

Poly[[diaquabis(μ_3 -isonicotinato- κ^3 N:O:O')bis(μ_2 -isonicotinato- κ^2 N:O)-gadolinium(III)disilver(I)] nitrate monohydrate]

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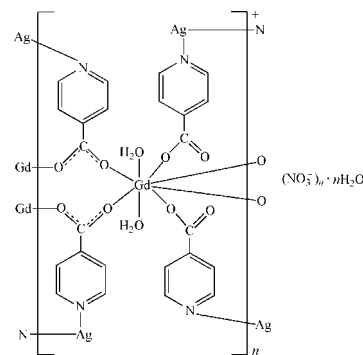
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.034; wR factor = 0.129; data-to-parameter ratio = 11.7.

In the title compound, $\{[\text{Ag}_2\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)_4(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}\}_n$, the Gd^{III} ion is coordinated by eight O atoms from six isonicotinate ligands and two water molecules in a distorted square antiprismatic geometry. Two Ag^{I} ions are each bonded to two N atoms from two isonicotinate ligands in a linear or bow-like fashion [$\text{N}-\text{Ag}-\text{N}$ angles = 178.6 (2) and 147.1 (2) $^\circ$]. These metal ions are connected by the isonicotinate ligands into a layer parallel to (010). O—H \cdots O hydrogen bonds donated by the coordinated and uncoordinated water molecules and intralayer π – π stacking interactions between the pyridine rings [centroid–centroid distances = 3.551 (4) and 3.555 (4) Å] are observed. The layers interact with each other by interlayer $\text{Ag}\cdots\text{O}(\text{aqua})$ contacts [2.731 (4) Å] and π – π stacking interactions between the pyridine rings [centroid–centroid distances = 3.466 (3) and 3.516 (3) Å], resulting in the formation of a three-dimensional supramolecular structure.

Related literature

For general background to the structures and properties of lanthanide–transition metal coordination polymers, see: Cheng *et al.* (2007, 2008); Fan & Wu (2010); Fang *et al.* (2009); Luo *et al.* (2007).



Experimental

Crystal data

$[\text{Ag}_2\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)_4(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$
 $M_r = 977.46$
 Monoclinic, $P2_1/c$
 $a = 16.889$ (8) Å
 $b = 24.744$ (11) Å
 $c = 6.750$ (3) Å

$\beta = 96.240$ (9) $^\circ$
 $V = 2804$ (2) Å 3
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.80$ mm $^{-1}$
 $T = 293$ K
 $0.30 \times 0.12 \times 0.08$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
 $T_{\text{min}} = 0.703$, $T_{\text{max}} = 1.000$

16445 measured reflections
 4859 independent reflections
 4370 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.129$
 $S = 1.08$
 4859 reflections

416 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.38$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -1.27$ e Å $^{-3}$

Table 1

Selected bond lengths (Å).

Gd1—O1	2.357 (4)	Gd1—O9	2.454 (4)
Gd1—O2 ⁱ	2.465 (4)	Gd1—O10	2.533 (4)
Gd1—O3	2.383 (4)	Ag1—N1	2.144 (5)
Gd1—O5	2.393 (4)	Ag1—N4 ⁱⁱ	2.147 (5)
Gd1—O7	2.399 (4)	Ag2—N2 ⁱⁱⁱ	2.189 (5)
Gd1—O8 ⁱ	2.386 (4)	Ag2—N3	2.199 (5)

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

Table 2

 Hydrogen-bond geometry (Å, $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O9—H9A \cdots O6	0.85	2.13	2.771 (7)	132
O9—H9B \cdots O2 ^{iv}	0.85	2.03	2.811 (6)	153
O10—H10A \cdots O6 ^v	0.85	2.12	2.954 (6)	165
O10—H10C \cdots O4	0.85	1.84	2.662 (6)	162
O14—H14B \cdots O12 ^{vi}	0.85	2.27	2.960 (9)	139
O14—H14C \cdots O13 ^{vii}	0.85	2.01	2.779 (10)	151

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2346).

