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

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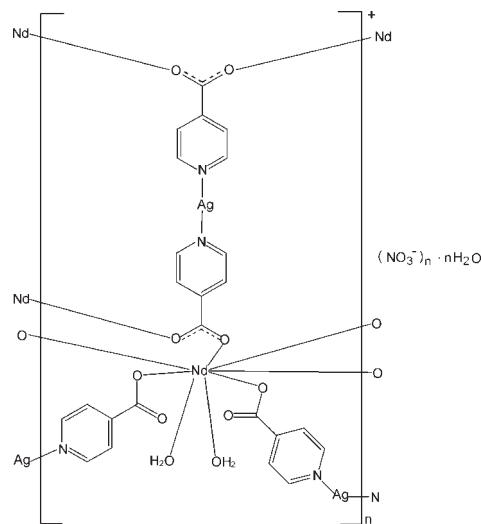
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.007$ Å; R factor = 0.032; wR factor = 0.067; data-to-parameter ratio = 11.8.

In the title complex, $\{[Ag_2Nd(C_6H_4NO_2)_4(H_2O)_2]NO_3 \cdot H_2O\}_n$, the Nd^{III} ion is coordinated by eight O atoms from six isonicotinate ligands and two water molecules in a distorted square antiprismatic geometry. Each Ag^I ion is coordinated by two N atoms from two different isonicotinate ligands. The crystal structure exhibits a two-dimensional heterometallic polymeric layer. $O-H \cdots O$ hydrogen bonds involving the coordinated and uncoordinated water molecules and intralayer $\pi-\pi$ interactions between the pyridine rings [centroid-centroid distances = 3.571 (2) and 3.569 (2) Å] are observed. Each layer interacts with two neighboring ones *via* $Ag \cdots O(H_2O)$ contacts and interlayer $\pi-\pi$ interactions [centroid-centroid distances = 3.479 (3) to 3.530 (3) Å], leading to a three-dimensional supramolecular network.

Related literature

For general background to metal organic frameworks, see: Batten & Robson (1998); Min & Suh (2000). For $4d-4f$ heterometallic coordination frameworks, see: Cai *et al.* (2009).



Experimental

Crystal data

$[Ag_2Nd(C_6H_4NO_2)_4(H_2O)_2]NO_3 \cdot H_2O$
 $M_r = 964.45$
 Monoclinic, $P2_1/c$
 $a = 16.9648$ (19) Å
 $b = 24.793$ (3) Å
 $c = 6.7770$ (8) Å

$\beta = 95.849$ (1)°
 $V = 2835.7$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.25$ mm⁻¹
 $T = 296$ K
 $0.23 \times 0.20 \times 0.18$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.522$, $T_{max} = 0.592$

14629 measured reflections
 5092 independent reflections
 4024 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.067$
 $S = 1.01$
 5092 reflections
 433 parameters
 9 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.57$ e Å⁻³
 $\Delta\rho_{min} = -0.91$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|-----------------------|-----------|--------------------------------------|-----------|
| Nd1—O1 ⁱ | 2.381 (3) | Ag1—N1 | 2.155 (4) |
| Nd1—O2 | 2.502 (3) | Ag1—N2 | 2.155 (4) |
| Nd1—O3 ⁱⁱ | 2.426 (3) | Ag1 ⁱ ···O1W ⁱ | 2.888 (4) |
| Nd1—O4 ⁱⁱⁱ | 2.432 (3) | Ag1 ⁱ ···O10 | 2.771 (5) |
| Nd1—O5 | 2.416 (3) | Ag2—N3 ^{iv} | 2.200 (4) |
| Nd1—O7 | 2.406 (3) | Ag2—N4 | 2.184 (4) |
| Nd1—O2W | 2.492 (4) | Ag2 ⁱ ···O3W ^v | 2.741 (4) |
| Nd1—O3W | 2.564 (3) | Ag2 ⁱ ···O9 ^{vi} | 2.950 (5) |

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x - 1, y, z$; (iii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $x + 1, y, z$; (v) $-x + 1, -y + 1, -z$; (vi) $x, y, z - 1$.

