A	−179.3 (3)	C11A—C12A—C7A—C6A	−174.5 (2)
C6—C1—C2—C3	−2.3 (4)	C9A—C8A—C7A—C12A	0.5 (5)
N03—C1—C2—C3	177.5 (3)	C9A—C8A—C7A—C6A	178.9 (3)
C1—C2—C3—C4	−0.9 (5)	C17—C18—C19—C14	−0.3 (4)
C5A—C4A—C3A—C2A	0.2 (4)	C17—C18—C19—C20	−178.5 (3)
C2—C3—C4—C5	1.8 (5)	O8—C14—C19—C18	−179.4 (2)
C4A—C3A—C2A—C1A	0.9 (5)	C15—C14—C19—C18	0.6 (4)
C3A—C2A—C1A—C20A	−1.0 (4)	O8—C14—C19—C20	−1.3 (4)
C3—C4—C5—C6	0.4 (5)	C15—C14—C19—C20	178.7 (2)
C4A—C5A—C20A—C1A	1.0 (4)	C12A—C7A—C6A—N02	−4.8 (4)
N02—C5A—C20A—C1A	179.3 (2)	C8A—C7A—C6A—N02	176.9 (3)
C4A—C5A—C20A—N01	−177.2 (2)	C18—C19—C20—N03	178.8 (3)
N02—C5A—C20A—N01	1.1 (3)	C14—C19—C20—N03	0.6 (4)
C2A—C1A—C20A—C5A	0.0 (4)	C18A—C19A—N01—C20A	−175.4 (2)
C2A—C1A—C20A—N01	178.1 (2)	C18A—C19A—N01—Al1	6.1 (3)
C4—C5—C6—C1	−3.6 (4)	C5A—C20A—N01—C19A	−171.3 (2)
C4—C5—C6—N04	176.5 (3)	C1A—C20A—N01—C19A	10.6 (4)
C2—C1—C6—C5	4.5 (4)	C5A—C20A—N01—Al1	7.3 (3)
N03—C1—C6—C5	−175.3 (2)	C1A—C20A—N01—Al1	−170.8 (2)
C2—C1—C6—N04	−175.6 (2)	C7A—C6A—N02—C5A	176.4 (2)
N03—C1—C6—N04	4.6 (3)	C7A—C6A—N02—Al1	−10.2 (4)
N01—C19A—C18A—C13A	4.1 (4)	C4A—C5A—N02—C6A	−16.8 (4)
N01—C19A—C18A—C17A	−179.3 (3)	C20A—C5A—N02—C6A	164.9 (2)
N04—C7—C8—C13	1.6 (4)	C4A—C5A—N02—Al1	169.2 (2)
N04—C7—C8—C9	−177.5 (3)	C20A—C5A—N02—Al1	−9.1 (3)
C13A—C18A—C17A—C16A	0.4 (4)	C19—C20—N03—C1	−178.6 (2)
C19A—C18A—C17A—C16A	−176.2 (3)	C19—C20—N03—Al2	4.2 (4)
C13—C8—C9—C10	0.3 (4)	C2—C1—N03—C20	0.2 (4)
C7—C8—C9—C10	179.4 (3)	C6—C1—N03—C20	180.0 (2)
C18A—C17A—C16A—C15A	1.8 (5)	C2—C1—N03—Al2	177.7 (2)
C8—C9—C10—C11	−0.4 (4)	C6—C1—N03—Al2	−2.6 (3)
C9—C10—C11—C12	−0.1 (4)	C8—C7—N04—C6	−179.3 (2)
C17A—C16A—C15A—C14A	−1.2 (5)	C8—C7—N04—Al2	−6.4 (4)
C16A—C15A—C14A—O3	179.2 (3)	C5—C6—N04—C7	−11.0 (4)
C16A—C15A—C14A—C13A	−1.8 (4)	C1—C6—N04—C7	169.1 (2)
C10—C11—C12—O10	−179.2 (3)	C5—C6—N04—Al2	175.4 (2)
C10—C11—C12—C13	0.9 (4)	C1—C6—N04—Al2	−4.5 (3)
C17A—C18A—C13A—O2	177.9 (2)	C7A—C12A—O1—Al1	13.5 (4)
C19A—C18A—C13A—O2	−5.7 (4)	C11A—C12A—O1—Al1	−167.85 (18)
C17A—C18A—C13A—C14A	−3.3 (4)	C18A—C13A—O2—Al1	−4.5 (3)
C19A—C18A—C13A—C14A	173.2 (2)	C14A—C13A—O2—Al1	176.65 (17)
O3—C14A—C13A—O2	2.1 (3)	C15A—C14A—O3—C022	−2.1 (4)
C15A—C14A—C13A—O2	−177.1 (2)	C13A—C14A—O3—C022	178.7 (2)
O3—C14A—C13A—C18A	−176.9 (2)	C10A—C11A—O4—C021	7.1 (4)
C15A—C14A—C13A—C18A	3.9 (4)	C12A—C11A—O4—C021	−174.5 (2)
C9—C8—C13—O7	179.7 (2)	C8—C13—O7—Al2	2.8 (4)
C7—C8—C13—O7	0.7 (4)	C12—C13—O7—Al2	−177.91 (18)
C9—C8—C13—C12	0.5 (4)	C19—C14—O8—Al2	−3.6 (4)