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supplementary materials

Acta Cryst. (2010). E66, m1234-m1235 [doi:10.1107/S1600536810035634]

Poly[[diaquabis(μ_3 -isonicotinato- $\kappa^3 N:O:O'$)bis(μ_2 -isonicotinato- $\kappa^2 N:O$)gadolinium(III)disilver(I)] nitrate monohydrate]

L.-Q. Fan and J.-H. Wu

Comment

In recent years, investigations on the design and synthesis of lanthanide-transition metal coordination polymers have attracted great interest not only for their fascinating structural topologies but also for their potential applications in magnetism, luminescence materials, molecular adsorption, and bimetallic catalysis (Cheng *et al.*, 2007, 2008; Fan & Wu, 2010; Fang *et al.*, 2009; Luo *et al.*, 2007). Isonicotinic acid, which acts as a multidentate ligand possessing N and O donor atoms, is utilized to construct lanthanide-transition metal coordination polymers *via* the carboxylate group coordinating to lanthanide ions and N atom bonding to transition metal ions, such as Ag^{I} or Cu^{I} ions. We report herein the crystal structure of the title 4d-4f compound by the reaction of Gd_2O_3 , isonicotinic acid and AgNO_3 under hydrothermal conditions.

As shown in Fig. 1, the asymmetric unit of the title compound contains one Gd^{III} ion, two Ag^{I} ions, four isonicotinate ligands, two coordinated water molecules, one nitrate ion, and one uncoordinated water molecule. The Gd^{III} ion is coordinated by eight O atoms from six isonicotinate ligands and two water molecules in a distorted square antiprismatic geometry, with the Gd—O bond lengths and O—Gd—O bond angles being from 2.356 (4) to 2.534 (4) Å and 71.22 (13) to 145.29 (14)°, respectively (Table 1). Each Ag^{I} ion is bonded to two N atoms from two different isonicotinate ligands in a linear or bow-like fashion, with the Ag—N bond lengths of 2.145 (5)–2.201 (5) Å and N—Ag—N bond angles of 178.5 (2)° and 147.30 (19) (Table 1). Adjacent Gd centers are connected by two carboxylate groups from two different isonicotinate ligands, forming one-dimensional chains, which are further linked by Ag^{I} ions to construct two-dimensional layers. The layers are stabilized by O—H \cdots O hydrogen bonds involving the coordinated and uncoordinated water molecules (Table 2) and intralayer π – π stacking interactions between the pyridine rings, with centroid–centroid distances of 3.551 (4) and 3.555 (4) Å (Spek, 2009). The layers interact each other by interlayer $\text{Ag}_2\cdots\text{O}10(\text{aqua})$ contacts [2.731 (4) Å] and π – π stacking interactions between the pyridine rings from two neighboring layers, with centroid–centroid distances of 3.466 (3) and 3.516 (3) Å, which result in the formation of a three-dimensional supramolecular structure (Fig. 2).

Experimental

A mixture of Gd_2O_3 (0.181 g, 0.5 mmol), isonicotinic acid (0.123 g, 1 mmol), AgNO_3 (0.170 g, 1 mmol) and H_2O (10 ml) was placed in a 23 ml Teflon-lined reactor, which was heated to 443 K for 7 d and then cooled to room temperature at a rate of 0.2 K h^{-1} . The colorless crystals obtained were washed with water and dried in air (yield 32% based on Gd).

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 and O—H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$. The highest residual electron density was found 1.18 Å from O10 and the deepest hole 0.81 Å from Gd1.

Figures

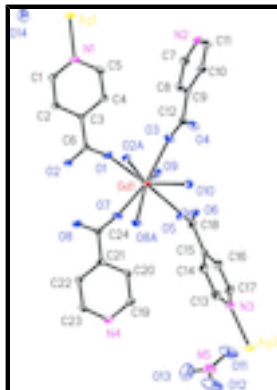


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Additional symmetry related atoms are included to complete the coordination geometry around the Gd atom. [Symmetry code: (A) $x, 1/2-y, 1/2+z$.]

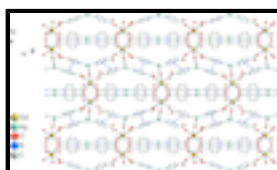


Fig. 2. The three-dimensional supramolecular structure viewed along the c axis, formed through weak interlayer $\text{Ag}\cdots\text{O}$ contacts and π - π stacking interactions (dashed lines).