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|--|-------------|---------------|-----------------------|-------------------------|
| O1 <i>W</i> —H1 <i>A</i> ···O10 ^{vii} | 0.85 (3) | 1.96 (2) | 2.796 (8) | 167 (7) |
| O1 <i>W</i> —H1 <i>B</i> ···O9 | 0.85 (4) | 2.12 (5) | 2.945 (8) | 164 (6) |
| O2 <i>W</i> —H2 <i>A</i> ···O6 | 0.85 (4) | 2.06 (3) | 2.799 (5) | 145 (5) |
| O2 <i>W</i> —H2 <i>B</i> ···O4 ⁱⁱⁱ | 0.84 (4) | 2.21 (4) | 3.033 (5) | 166 (5) |
| O3 <i>W</i> —H3 <i>A</i> ···O8 | 0.85 (3) | 1.87 (2) | 2.653 (5) | 153 (4) |
| O3 <i>W</i> —H3 <i>B</i> ···O6 ^{vii} | 0.85 (3) | 2.11 (3) | 2.951 (5) | 174 (5) |

Symmetry codes: (iii) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (vii) $x, y, z + 1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2237).

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supplementary materials

Acta Cryst. (2009). E65, m1434-m1435 [doi:10.1107/S1600536809042342]

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

Q.-G. Zhan, J.-X. Huang and R.-H. Zeng

Comment

In recent years, assembly processes directed by metal–ligand ligation have been extensively utilized to construct metal organic frameworks with novel topologies and potentially interesting functions in magnetism, photoluminescence, sorption, catalysis (Batten & Robson, 1998; Min & Suh, 2000). However, metal-directed assembly of 4d–4f heterometallic coordination frameworks with fascinating topological networks and potential applications have been few reported (Cai *et al.*, 2009). We utilized isonicotinate as multifunctional ligand with O and N atoms on opposite sites. Here, a new metal-directed assembly of 4d–4f coordination polymer, which was synthesized under hydrothermal conditions, is reported.

The asymmetric unit of the title complex contains one Nd^{III} ion, two Ag^I ions, four crystallographically unique isonicotinate ligands, one nitrate anion, two coordinated water molecules and one uncoordinated water molecule (Fig. 1). The Nd^{III} ion is in a distorted square antiprismatic geometry, defined by eight O atoms from six isonicotinate ligands and two water molecules. The Nd–O bond distances and O–Nd–O bond angles range from 2.381 (3) to 2.564 (3) Å and 71.79 (11) to 145.83 (12)°, respectively (Table 1). The Ag^I ion exhibits an approximately linear or bow-like configuration, being coordinated by two N atoms from two different isonicotinate ligands. The isonicotinate ligands link Nd and Ag metal centers, forming a layer in the (010) plane, which are stabilized by O–H···O hydrogen bonds involving the coordinated and uncoordinated water molecules (Table 2) and intralayer π – π stacking interactions between the pyridine rings, with a centroid–centroid distances of 3.571 (2) and 3.569 (2) Å. These layers are further connected by Ag···O(H₂O) contacts and interlayer π – π stacking interactions [centroid–centroid distances = 3.479 (3) to 3.530 (3) Å] between the pyridine rings of two adjacent layers, assembling a three-dimensional supramolecular architecture (Fig. 2).

Experimental

A mixture of Nd₂O₃ (0.183 g, 0.5 mmol), AgNO₃ (0.170 g, 1 mmol), isonicotinic acid (0.135 g, 1.5 mmol), water (10 ml) in the presence of HNO₃ (0.024 g, 0.385 mmol) was stirred vigorously for 20 min and then sealed in a Teflon-lined stainless-steel autoclave (20 ml capacity). The autoclave was heated and maintained at 443 K for 3 d, and then cooled to room temperature at 5 K h⁻¹. The colorless block crystals of the title compound were obtained.

Refinement

Water H atoms were tentatively located in difference Fourier maps and refined with distance restraints of O–H = 0.85 (1) Å and H···H = 1.35 (1) Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. H atoms attached to C atoms were placed at calculated positions and treated as riding on their parent atoms, with C–H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

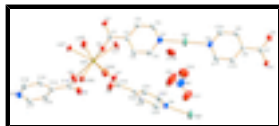


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $x, 3/2-y, -1/2+z$; (ii) $-1+x, y, z$; (iii) $-1+x, 3/2-y, -1/2+z$.]