C7—C8—C13—C12	−178.6 (2)	C15—C14—O8—Al2	176.38 (17)
C11—C12—C13—O7	179.6 (2)	C16—C15—O9—C22	13.3 (4)
O10—C12—C13—O7	−0.3 (3)	C14—C15—O9—C22	−167.7 (2)
C11—C12—C13—C8	−1.1 (4)	C11—C12—O10—C21	0.1 (4)
O10—C12—C13—C8	179.0 (2)	C13—C12—O10—C21	180.0 (2)
O1—C12A—C11A—O4	−2.5 (3)	C13A—O2—Al1—O1	−172.4 (2)
C7A—C12A—C11A—O4	176.2 (2)	C13A—O2—Al1—O5	−78.5 (2)
O1—C12A—C11A—C10A	176.0 (2)	C13A—O2—Al1—O6	96.9 (2)
C7A—C12A—C11A—C10A	−5.3 (4)	C13A—O2—Al1—N01	10.8 (2)
O8—C14—C15—O9	0.3 (3)	C12A—O1—Al1—O2	159.5 (2)
C19—C14—C15—O9	−179.7 (2)	C12A—O1—Al1—O5	67.4 (2)
O8—C14—C15—C16	179.3 (2)	C12A—O1—Al1—O6	−109.9 (2)
C19—C14—C15—C16	−0.6 (4)	C12A—O1—Al1—N02	−21.2 (2)
O4—C11A—C10A—C9A	−179.2 (3)	C14—O8—Al2—O7	−172.2 (2)
C12A—C11A—C10A—C9A	2.4 (5)	C14—O8—Al2—O11	−81.1 (2)
O9—C15—C16—C17	179.3 (2)	C14—O8—Al2—O12	95.4 (2)
C14—C15—C16—C17	0.4 (4)	C14—O8—Al2—N03	6.3 (2)
C11A—C10A—C9A—C8A	2.1 (5)	C13—O7—Al2—O8	178.1 (2)
C15—C16—C17—C18	−0.1 (4)	C13—O7—Al2—O11	84.8 (2)
C10A—C9A—C8A—C7A	−3.5 (5)	C13—O7—Al2—O12	−91.7 (2)
C16—C17—C18—C19	0.1 (4)	C13—O7—Al2—N04	−5.6 (2)
O1—C12A—C7A—C8A	−177.5 (3)	C4U—C4R—C4T—O4T	−171 (6)
C11A—C12A—C7A—C8A	3.8 (4)	C4T—C4R—C4U—O4U	7 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H52···O16	0.87 (2)	1.83 (3)	2.684 (3)	169 (3)
O11—H11*B*···O1*A*	0.85 (3)	1.73 (3)	2.573 (4)	178 (7)

Diaqua(6,6′-{(1*E*,1′*E*)-[1,2-phenylenebis(azanylylidene)]bis(methanylylidene)}bis(2-methoxyphenolato)-$\kappa^4O^1,N,N',O^{1'}$)gallium(III) nitrate ethanol monosolvate (16rjt1_0m)

Crystal data

$[Ga(C_{22}H_{18}N_2O_4)(H_2O)_2]NO_3\cdot C_2H_6O$	$Z = 4$
$M_r = 588.21$	$F(000) = 1216$
Triclinic, $P\overline{1}$	$D_x = 1.576$ Mg m^{-3}
$a = 12.399$ (5) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 13.580$ (5) Å	Cell parameters from 11972 reflections
$c = 16.419$ (5) Å	$\theta = 1.0$–$1.0°$
$\alpha = 86.818$ (5)°	$\mu = 1.17$ mm^{-1}
$\beta = 78.871$ (5)°	$T = 100$ K
$\gamma = 66.124$ (5)°	Cuboid, yellow
$V = 2479.7$ (16) Å^3	0.57 × 0.24 × 0.23 mm

Data collection

Bruker APEXII CCD diffractometer	47407 measured reflections
φ and ω scans	11972 independent reflections
	10426 reflections with $I > 2\sigma(I)$

R_{int} = 0.027
θ_{max} = 28.0°, θ_{min} = 1.6°
h = −16→16
k = −16→17
l = −21→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.114
S = 1.06
11886 reflections
682 parameters
20 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 5.8146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.84 e Å^{-3}
$\Delta\rho_{min}$ = −2.07 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ga01	0.45155 (2)	0.17569 (2)	0.95269 (2)	0.01661 (6)	
Ga02	0.08156 (2)	0.32174 (2)	0.54724 (2)	0.01661 (6)	
O6	0.29643 (18)	−0.05042 (15)	0.90092 (12)	0.0244 (4)	
N2A	0.0987 (2)	0.28745 (17)	0.66651 (13)	0.0206 (4)	
C7A	−0.0959 (3)	0.2234 (2)	0.29245 (18)	0.0292 (5)	
H7A	−0.1286	0.1951	0.2584	0.035*	
O4	0.39050 (16)	0.08262 (14)	0.91687 (10)	0.0185 (3)	
C15A	0.2812 (2)	0.4138 (2)	0.72964 (17)	0.0247 (5)	
H15A	0.2812	0.3858	0.7826	0.030*	
C12A	0.2796 (2)	0.4998 (2)	0.57193 (16)	0.0224 (5)	
O3	0.40813 (16)	0.14689 (14)	1.06566 (10)	0.0187 (3)	
O5	0.31225 (16)	0.09519 (14)	1.20518 (11)	0.0213 (4)	
C4	0.4966 (2)	0.3212 (2)	1.05411 (17)	0.0225 (5)	
H4	0.5227	0.3755	1.0593	0.027*	
C21	0.2664 (3)	0.0603 (2)	1.28266 (17)	0.0263 (6)	
H21A	0.2509	−0.0015	1.2734	0.039*	
H21B	0.1932	0.1174	1.3084	0.039*	
H21C	0.3243	0.0417	1.3184	0.039*	
C18	0.5848 (2)	0.26915 (19)	0.83385 (16)	0.0199 (5)	
O25	0.2711 (2)	0.53867 (18)	0.49337 (14)	0.0349 (3)	
O6A	0.04001 (17)	0.42112 (15)	0.28984 (11)	0.0231 (4)	
O1	0.61681 (16)	0.04865 (14)	0.94634 (11)	0.0188 (3)	
C17	0.4886 (2)	0.1814 (2)	0.77038 (15)	0.0210 (5)	
H17	0.5152	0.2061	0.7198	0.025*	
O16	0.32134 (19)	0.49178 (16)	0.92363 (15)	0.0351 (5)	
C22	0.2458 (3)	−0.1268 (2)	0.8949 (2)	0.0314 (6)	
H22A	0.2277	−0.1531	0.9490	0.047*	