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Crystal data

$[\text{Ag}_2\text{Gd}(\text{C}_6\text{H}_4\text{NO}_2)_4(\text{H}_2\text{O})_2]\text{NO}_3\cdot\text{H}_2\text{O}$

$M_r = 977.46$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 16.889$ (8) Å

$b = 24.744$ (11) Å

$c = 6.750$ (3) Å

$\beta = 96.240$ (9)°

$V = 2804$ (2) Å³

$Z = 4$

$F(000) = 1884$

$D_x = 2.315$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6663 reflections

$\theta = 3.0$ – 27.5 °

$\mu = 3.80$ mm⁻¹

$T = 293$ K

Block, colorless

$0.30 \times 0.12 \times 0.08$ mm

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

ω scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2007)

$T_{\min} = 0.703$, $T_{\max} = 1.000$

16445 measured reflections

4859 independent reflections

4370 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 25.0$ °, $\theta_{\text{min}} = 2.6$ °

$h = -20 \rightarrow 19$

$k = -28 \rightarrow 29$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2 + 0.0116P]$
4859 reflections	where $P = (F_o^2 + 2F_c^2)/3$
416 parameters	$(\Delta/\sigma)_{\max} = 0.002$
0 restraints	$\Delta\rho_{\max} = 1.38 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -1.27 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Gd1	0.769985 (15)	0.162835 (10)	0.61682 (4)	0.01965 (14)
Ag1	1.27129 (3)	0.27098 (2)	0.49007 (9)	0.04268 (18)
Ag2	0.26502 (3)	0.00962 (2)	0.40147 (9)	0.04637 (19)
O1	0.8613 (2)	0.23037 (17)	0.5464 (8)	0.0399 (11)
O2	0.8530 (2)	0.31392 (15)	0.4284 (6)	0.0255 (8)
O3	0.8850 (2)	0.10782 (16)	0.6024 (6)	0.0309 (9)
O4	0.9135 (3)	0.05792 (18)	0.8754 (6)	0.0342 (10)
O5	0.6664 (3)	0.1044 (2)	0.4728 (6)	0.0412 (12)
O6	0.6514 (3)	0.08461 (19)	0.1515 (7)	0.0380 (11)
O7	0.6853 (2)	0.22994 (18)	0.4473 (7)	0.0394 (11)
O8	0.6733 (2)	0.31472 (17)	0.3362 (6)	0.0305 (9)
O9	0.7837 (3)	0.1483 (2)	0.2626 (6)	0.0419 (12)
H9A	0.7661	0.1161	0.2502	0.050*
H9B	0.8157	0.1639	0.1924	0.050*
O10	0.7581 (2)	0.08017 (15)	0.8329 (6)	0.0293 (9)
H10C	0.8059	0.0717	0.8722	0.035*
H10A	0.7353	0.0817	0.9390	0.035*
O11	0.2993 (4)	0.0486 (3)	0.8246 (9)	0.076 (2)
O12	0.2422 (4)	0.0839 (3)	1.0578 (9)	0.084 (2)
O13	0.2575 (5)	0.1295 (3)	0.7976 (11)	0.083 (2)
O14	1.2728 (4)	0.3429 (2)	0.9058 (12)	0.0660 (18)
H14C	1.2816	0.3432	1.0322	0.08 (4)*
H14B	1.2406	0.3619	0.8292	0.095*
N1	1.1448 (3)	0.2720 (2)	0.4982 (7)	0.0295 (11)
N2	1.1488 (3)	0.0291 (2)	0.4987 (8)	0.0319 (12)
N3	0.3875 (3)	0.0365 (2)	0.3745 (8)	0.0317 (11)
N4	0.3979 (3)	0.2720 (2)	0.4807 (8)	0.0326 (12)
N5	0.2680 (4)	0.0875 (3)	0.8983 (11)	0.0524 (17)
C1	1.1038 (3)	0.3187 (3)	0.4945 (9)	0.0300 (13)
H1A	1.1321	0.3510	0.4970	0.036*

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C2	1.0215 (3)	0.3210 (2)	0.4872 (9)	0.0254 (12)
H2A	0.9952	0.3541	0.4804	0.030*
C3	0.9793 (3)	0.2732 (2)	0.4900 (8)	0.0192 (11)
C4	1.0219 (3)	0.2248 (2)	0.4990 (9)	0.0244 (12)
H4A	0.9951	0.1920	0.5020	0.029*
C5	1.1036 (4)	0.2255 (3)	0.5035 (9)	0.0306 (13)
H5A	1.1312	0.1929	0.5103	0.037*
C6	0.8906 (3)	0.2727 (2)	0.4838 (7)	0.0202 (11)
C7	1.0969 (4)	0.0607 (2)	0.3909 (10)	0.0319 (13)
H7A	1.1093	0.0724	0.2670	0.038*
C8	1.0253 (4)	0.0770 (2)	0.4541 (9)	0.0286 (13)
H8A	0.9897	0.0980	0.3723	0.034*
C9	1.0080 (3)	0.0614 (2)	0.6418 (8)	0.0209 (11)
C10	1.0615 (3)	0.0291 (2)	0.7561 (9)	0.0299 (13)
H10B	1.0514	0.0180	0.8826	0.036*
C11	1.1301 (4)	0.0136 (2)	0.6792 (10)	0.0325 (14)
H11A	1.1654	-0.0089	0.7558	0.039*
C12	0.9283 (3)	0.0766 (2)	0.7152 (8)	0.0229 (12)
C13	0.4339 (4)	0.0597 (3)	0.5286 (9)	0.0327 (14)
H13A	0.4127	0.0643	0.6490	0.039*
C14	0.5102 (4)	0.0765 (2)	0.5146 (10)	0.0326 (14)
H14A	0.5406	0.0910	0.6250	0.039*
C15	0.5418 (3)	0.0717 (2)	0.3342 (8)	0.0219 (11)
C16	0.4947 (4)	0.0496 (2)	0.1764 (8)	0.0294 (13)
H16A	0.5139	0.0462	0.0530	0.035*
C17	0.4192 (4)	0.0327 (3)	0.2018 (10)	0.0328 (14)
H17A	0.3883	0.0178	0.0930	0.039*
C18	0.6282 (3)	0.0883 (2)	0.3187 (8)	0.0231 (12)
C19	0.4396 (3)	0.2255 (2)	0.4717 (9)	0.0288 (13)
H19A	0.4125	0.1928	0.4741	0.035*
C20	0.5204 (3)	0.2245 (2)	0.4593 (8)	0.0234 (12)
H20A	0.5476	0.1918	0.4597	0.028*
C21	0.4397 (4)	0.3187 (3)	0.4771 (9)	0.0323 (14)
H21A	0.4130	0.3511	0.4912	0.039*
C22	0.5186 (3)	0.3206 (2)	0.4539 (9)	0.0260 (12)
H22A	0.5441	0.3536	0.4434	0.031*
C23	0.5604 (3)	0.2726 (2)	0.4462 (7)	0.0202 (11)
C24	0.6471 (3)	0.2728 (2)	0.4095 (8)	0.0232 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Gd1	0.0133 (2)	0.0206 (2)	0.0256 (2)	-0.00073 (9)	0.00462 (13)	0.00042 (9)
Ag1	0.0119 (3)	0.0577 (4)	0.0593 (4)	-0.0001 (2)	0.0077 (2)	0.0006 (3)
Ag2	0.0197 (3)	0.0572 (4)	0.0642 (4)	0.0012 (2)	0.0137 (2)	0.0041 (3)
O1	0.016 (2)	0.032 (2)	0.071 (3)	-0.0077 (18)	0.004 (2)	0.019 (2)
O2	0.0152 (19)	0.028 (2)	0.033 (2)	0.0050 (17)	-0.0015 (16)	0.0059 (17)
O3	0.027 (2)	0.030 (2)	0.037 (2)	0.0107 (18)	0.0090 (19)	0.0024 (18)