H22B	0.3023	−0.1858	0.8588	0.047*
H22C	0.1735	−0.0927	0.8728	0.047*
O2A	−0.08101 (17)	0.44875 (14)	0.59385 (11)	0.0209 (4)
C2A	−0.0556 (3)	0.1040 (2)	0.67441 (18)	0.0274 (6)
H2AC	−0.0852	0.0755	0.6381	0.033*
O5A	0.16622 (17)	0.41135 (14)	0.53847 (11)	0.0216 (4)
C15	0.4045 (3)	0.0944 (2)	0.69046 (17)	0.0293 (6)
H15	0.4309	0.1262	0.6437	0.035*
O4A	0.04988 (17)	0.35558 (14)	0.43888 (11)	0.0208 (4)
O10	0.3168 (2)	0.84316 (16)	0.42534 (14)	0.0324 (4)
C22A	0.3271 (3)	0.6109 (3)	0.4661 (2)	0.0349 (3)
H22D	0.3154	0.6327	0.4107	0.052*
H22E	0.4115	0.5756	0.4666	0.052*
H22F	0.2921	0.6732	0.5026	0.052*
C11A	0.2196 (2)	0.42986 (19)	0.59469 (16)	0.0198 (5)
O2	0.29328 (17)	0.30294 (15)	0.95132 (13)	0.0265 (4)
O11	0.3445 (2)	0.9705 (2)	0.48120 (15)	0.0409 (5)
C3A	−0.0052 (2)	0.1777 (2)	0.64648 (16)	0.0217 (5)
O12	0.1678 (2)	0.99308 (18)	0.46706 (17)	0.0440 (6)
C16	0.4232 (2)	0.1152 (2)	0.76905 (15)	0.0210 (5)
C5A	−0.0401 (2)	0.2303 (2)	0.42517 (15)	0.0196 (5)
C16A	0.2210 (2)	0.3868 (2)	0.67492 (16)	0.0214 (5)
O7	0.1295 (2)	0.54519 (18)	0.93591 (18)	0.0443 (6)
C6A	−0.0894 (2)	0.1882 (2)	0.37179 (17)	0.0245 (5)
H6A	−0.1178	0.1358	0.3910	0.029*
N1	0.52160 (19)	0.27638 (16)	0.98134 (13)	0.0180 (4)
C14	0.3483 (3)	0.0283 (3)	0.68225 (18)	0.0339 (7)
H14	0.3352	0.0168	0.6304	0.041*
C11	0.3817 (2)	0.06723 (19)	0.84022 (15)	0.0181 (5)
N1A	0.00006 (19)	0.21935 (16)	0.56512 (13)	0.0197 (4)
N3	0.2764 (2)	0.93433 (18)	0.45785 (13)	0.0235 (5)
C21A	0.0575 (3)	0.4449 (2)	0.20350 (16)	0.0287 (6)
H21D	0.0885	0.4997	0.1953	0.043*
H21E	−0.0178	0.4699	0.1849	0.043*
H21F	0.1135	0.3810	0.1723	0.043*
N4	0.2209 (2)	0.56655 (18)	0.92205 (16)	0.0278 (5)
O9	0.2115 (2)	0.65943 (17)	0.90632 (17)	0.0430 (6)
C4A	−0.0400 (2)	0.1895 (2)	0.50775 (16)	0.0217 (5)
H4A	−0.0711	0.1376	0.5212	0.026*
N2	0.51356 (18)	0.20938 (16)	0.83601 (13)	0.0177 (4)
C10A	0.0034 (2)	0.30990 (19)	0.39546 (15)	0.0181 (5)
C19	0.6505 (3)	0.2923 (2)	0.76180 (18)	0.0270 (6)
H19	0.6480	0.2693	0.7101	0.032*
C18A	0.0431 (2)	0.2177 (2)	0.70141 (16)	0.0219 (5)
C12	0.3280 (2)	−0.0041 (2)	0.82891 (16)	0.0210 (5)
C13	0.3104 (3)	−0.0219 (2)	0.75171 (18)	0.0292 (6)
H13	0.2732	−0.0676	0.7457	0.035*
C8	0.3146 (3)	0.2457 (2)	1.27768 (17)	0.0310 (6)

H8	0.2764	0.2298	1.3280	0.037*	
C10	0.3942 (2)	0.20751 (19)	1.12989 (15)	0.0181 (5)	
C5	0.4317 (2)	0.2934 (2)	1.12719 (16)	0.0230 (5)	
C9	0.3389 (2)	0.1830 (2)	1.20792 (16)	0.0206 (5)	
C8A	−0.0531 (2)	0.3023 (2)	0.26230 (16)	0.0246 (5)	
H8A	−0.0579	0.3263	0.2084	0.030*	
C19A	0.0328 (3)	0.1886 (2)	0.78431 (17)	0.0280 (6)	
H19A	0.0609	0.2175	0.8215	0.034*	
C1A	−0.0613 (3)	0.0734 (2)	0.75655 (19)	0.0317 (6)	
H1AA	−0.0936	0.0234	0.7750	0.038*	
C9A	−0.0041 (2)	0.3440 (2)	0.31235 (15)	0.0196 (5)	
C17A	0.1613 (2)	0.3171 (2)	0.70624 (16)	0.0222 (5)	
H17A	0.1683	0.2914	0.7595	0.027*	
C13A	0.3384 (2)	0.5236 (2)	0.62578 (18)	0.0264 (6)	
H13A	0.3781	0.5687	0.6093	0.032*	
C14A	0.3390 (3)	0.4803 (2)	0.70562 (18)	0.0280 (6)	
H14A	0.3786	0.4969	0.7419	0.034*	
C20A	−0.0192 (3)	0.1167 (2)	0.81145 (18)	0.0315 (6)	
H20A	−0.0259	0.0973	0.8668	0.038*	
C3	0.5900 (2)	0.30404 (19)	0.91141 (16)	0.0203 (5)	
C2	0.6618 (3)	0.3594 (2)	0.91662 (19)	0.0285 (6)	
H2	0.6666	0.3810	0.9681	0.034*	
C20	0.7193 (3)	0.3496 (2)	0.7677 (2)	0.0325 (6)	
H20	0.7615	0.3666	0.7197	0.039*	
C1	0.7257 (3)	0.3818 (3)	0.8447 (2)	0.0341 (7)	
H1	0.7736	0.4188	0.8480	0.041*	
C6	0.4077 (3)	0.3553 (2)	1.2003 (2)	0.0354 (7)	
H6	0.4333	0.4111	1.1988	0.042*	
C7	0.3474 (3)	0.3337 (3)	1.2728 (2)	0.0417 (8)	
H7	0.3278	0.3776	1.3195	0.050*	
C6B	0.5687 (4)	0.2399 (3)	0.3791 (3)	0.0535 (9)	
H6BA	0.5848	0.3000	0.3556	0.080*	
H6BB	0.5405	0.2110	0.3396	0.080*	
H6BC	0.6410	0.1853	0.3925	0.080*	
C5B	0.4736 (3)	0.2769 (3)	0.4573 (2)	0.0349 (3)	
H5BA	0.5019	0.3074	0.4964	0.042*	
H5BB	0.4014	0.3332	0.4436	0.042*	
C2B	0.0900 (6)	0.1407 (6)	0.0735 (4)	0.0292 (5)	0.492 (6)
H2BA	0.1568	0.1376	0.0966	0.044*	0.492 (6)
H2BB	0.1002	0.0689	0.0607	0.044*	0.492 (6)
H2BC	0.0170	0.1746	0.1130	0.044*	0.492 (6)
O13	0.0912 (4)	0.2902 (3)	0.0223 (4)	0.0324 (4)	0.492 (6)
H13B	0.1064	0.2909	0.0686	0.049*	0.492 (6)
C4B	0.0849 (8)	0.1940 (6)	0.0085 (5)	0.0349 (3)	0.492 (6)
H4BA	0.0103	0.2076	−0.0097	0.042*	0.492 (6)
H4BB	0.1508	0.1529	−0.0351	0.042*	0.492 (6)
C3B	0.0713 (5)	0.1925 (5)	−0.0128 (4)	0.0217 (5)	0.508 (6)
H3BA	0.1363	0.1454	−0.0542	0.026*	0.508 (6)