O4	0.033 (2)	0.042 (3)	0.029 (2)	0.016 (2)	0.0073 (19)	0.0101 (19)
O5	0.036 (3)	0.056 (3)	0.030 (2)	-0.026 (2)	-0.002 (2)	-0.001 (2)
O6	0.029 (2)	0.054 (3)	0.033 (2)	-0.010 (2)	0.0116 (19)	-0.005 (2)
O7	0.016 (2)	0.041 (3)	0.061 (3)	0.0114 (19)	0.004 (2)	0.015 (2)
O8	0.019 (2)	0.035 (2)	0.039 (2)	-0.0045 (18)	0.0097 (18)	0.0090 (19)
O9	0.041 (3)	0.063 (3)	0.023 (2)	-0.022 (2)	0.0083 (19)	-0.002 (2)
O10	0.026 (2)	0.025 (2)	0.038 (2)	0.0025 (18)	0.0141 (18)	0.0036 (17)
O11	0.051 (4)	0.112 (6)	0.063 (4)	0.029 (4)	0.002 (3)	-0.033 (4)
O12	0.065 (4)	0.143 (7)	0.042 (3)	0.047 (4)	-0.002 (3)	-0.002 (3)
O13	0.102 (6)	0.068 (5)	0.081 (4)	-0.019 (4)	0.020 (4)	-0.007 (4)
O14	0.062 (4)	0.038 (3)	0.098 (6)	-0.002 (3)	0.007 (4)	-0.001 (3)
N1	0.015 (2)	0.042 (3)	0.032 (3)	-0.001 (2)	0.005 (2)	0.000 (2)
N2	0.018 (3)	0.034 (3)	0.045 (3)	-0.002 (2)	0.009 (2)	-0.006 (2)
N3	0.016 (2)	0.032 (3)	0.047 (3)	0.002 (2)	0.003 (2)	0.002 (2)
N4	0.018 (3)	0.036 (3)	0.045 (3)	0.001 (2)	0.012 (2)	-0.003 (2)
N5	0.030 (3)	0.063 (4)	0.064 (5)	0.002 (3)	0.006 (3)	-0.018 (4)
C1	0.016 (3)	0.030 (3)	0.044 (3)	-0.008 (3)	0.006 (3)	0.000 (3)
C2	0.015 (3)	0.023 (3)	0.039 (3)	-0.001 (2)	0.008 (2)	0.005 (2)
C3	0.014 (3)	0.022 (3)	0.022 (3)	-0.001 (2)	0.002 (2)	0.002 (2)
C4	0.016 (3)	0.023 (3)	0.034 (3)	0.000 (2)	0.003 (2)	0.001 (2)
C5	0.024 (3)	0.031 (3)	0.037 (3)	0.007 (3)	0.005 (3)	0.003 (3)
C6	0.016 (3)	0.027 (3)	0.018 (2)	-0.004 (2)	0.003 (2)	-0.004 (2)
C7	0.028 (3)	0.031 (3)	0.039 (3)	0.002 (3)	0.012 (3)	0.002 (3)
C8	0.023 (3)	0.024 (3)	0.040 (3)	0.004 (2)	0.006 (3)	-0.005 (2)
C9	0.020 (3)	0.021 (3)	0.022 (3)	0.001 (2)	-0.001 (2)	-0.001 (2)
C10	0.019 (3)	0.034 (3)	0.037 (3)	-0.003 (3)	0.007 (3)	0.003 (3)
C11	0.021 (3)	0.032 (3)	0.044 (4)	0.010 (3)	0.001 (3)	0.003 (3)
C12	0.022 (3)	0.022 (3)	0.025 (3)	0.004 (2)	0.006 (2)	-0.003 (2)
C13	0.034 (3)	0.034 (3)	0.032 (3)	-0.001 (3)	0.009 (3)	-0.006 (3)
C14	0.031 (3)	0.030 (3)	0.038 (3)	-0.008 (3)	0.009 (3)	-0.008 (3)
C15	0.020 (3)	0.013 (2)	0.033 (3)	-0.001 (2)	0.004 (2)	0.002 (2)
C16	0.031 (3)	0.033 (3)	0.023 (3)	-0.003 (3)	0.001 (2)	0.000 (2)
C17	0.022 (3)	0.036 (3)	0.039 (3)	-0.007 (3)	0.000 (3)	0.003 (3)
C18	0.024 (3)	0.021 (3)	0.024 (3)	-0.006 (2)	0.000 (2)	-0.002 (2)
C19	0.018 (3)	0.030 (3)	0.038 (3)	-0.004 (2)	0.002 (3)	0.003 (2)
C20	0.021 (3)	0.028 (3)	0.022 (3)	0.002 (2)	0.004 (2)	0.001 (2)
C21	0.023 (3)	0.028 (3)	0.048 (4)	0.004 (3)	0.015 (3)	-0.002 (3)
C22	0.021 (3)	0.024 (3)	0.032 (3)	-0.004 (2)	0.003 (2)	0.001 (2)
C23	0.017 (3)	0.029 (3)	0.015 (2)	-0.003 (2)	0.005 (2)	0.002 (2)
C24	0.018 (3)	0.028 (3)	0.025 (3)	-0.001 (2)	0.007 (2)	0.003 (2)

Geometric parameters (Å, °)

Gd1—O1	2.357 (4)	N4—C19	1.354 (8)
Gd1—O2 ⁱ	2.465 (4)	N4—Ag1 ⁱⁱⁱ	2.147 (5)
Gd1—O3	2.383 (4)	C1—C2	1.388 (8)
Gd1—O5	2.393 (4)	C1—H1A	0.9300
Gd1—O7	2.399 (4)	C2—C3	1.383 (8)
Gd1—O8 ⁱ	2.386 (4)	C2—H2A	0.9300

supplementary materials

Gd1—O9	2.454 (4)	C3—C4	1.395 (7)
Gd1—O10	2.533 (4)	C3—C6	1.494 (7)
Ag1—N1	2.144 (5)	C4—C5	1.377 (8)
Ag1—N4 ⁱⁱ	2.147 (5)	C4—H4A	0.9300
Ag2—N2 ⁱⁱⁱ	2.189 (5)	C5—H5A	0.9300
Ag2—N3	2.199 (5)	C7—C8	1.385 (9)
O1—C6	1.252 (7)	C7—H7A	0.9300
O2—C6	1.238 (7)	C8—C9	1.386 (8)
O2—Gd1 ^{iv}	2.465 (4)	C8—H8A	0.9300
O3—C12	1.261 (7)	C9—C10	1.378 (8)
O4—C12	1.227 (7)	C9—C12	1.530 (8)
O5—C18	1.229 (7)	C10—C11	1.374 (8)
O6—C18	1.238 (7)	C10—H10B	0.9300
O7—C24	1.253 (7)	C11—H11A	0.9300
O8—C24	1.251 (7)	C13—C14	1.367 (9)
O8—Gd1 ^{iv}	2.386 (4)	C13—H13A	0.9300
O9—H9A	0.8500	C14—C15	1.387 (8)
O9—H9B	0.8500	C14—H14A	0.9300
O10—H10C	0.8500	C15—C16	1.371 (8)
O10—H10A	0.8500	C15—C18	1.531 (8)
O11—N5	1.229 (9)	C16—C17	1.370 (9)
O12—N5	1.208 (9)	C16—H16A	0.9300
O13—N5	1.244 (10)	C17—H17A	0.9300
O14—H14C	0.8500	C19—C20	1.377 (8)
O14—H14B	0.8500	C19—H19A	0.9300
N1—C1	1.345 (8)	C20—C23	1.377 (8)
N1—C5	1.348 (8)	C20—H20A	0.9300
N2—C7	1.331 (8)	C21—C22	1.359 (9)
N2—C11	1.348 (8)	C21—H21A	0.9300
N2—Ag2 ⁱⁱ	2.189 (5)	C22—C23	1.384 (8)
N3—C17	1.338 (8)	C22—H22A	0.9300
N3—C13	1.359 (8)	C23—C24	1.512 (7)
N4—C21	1.354 (8)		
O1—Gd1—O3	80.95 (15)	C2—C3—C6	121.5 (5)
O1—Gd1—O8 ⁱ	117.84 (16)	C4—C3—C6	120.4 (5)
O3—Gd1—O8 ⁱ	140.74 (14)	C5—C4—C3	120.1 (5)
O1—Gd1—O5	144.27 (17)	C5—C4—H4A	120.0
O3—Gd1—O5	101.65 (17)	C3—C4—H4A	120.0
O8 ⁱ —Gd1—O5	82.71 (15)	N1—C5—C4	121.9 (6)
O1—Gd1—O7	77.42 (16)	N1—C5—H5A	119.1
O3—Gd1—O7	145.32 (15)	C4—C5—H5A	119.1
O8 ⁱ —Gd1—O7	73.87 (15)	O2—C6—O1	125.6 (5)
O5—Gd1—O7	81.52 (18)	O2—C6—C3	118.8 (5)
O1—Gd1—O9	76.97 (17)	O1—C6—C3	115.4 (5)
O3—Gd1—O9	73.28 (16)	N2—C7—C8	123.3 (6)
O8 ⁱ —Gd1—O9	141.49 (16)	N2—C7—H7A	118.4
O5—Gd1—O9	69.98 (15)	C8—C7—H7A	118.4