H3BB	−0.0019	0.2048	−0.0326	0.026*	0.508 (6)
C1B	0.0688 (9)	0.1200 (7)	0.0651 (6)	0.0535 (9)	0.508 (6)
H1BA	0.0606	0.0566	0.0495	0.080*	0.508 (6)
H1BB	0.0020	0.1597	0.1077	0.080*	0.508 (6)
H1BC	0.1421	0.0994	0.0857	0.080*	0.508 (6)
O15	0.0815 (5)	0.2894 (4)	−0.0210 (4)	0.0409 (5)	0.508 (6)
H15B	0.0410	0.3283	0.0197	0.061*	0.508 (6)
O14	0.4471 (2)	0.1992 (3)	0.4926 (2)	0.0653 (9)	
H14B	0.5091	0.1478	0.4985	0.098*	
H1A	0.614 (5)	−0.004 (3)	0.922 (3)	0.098*	
H1B	0.626 (5)	0.033 (4)	0.9960 (16)	0.098*	
H2A	0.223 (3)	0.304 (4)	0.971 (4)	0.098*	
H2B	0.289 (5)	0.367 (2)	0.952 (4)	0.098*	
H2AA	−0.070 (5)	0.498 (3)	0.613 (3)	0.098*	
H2AB	−0.122 (5)	0.468 (4)	0.556 (3)	0.098*	
O0AA	0.23809 (18)	0.19361 (15)	0.50397 (13)	0.0288 (4)	
H0AA	0.2378	0.1355	0.5278	0.043*	
H0AB	0.2974	0.2011	0.5188	0.043*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga01	0.02039 (10)	0.01428 (10)	0.01347 (10)	−0.00593 (7)	−0.00250 (7)	0.00317 (7)
Ga02	0.02039 (10)	0.01428 (10)	0.01347 (10)	−0.00593 (7)	−0.00250 (7)	0.00317 (7)
O6	0.0307 (10)	0.0245 (9)	0.0236 (9)	−0.0170 (8)	−0.0055 (8)	0.0036 (7)
N2A	0.0242 (11)	0.0177 (10)	0.0166 (10)	−0.0055 (8)	−0.0040 (8)	0.0040 (8)
C7A	0.0301 (13)	0.0338 (14)	0.0239 (12)	−0.0119 (11)	−0.0061 (10)	−0.0046 (10)
O4	0.0250 (9)	0.0179 (8)	0.0142 (8)	−0.0104 (7)	−0.0046 (7)	0.0041 (6)
C15A	0.0257 (13)	0.0247 (13)	0.0198 (12)	−0.0056 (11)	−0.0060 (10)	0.0026 (10)
C12A	0.0210 (12)	0.0186 (12)	0.0214 (12)	−0.0032 (10)	−0.0002 (9)	0.0007 (9)
O3	0.0258 (9)	0.0160 (8)	0.0140 (8)	−0.0096 (7)	−0.0004 (7)	0.0015 (6)
O5	0.0249 (9)	0.0218 (9)	0.0151 (8)	−0.0098 (7)	0.0012 (7)	0.0035 (7)
C4	0.0256 (13)	0.0138 (11)	0.0274 (13)	−0.0075 (10)	−0.0044 (10)	0.0012 (9)
C21	0.0255 (13)	0.0271 (13)	0.0198 (12)	−0.0080 (11)	0.0033 (10)	0.0065 (10)
C18	0.0194 (11)	0.0144 (11)	0.0225 (12)	−0.0052 (9)	−0.0012 (9)	0.0068 (9)
O25	0.0359 (8)	0.0359 (8)	0.0299 (8)	−0.0133 (7)	−0.0031 (6)	0.0044 (6)
O6A	0.0306 (10)	0.0239 (9)	0.0153 (8)	−0.0117 (8)	−0.0042 (7)	0.0029 (7)
O1	0.0202 (8)	0.0159 (8)	0.0170 (8)	−0.0049 (7)	−0.0022 (7)	0.0030 (6)
C17	0.0214 (12)	0.0198 (12)	0.0155 (11)	−0.0036 (10)	−0.0013 (9)	0.0065 (9)
O16	0.0285 (11)	0.0205 (10)	0.0529 (14)	−0.0028 (8)	−0.0160 (10)	0.0012 (9)
C22	0.0360 (16)	0.0267 (14)	0.0392 (17)	−0.0183 (12)	−0.0135 (13)	0.0051 (12)
O2A	0.0253 (9)	0.0169 (8)	0.0174 (9)	−0.0055 (7)	−0.0034 (7)	0.0006 (7)
C2A	0.0365 (15)	0.0216 (13)	0.0245 (13)	−0.0122 (11)	−0.0072 (11)	0.0051 (10)
O5A	0.0266 (9)	0.0206 (9)	0.0166 (8)	−0.0081 (7)	−0.0058 (7)	0.0038 (7)
C15	0.0347 (15)	0.0346 (15)	0.0170 (12)	−0.0117 (12)	−0.0079 (11)	0.0058 (11)
O4A	0.0291 (10)	0.0182 (8)	0.0145 (8)	−0.0087 (7)	−0.0048 (7)	0.0012 (6)
O10	0.0352 (10)	0.0208 (9)	0.0377 (11)	−0.0085 (8)	−0.0035 (8)	−0.0055 (8)
C22A	0.0359 (8)	0.0359 (8)	0.0299 (8)	−0.0133 (7)	−0.0031 (6)	0.0044 (6)