O7—Gd1—O9	75.62 (18)	C9—C8—C7	118.6 (6)
O1—Gd1—O2 ⁱ	71.51 (16)	C9—C8—H8A	120.7
O3—Gd1—O2 ⁱ	77.15 (14)	C7—C8—H8A	120.7
O8 ⁱ —Gd1—O2 ⁱ	77.31 (14)	C8—C9—C10	118.9 (5)
O5—Gd1—O2 ⁱ	144.13 (14)	C8—C9—C12	120.6 (5)
O7—Gd1—O2 ⁱ	119.97 (15)	C10—C9—C12	120.5 (5)
O9—Gd1—O2 ⁱ	139.49 (14)	C11—C10—C9	118.6 (6)
O1—Gd1—O10	141.58 (15)	C11—C10—H10B	120.7
O3—Gd1—O10	71.24 (14)	C9—C10—H10B	120.7
O8 ⁱ —Gd1—O10	74.21 (14)	N2—C11—C10	123.5 (6)
O5—Gd1—O10	69.25 (15)	N2—C11—H11A	118.2
O7—Gd1—O10	138.84 (14)	C10—C11—H11A	118.2
O9—Gd1—O10	117.66 (16)	O4—C12—O3	127.1 (5)
O2 ⁱ —Gd1—O10	76.74 (14)	O4—C12—C9	117.6 (5)
N4 ⁱⁱ —Ag1—N1	178.6 (2)	O3—C12—C9	115.3 (5)
N2 ⁱⁱⁱ —Ag2—N3	147.1 (2)	N3—C13—C14	123.0 (6)
C6—O1—Gd1	162.4 (4)	N3—C13—H13A	118.5
C6—O2—Gd1 ^{iv}	132.5 (3)	C14—C13—H13A	118.5
C12—O3—Gd1	138.3 (4)	C13—C14—C15	119.3 (6)
C18—O5—Gd1	146.4 (4)	C13—C14—H14A	120.3
C24—O7—Gd1	161.8 (4)	C15—C14—H14A	120.3
C24—O8—Gd1 ^{iv}	137.2 (4)	C16—C15—C14	118.0 (5)
Gd1—O9—H9A	99.5	C16—C15—C18	122.1 (5)
Gd1—O9—H9B	127.5	C14—C15—C18	119.8 (5)
H9A—O9—H9B	127.5	C17—C16—C15	119.6 (5)
Gd1—O10—H10C	104.3	C17—C16—H16A	120.2
Gd1—O10—H10A	121.4	C15—C16—H16A	120.2
H10C—O10—H10A	104.5	N3—C17—C16	123.6 (6)
H14C—O14—H14B	129.5	N3—C17—H17A	118.2
C1—N1—C5	118.0 (5)	C16—C17—H17A	118.2
C1—N1—Ag1	121.4 (4)	O5—C18—O6	127.3 (6)
C5—N1—Ag1	120.6 (4)	O5—C18—C15	116.5 (5)
C7—N2—C11	117.1 (5)	O6—C18—C15	116.2 (5)
C7—N2—Ag2 ⁱⁱ	121.6 (4)	N4—C19—C20	122.8 (5)
C11—N2—Ag2 ⁱⁱ	121.0 (4)	N4—C19—H19A	118.6
C17—N3—C13	116.4 (5)	C20—C19—H19A	118.6
C17—N3—Ag2	121.3 (4)	C23—C20—C19	118.9 (5)
C13—N3—Ag2	122.2 (4)	C23—C20—H20A	120.5
C21—N4—C19	116.7 (5)	C19—C20—H20A	120.5
C21—N4—Ag1 ⁱⁱⁱ	122.2 (4)	N4—C21—C22	123.4 (6)
C19—N4—Ag1 ⁱⁱⁱ	121.0 (4)	N4—C21—H21A	118.3
O12—N5—O11	121.1 (9)	C22—C21—H21A	118.3
O12—N5—O13	120.3 (7)	C21—C22—C23	119.0 (5)
O11—N5—O13	118.4 (8)	C21—C22—H22A	120.5
N1—C1—C2	123.3 (6)	C23—C22—H22A	120.5
N1—C1—H1A	118.4	C20—C23—C22	118.9 (5)

supplementary materials

C2—C1—H1A	118.4	C20—C23—C24	120.2 (5)
C3—C2—C1	118.6 (5)	C22—C23—C24	120.8 (5)
C3—C2—H2A	120.7	O7—C24—O8	125.9 (5)
C1—C2—H2A	120.7	O7—C24—C23	116.8 (5)
C2—C3—C4	118.1 (5)	O8—C24—C23	117.2 (5)

Symmetry codes: (i) $x, -y+1/2, z+1/2$; (ii) $x+1, y, z$; (iii) $x-1, y, z$; (iv) $x, -y+1/2, z-1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9A \cdots O6	0.85	2.13	2.771 (7)	132
O9—H9B \cdots O2 ^{iv}	0.85	2.03	2.811 (6)	153
O10—H10A \cdots O6 ^v	0.85	2.12	2.954 (6)	165
O10—H10C \cdots O4	0.85	1.84	2.662 (6)	162
O14—H14B \cdots O12 ^{vi}	0.85	2.27	2.960 (9)	139
O14—H14C \cdots O13 ^{vii}	0.85	2.01	2.779 (10)	151

Symmetry codes: (iv) $x, -y+1/2, z-1/2$; (v) $x, y, z+1$; (vi) $x+1, -y+1/2, z-1/2$; (vii) $x+1, -y+1/2, z+1/2$.

Fig. 1

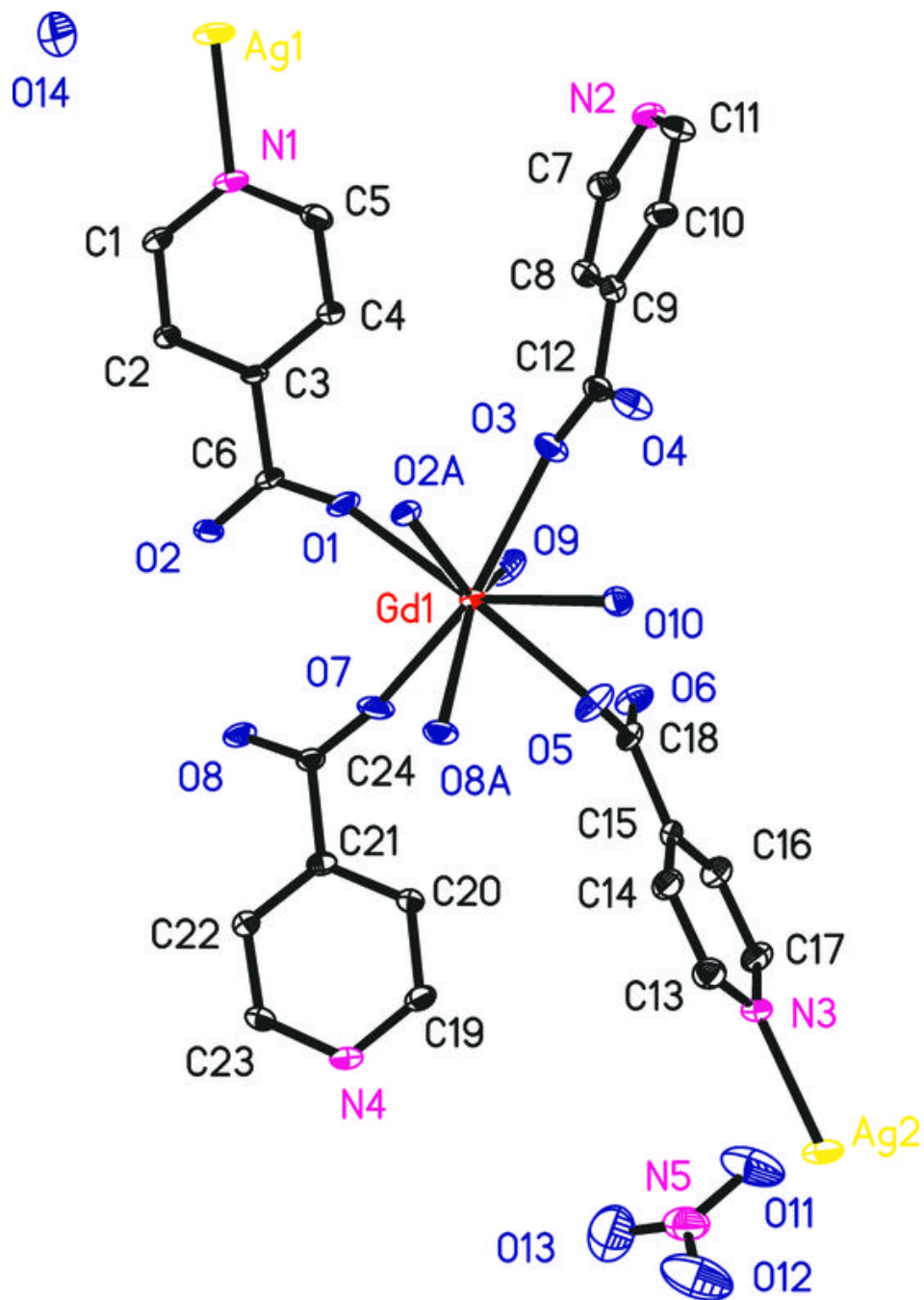


Fig. 2