C11A	0.0184 (11)	0.0165 (11)	0.0191 (12)	−0.0025 (9)	−0.0010 (9)	−0.0001 (9)
O2	0.0202 (9)	0.0159 (8)	0.0388 (11)	−0.0048 (7)	−0.0026 (8)	0.0068 (8)
O11	0.0513 (13)	0.0439 (12)	0.0392 (12)	−0.0288 (11)	−0.0124 (10)	−0.0003 (9)
C3A	0.0250 (13)	0.0161 (11)	0.0186 (12)	−0.0043 (10)	−0.0018 (9)	0.0038 (9)
O12	0.0339 (12)	0.0271 (11)	0.0552 (15)	0.0013 (9)	−0.0029 (11)	−0.0004 (10)
C16	0.0222 (12)	0.0196 (12)	0.0163 (11)	−0.0032 (10)	−0.0048 (9)	0.0037 (9)
C5A	0.0174 (11)	0.0174 (11)	0.0184 (12)	−0.0024 (9)	−0.0002 (9)	−0.0011 (9)
C16A	0.0211 (12)	0.0187 (11)	0.0203 (12)	−0.0039 (10)	−0.0040 (9)	0.0025 (9)
O7	0.0298 (12)	0.0285 (11)	0.0762 (18)	−0.0123 (9)	−0.0111 (11)	−0.0031 (11)
C6A	0.0239 (13)	0.0249 (13)	0.0239 (13)	−0.0100 (11)	−0.0012 (10)	−0.0018 (10)
N1	0.0192 (10)	0.0142 (9)	0.0199 (10)	−0.0068 (8)	−0.0031 (8)	0.0042 (8)
C14	0.0410 (17)	0.0439 (17)	0.0203 (13)	−0.0174 (14)	−0.0131 (12)	0.0019 (12)
C11	0.0176 (11)	0.0162 (11)	0.0166 (11)	−0.0025 (9)	−0.0047 (9)	0.0020 (9)
N1A	0.0219 (10)	0.0153 (9)	0.0168 (10)	−0.0036 (8)	−0.0012 (8)	0.0019 (8)
N3	0.0350 (13)	0.0196 (10)	0.0160 (10)	−0.0122 (9)	−0.0036 (9)	0.0042 (8)
C21A	0.0353 (15)	0.0369 (15)	0.0167 (12)	−0.0184 (13)	−0.0041 (11)	0.0060 (11)
N4	0.0312 (12)	0.0172 (10)	0.0353 (13)	−0.0069 (9)	−0.0136 (10)	0.0012 (9)
O9	0.0496 (14)	0.0171 (10)	0.0662 (17)	−0.0134 (10)	−0.0217 (12)	0.0076 (10)
C4A	0.0210 (11)	0.0203 (10)	0.0191 (11)	−0.0044 (9)	−0.0017 (9)	−0.0001 (9)
N2	0.0176 (10)	0.0151 (9)	0.0172 (10)	−0.0049 (8)	−0.0011 (8)	0.0054 (7)
C10A	0.0168 (11)	0.0154 (11)	0.0160 (11)	−0.0010 (9)	−0.0006 (9)	−0.0023 (9)
C19	0.0273 (14)	0.0251 (13)	0.0239 (13)	−0.0098 (11)	0.0025 (11)	0.0062 (10)
C18A	0.0245 (12)	0.0177 (11)	0.0196 (12)	−0.0054 (10)	−0.0032 (10)	0.0049 (9)
C12	0.0202 (12)	0.0202 (12)	0.0207 (12)	−0.0057 (10)	−0.0050 (9)	0.0023 (9)
C13	0.0301 (14)	0.0345 (15)	0.0272 (14)	−0.0150 (12)	−0.0098 (11)	−0.0012 (11)
C8	0.0369 (16)	0.0331 (15)	0.0179 (13)	−0.0128 (13)	0.0054 (11)	−0.0049 (11)
C10	0.0187 (11)	0.0142 (10)	0.0157 (11)	−0.0019 (9)	−0.0008 (9)	0.0007 (8)
C5	0.0277 (13)	0.0174 (11)	0.0207 (12)	−0.0071 (10)	−0.0009 (10)	−0.0017 (9)
C9	0.0199 (12)	0.0192 (11)	0.0177 (12)	−0.0040 (9)	−0.0008 (9)	0.0001 (9)
C8A	0.0271 (13)	0.0281 (13)	0.0158 (12)	−0.0085 (11)	−0.0033 (10)	−0.0004 (10)
C19A	0.0354 (15)	0.0293 (14)	0.0195 (13)	−0.0131 (12)	−0.0072 (11)	0.0062 (10)
C1A	0.0424 (17)	0.0262 (14)	0.0288 (15)	−0.0172 (13)	−0.0071 (12)	0.0120 (11)
C9A	0.0196 (11)	0.0187 (11)	0.0160 (11)	−0.0042 (9)	−0.0008 (9)	−0.0005 (9)
C17A	0.0252 (13)	0.0208 (12)	0.0161 (11)	−0.0054 (10)	−0.0037 (9)	0.0046 (9)
C13A	0.0230 (13)	0.0244 (13)	0.0291 (14)	−0.0082 (11)	−0.0018 (10)	0.0012 (11)
C14A	0.0257 (14)	0.0306 (14)	0.0272 (14)	−0.0099 (11)	−0.0071 (11)	0.0003 (11)
C20A	0.0431 (17)	0.0305 (15)	0.0202 (13)	−0.0151 (13)	−0.0075 (12)	0.0121 (11)
C3	0.0202 (12)	0.0150 (11)	0.0234 (12)	−0.0062 (9)	−0.0023 (9)	0.0056 (9)
C2	0.0300 (14)	0.0283 (14)	0.0313 (15)	−0.0169 (12)	−0.0048 (11)	0.0043 (11)
C20	0.0313 (15)	0.0313 (15)	0.0333 (16)	−0.0165 (12)	0.0042 (12)	0.0093 (12)
C1	0.0322 (15)	0.0346 (16)	0.0412 (17)	−0.0225 (13)	−0.0016 (13)	0.0076 (13)
C6	0.0493 (19)	0.0254 (14)	0.0317 (16)	−0.0184 (14)	0.0024 (13)	−0.0095 (12)
C7	0.060 (2)	0.0389 (18)	0.0242 (15)	−0.0228 (16)	0.0069 (14)	−0.0146 (13)
C6B	0.050 (2)	0.047 (2)	0.064 (2)	−0.0221 (16)	−0.0032 (17)	−0.0032 (17)
C5B	0.0359 (8)	0.0359 (8)	0.0299 (8)	−0.0133 (7)	−0.0031 (6)	0.0044 (6)
C2B	0.0301 (13)	0.0338 (14)	0.0239 (12)	−0.0119 (11)	−0.0061 (10)	−0.0046 (10)
O13	0.0352 (10)	0.0208 (9)	0.0377 (11)	−0.0085 (8)	−0.0035 (8)	−0.0055 (8)
C4B	0.0359 (8)	0.0359 (8)	0.0299 (8)	−0.0133 (7)	−0.0031 (6)	0.0044 (6)

C3B	0.0210 (11)	0.0203 (10)	0.0191 (11)	−0.0044 (9)	−0.0017 (9)	−0.0001 (9)
C1B	0.050 (2)	0.047 (2)	0.064 (2)	−0.0221 (16)	−0.0032 (17)	−0.0032 (17)
O15	0.0513 (13)	0.0439 (12)	0.0392 (12)	−0.0288 (11)	−0.0124 (10)	−0.0003 (9)
O14	0.0270 (13)	0.092 (2)	0.0654 (19)	−0.0124 (14)	−0.0095 (13)	0.0062 (17)
O0AA	0.0275 (10)	0.0191 (9)	0.0322 (11)	−0.0039 (8)	−0.0013 (8)	0.0030 (8)

Geometric parameters (Å, º)

Ga01—O4	1.8829 (18)	C5A—C6A	1.419 (4)
Ga01—O3	1.8941 (18)	C5A—C4A	1.436 (3)
Ga01—N1	2.009 (2)	C16A—C17A	1.441 (4)
Ga01—N2	2.022 (2)	O7—N4	1.257 (3)
Ga01—O2	2.0262 (19)	C6A—H6A	0.9300
Ga01—O1	2.0644 (19)	N1—C3	1.419 (3)
Ga02—O5A	1.887 (2)	C14—C13	1.397 (4)
Ga02—O4A	1.8878 (18)	C14—H14	0.9300
Ga02—N1A	2.005 (2)	C11—C12	1.417 (4)
Ga02—N2A	2.019 (2)	N1A—C4A	1.298 (3)
Ga02—O0AA	2.042 (2)	C21A—H21D	0.9600
Ga02—O2A	2.0881 (19)	C21A—H21E	0.9600
O6—C12	1.373 (3)	C21A—H21F	0.9600
O6—C22	1.428 (3)	N4—O9	1.236 (3)
N2A—C17A	1.291 (4)	C4A—H4A	0.9300
N2A—C18A	1.420 (3)	C10A—C9A	1.425 (3)
C7A—C6A	1.368 (4)	C19—C20	1.386 (4)
C7A—C8A	1.405 (4)	C19—H19	0.9300
C7A—H7A	0.9300	C18A—C19A	1.393 (4)
O4—C11	1.319 (3)	C12—C13	1.376 (4)
C15A—C14A	1.363 (4)	C13—H13	0.9300
C15A—C16A	1.419 (4)	C8—C9	1.377 (4)
C15A—H15A	0.9300	C8—C7	1.403 (5)
C12A—O25	1.373 (3)	C8—H8	0.9300
C12A—C13A	1.375 (4)	C10—C5	1.415 (4)
C12A—C11A	1.421 (4)	C10—C9	1.422 (3)
O3—C10	1.315 (3)	C5—C6	1.417 (4)
O5—C9	1.365 (3)	C8A—C9A	1.374 (4)
O5—C21	1.427 (3)	C8A—H8A	0.9300
C4—N1	1.296 (3)	C19A—C20A	1.386 (4)
C4—C5	1.433 (4)	C19A—H19A	0.9300
C4—H4	0.9300	C1A—C20A	1.385 (4)
C21—H21A	0.9600	C1A—H1AA	0.9300
C21—H21B	0.9600	C17A—H17A	0.9300
C21—H21C	0.9600	C13A—C14A	1.407 (4)
C18—C19	1.398 (3)	C13A—H13A	0.9300
C18—C3	1.405 (4)	C14A—H14A	0.9300
C18—N2	1.417 (3)	C20A—H20A	0.9300
O25—C22A	1.424 (4)	C3—C2	1.393 (4)
O6A—C9A	1.369 (3)	C2—C1	1.382 (4)

O6A—C21A	1.431 (3)	C2—H2	0.9300
O1—H1A	0.854 (19)	C20—C1	1.388 (5)
O1—H1B	0.850 (19)	C20—H20	0.9300
C17—N2	1.293 (3)	C1—H1	0.9300
C17—C16	1.437 (4)	C6—C7	1.364 (5)
C17—H17	0.9300	C6—H6	0.9300
O16—N4	1.253 (3)	C7—H7	0.9300
C22—H22A	0.9600	C6B—C5B	1.517 (5)
C22—H22B	0.9600	C6B—H6BA	0.9600
C22—H22C	0.9600	C6B—H6BB	0.9600
O2A—H2AA	0.832 (19)	C6B—H6BC	0.9600
O2A—H2AB	0.838 (19)	C5B—O14	1.302 (5)
C2A—C1A	1.386 (4)	C5B—H5BA	0.9700
C2A—C3A	1.395 (4)	C5B—H5BB	0.9700
C2A—H2AC	0.9300	C2B—C4B	1.252 (10)
O5A—C11A	1.323 (3)	C2B—H2BA	0.9600
C15—C14	1.365 (4)	C2B—H2BB	0.9600
C15—C16	1.417 (4)	C2B—H2BC	0.9600
C15—H15	0.9300	O13—C4B	1.373 (8)
O4A—C10A	1.313 (3)	O13—H13B	0.8200
O10—N3	1.240 (3)	C4B—H4BA	0.9700
C22A—H22D	0.9600	C4B—H4BB	0.9700
C22A—H22E	0.9600	C3B—O15	1.369 (7)
C22A—H22F	0.9600	C3B—C1B	1.575 (11)
C11A—C16A	1.412 (3)	C3B—H3BA	0.9700
O2—H2A	0.855 (19)	C3B—H3BB	0.9700
O2—H2B	0.854 (19)	C1B—H1BA	0.9600
O11—N3	1.259 (3)	C1B—H1BB	0.9600
C3A—C18A	1.412 (4)	C1B—H1BC	0.9600
C3A—N1A	1.422 (3)	O15—H15B	0.8200
O12—N3	1.240 (3)	O14—H14B	0.8200
C16—C11	1.417 (3)	O0AA—H0AA	0.8624
C5A—C10A	1.418 (4)	O0AA—H0AB	0.8623

O4—Ga01—O3	91.95 (8)	O6A—C21A—H21E	109.5
O4—Ga01—N1	175.43 (8)	H21D—C21A—H21E	109.5
O3—Ga01—N1	92.60 (8)	O6A—C21A—H21F	109.5
O4—Ga01—N2	93.84 (8)	H21D—C21A—H21F	109.5
O3—Ga01—N2	173.36 (8)	H21E—C21A—H21F	109.5
N1—Ga01—N2	81.59 (9)	O9—N4—O16	120.9 (3)
O4—Ga01—O2	90.60 (9)	O9—N4—O7	120.4 (2)
O3—Ga01—O2	93.72 (8)	O16—N4—O7	118.7 (2)
N1—Ga01—O2	89.56 (9)	N1A—C4A—C5A	125.2 (2)
N2—Ga01—O2	89.48 (8)	N1A—C4A—H4A	117.4
O4—Ga01—O1	89.74 (8)	C5A—C4A—H4A	117.4
O3—Ga01—O1	90.02 (7)	C17—N2—C18	123.5 (2)
N1—Ga01—O1	89.80 (8)	C17—N2—Ga01	123.54 (18)
N2—Ga01—O1	86.76 (8)	C18—N2—Ga01	112.92 (16)

O2—Ga01—O1	176.23 (8)	O4A—C10A—C5A	125.0 (2)
O5A—Ga02—O4A	91.11 (8)	O4A—C10A—C9A	117.0 (2)
O5A—Ga02—N1A	174.56 (8)	C5A—C10A—C9A	118.0 (2)
O4A—Ga02—N1A	93.96 (8)	C20—C19—C18	119.7 (3)
O5A—Ga02—N2A	92.88 (8)	C20—C19—H19	120.1
O4A—Ga02—N2A	174.46 (9)	C18—C19—H19	120.1
N1A—Ga02—N2A	82.20 (9)	C19A—C18A—C3A	119.5 (2)
O5A—Ga02—O0AA	89.90 (9)	C19A—C18A—N2A	124.5 (3)
O4A—Ga02—O0AA	91.77 (8)	C3A—C18A—N2A	115.9 (2)
N1A—Ga02—O0AA	87.98 (9)	O6—C12—C13	125.4 (2)
N2A—Ga02—O0AA	92.08 (9)	O6—C12—C11	113.6 (2)
O5A—Ga02—O2A	92.01 (8)	C13—C12—C11	121.0 (2)
O4A—Ga02—O2A	89.17 (8)	C12—C13—C14	120.4 (3)
N1A—Ga02—O2A	90.03 (9)	C12—C13—H13	119.8
N2A—Ga02—O2A	86.84 (8)	C14—C13—H13	119.8
O0AA—Ga02—O2A	177.85 (8)	C9—C8—C7	120.0 (3)
C12—O6—C22	117.4 (2)	C9—C8—H8	120.0
C17A—N2A—C18A	122.1 (2)	C7—C8—H8	120.0
C17A—N2A—Ga02	124.87 (18)	O3—C10—C5	125.0 (2)
C18A—N2A—Ga02	112.76 (17)	O3—C10—C9	116.9 (2)
C6A—C7A—C8A	120.2 (3)	C5—C10—C9	118.0 (2)
C6A—C7A—H7A	119.9	C10—C5—C6	119.7 (2)
C8A—C7A—H7A	119.9	C10—C5—C4	123.7 (2)
C11—O4—Ga01	127.10 (16)	C6—C5—C4	116.5 (2)
C14A—C15A—C16A	120.9 (3)	O5—C9—C8	125.3 (2)
C14A—C15A—H15A	119.5	O5—C9—C10	113.8 (2)
C16A—C15A—H15A	119.5	C8—C9—C10	121.0 (2)
O25—C12A—C13A	125.7 (3)	C9A—C8A—C7A	120.0 (2)
O25—C12A—C11A	113.2 (2)	C9A—C8A—H8A	120.0
C13A—C12A—C11A	121.2 (2)	C7A—C8A—H8A	120.0
C10—O3—Ga01	126.03 (15)	C20A—C19A—C18A	120.0 (3)
C9—O5—C21	116.6 (2)	C20A—C19A—H19A	120.0
N1—C4—C5	124.8 (2)	C18A—C19A—H19A	120.0
N1—C4—H4	117.6	C20A—C1A—C2A	120.6 (3)
C5—C4—H4	117.6	C20A—C1A—H1AA	119.7
O5—C21—H21A	109.5	C2A—C1A—H1AA	119.7
O5—C21—H21B	109.5	O6A—C9A—C8A	125.2 (2)
H21A—C21—H21B	109.5	O6A—C9A—C10A	113.4 (2)
O5—C21—H21C	109.5	C8A—C9A—C10A	121.4 (2)
H21A—C21—H21C	109.5	N2A—C17A—C16A	125.4 (2)
H21B—C21—H21C	109.5	N2A—C17A—H17A	117.3
C19—C18—C3	119.4 (2)	C16A—C17A—H17A	117.3
C19—C18—N2	125.0 (2)	C12A—C13A—C14A	120.5 (3)
C3—C18—N2	115.6 (2)	C12A—C13A—H13A	119.8
C12A—O25—C22A	116.8 (2)	C14A—C13A—H13A	119.8
C9A—O6A—C21A	117.0 (2)	C15A—C14A—C13A	119.7 (3)
Ga01—O1—H1A	107 (4)	C15A—C14A—H14A	120.1
Ga01—O1—H1B	107 (4)	C13A—C14A—H14A	120.1

H1A—O1—H1B	110 (3)	C1A—C20A—C19A	120.4 (3)
N2—C17—C16	125.5 (2)	C1A—C20A—H20A	119.8
N2—C17—H17	117.3	C19A—C20A—H20A	119.8
C16—C17—H17	117.3	C2—C3—C18	120.3 (2)
O6—C22—H22A	109.5	C2—C3—N1	123.9 (2)
O6—C22—H22B	109.5	C18—C3—N1	115.8 (2)
H22A—C22—H22B	109.5	C1—C2—C3	119.5 (3)
O6—C22—H22C	109.5	C1—C2—H2	120.3
H22A—C22—H22C	109.5	C3—C2—H2	120.3
H22B—C22—H22C	109.5	C19—C20—C1	120.4 (3)
Ga02—O2A—H2AA	111 (4)	C19—C20—H20	119.8
Ga02—O2A—H2AB	109 (4)	C1—C20—H20	119.8
H2AA—O2A—H2AB	113 (3)	C2—C1—C20	120.7 (3)
C1A—C2A—C3A	119.7 (3)	C2—C1—H1	119.6
C1A—C2A—H2AC	120.2	C20—C1—H1	119.6
C3A—C2A—H2AC	120.2	C7—C6—C5	120.4 (3)
C11A—O5A—Ga02	127.81 (16)	C7—C6—H6	119.8
C14—C15—C16	121.1 (3)	C5—C6—H6	119.8
C14—C15—H15	119.4	C6—C7—C8	120.6 (3)
C16—C15—H15	119.4	C6—C7—H7	119.7
C10A—O4A—Ga02	127.15 (16)	C8—C7—H7	119.7
O25—C22A—H22D	109.5	C5B—C6B—H6BA	109.5
O25—C22A—H22E	109.5	C5B—C6B—H6BB	109.5
H22D—C22A—H22E	109.5	H6BA—C6B—H6BB	109.5
O25—C22A—H22F	109.5	C5B—C6B—H6BC	109.5
H22D—C22A—H22F	109.5	H6BA—C6B—H6BC	109.5
H22E—C22A—H22F	109.5	H6BB—C6B—H6BC	109.5
O5A—C11A—C16A	125.6 (2)	O14—C5B—C6B	112.8 (3)
O5A—C11A—C12A	116.7 (2)	O14—C5B—H5BA	109.0
C16A—C11A—C12A	117.8 (2)	C6B—C5B—H5BA	109.0
Ga01—O2—H2A	126 (3)	O14—C5B—H5BB	109.0
Ga01—O2—H2B	121 (3)	C6B—C5B—H5BB	109.0
H2A—O2—H2B	108 (3)	H5BA—C5B—H5BB	107.8
C2A—C3A—C18A	119.7 (2)	C4B—C2B—H2BA	109.5
C2A—C3A—N1A	124.9 (3)	C4B—C2B—H2BB	109.5
C18A—C3A—N1A	115.4 (2)	H2BA—C2B—H2BB	109.5
C15—C16—C11	119.2 (3)	C4B—C2B—H2BC	109.5
C15—C16—C17	116.7 (2)	H2BA—C2B—H2BC	109.5
C11—C16—C17	124.0 (2)	H2BB—C2B—H2BC	109.5
C10A—C5A—C6A	119.3 (2)	C4B—O13—H13B	109.5
C10A—C5A—C4A	124.1 (2)	C2B—C4B—O13	110.5 (6)
C6A—C5A—C4A	116.6 (2)	C2B—C4B—H4BA	109.5
C11A—C16A—C15A	119.9 (2)	O13—C4B—H4BA	109.5
C11A—C16A—C17A	123.2 (2)	C2B—C4B—H4BB	109.5
C15A—C16A—C17A	116.9 (2)	O13—C4B—H4BB	109.5
C7A—C6A—C5A	121.1 (3)	H4BA—C4B—H4BB	108.1
C7A—C6A—H6A	119.5	O15—C3B—C1B	130.8 (6)
C5A—C6A—H6A	119.5	O15—C3B—H3BA	104.6

C4—N1—C3	122.7 (2)	C1B—C3B—H3BA	104.6
C4—N1—Ga01	123.77 (18)	O15—C3B—H3BB	104.6
C3—N1—Ga01	113.12 (17)	C1B—C3B—H3BB	104.6
C15—C14—C13	120.0 (3)	H3BA—C3B—H3BB	105.7
C15—C14—H14	120.0	C3B—C1B—H1BA	109.5
C13—C14—H14	120.0	C3B—C1B—H1BB	109.5
O4—C11—C12	116.8 (2)	H1BA—C1B—H1BB	109.5
O4—C11—C16	125.0 (2)	C3B—C1B—H1BC	109.5
C12—C11—C16	118.1 (2)	H1BA—C1B—H1BC	109.5
C4A—N1A—C3A	122.4 (2)	H1BB—C1B—H1BC	109.5
C4A—N1A—Ga02	124.02 (18)	C3B—O15—H15B	109.5
C3A—N1A—Ga02	113.50 (17)	C5B—O14—H14B	109.5
O12—N3—O10	120.8 (3)	Ga02—O0AA—H0AA	110.3
O12—N3—O11	118.1 (2)	Ga02—O0AA—H0AB	110.0
O10—N3—O11	121.0 (3)	H0AA—O0AA—H0AB	103.7
O6A—C21A—H21D	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O4^{i}	0.85 (2)	2.11 (4)	2.800 (2)	138 (4)
O1—H1*A*···O3^{i}	0.85 (2)	2.06 (3)	2.816 (3)	147 (5)
O2*A*—H2*AB*···O5*A*^{ii}	0.84 (2)	2.17 (4)	2.872 (3)	141 (5)
O2*A*—H2*AA*···O4*A*^{ii}	0.83 (2)	2.20 (4)	2.844 (3)	134 (5)
O2—H2*B*···O16	0.85 (2)	1.90 (2)	2.727 (3)	161 (5)
O2—H2*A*···O13^{iii}	0.86 (2)	1.77 (2)	2.620 (5)	170 (6)
O2—H2*A*···O15^{iii}	0.86 (2)	1.83 (3)	2.656 (6)	162 (6)

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