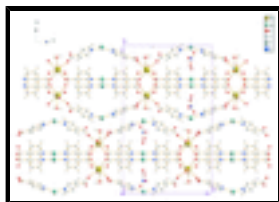


Fig. 2. A view of the layered networks in the title compound.

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

Crystal data

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

$M_r = 964.45$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 16.9648\ (19)\ \text{\AA}$

$b = 24.793\ (3)\ \text{\AA}$

$c = 6.7770\ (8)\ \text{\AA}$

$\beta = 95.849\ (1)^\circ$

$V = 2835.7\ (6)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1868$

$D_x = 2.259\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3327 reflections

$\theta = 2.4\text{--}25.9^\circ$

$\mu = 3.25\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colorless

$0.23 \times 0.20 \times 0.18\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.522, T_{\max} = 0.592$

14629 measured reflections

5092 independent reflections

4024 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 25.2^\circ$

$\theta_{\min} = 1.6^\circ$

$h = -17 \rightarrow 20$

$k = -29 \rightarrow 29$

$l = -8 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.032$$

$$wR(F^2) = 0.067$$

$$S = 1.01$$

5092 reflections

433 parameters

9 restraints

Primary atom site location: structure-invariant direct methods

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|--------------|----------------------------------|
| Nd1 | 0.269306 (14) | 0.662399 (10) | 0.11749 (4) | 0.01959 (8) |
| Ag1 | 0.77067 (2) | 0.728604 (19) | 0.49039 (7) | 0.04705 (14) |
| Ag2 | 0.76495 (3) | 0.510435 (19) | -0.09689 (7) | 0.05046 (14) |
| O7 | 0.38451 (19) | 0.60656 (13) | 0.1017 (5) | 0.0338 (9) |
| O2 | 0.35364 (18) | 0.68568 (12) | 0.4305 (5) | 0.0289 (8) |
| O5 | 0.1656 (2) | 0.60334 (15) | -0.0262 (5) | 0.0456 (10) |
| C3 | 0.5223 (3) | 0.77468 (17) | 0.5011 (7) | 0.0242 (11) |
| H3 | 0.4958 | 0.8074 | 0.5054 | 0.029* |
| C1 | 0.3912 (3) | 0.72711 (19) | 0.4857 (7) | 0.0229 (11) |
| C2 | 0.4801 (3) | 0.72666 (17) | 0.4924 (6) | 0.0197 (10) |
| N2 | 0.8974 (2) | 0.72776 (16) | 0.4834 (6) | 0.0341 (10) |
| N1 | 0.6441 (2) | 0.72777 (16) | 0.4996 (6) | 0.0327 (10) |
| C6 | 0.5224 (3) | 0.67929 (18) | 0.4894 (7) | 0.0246 (11) |
| H6 | 0.4963 | 0.6462 | 0.4835 | 0.030* |
| C10 | 0.9388 (3) | 0.77404 (19) | 0.4767 (7) | 0.0308 (12) |
| H10 | 0.9122 | 0.8067 | 0.4841 | 0.037* |
| C9 | 1.0183 (3) | 0.77478 (18) | 0.4595 (7) | 0.0275 (12) |
| H9 | 1.0448 | 0.8076 | 0.4563 | 0.033* |
| C20 | 0.5069 (3) | 0.56100 (17) | 0.1414 (7) | 0.0258 (11) |
| C19 | 0.4289 (3) | 0.57592 (18) | 0.2152 (8) | 0.0259 (11) |
| O8 | 0.4127 (2) | 0.55701 (14) | 0.3746 (5) | 0.0371 (9) |
| N4 | 0.6493 (2) | 0.52916 (15) | 0.0010 (6) | 0.0316 (10) |
| C22 | 0.5972 (3) | 0.56051 (19) | -0.1083 (8) | 0.0337 (13) |
| H22 | 0.6094 | 0.5719 | -0.2323 | 0.040* |
| C23 | 0.6300 (3) | 0.5135 (2) | 0.1793 (8) | 0.0341 (13) |
| H23 | 0.6649 | 0.4912 | 0.2561 | 0.041* |
| C5 | 0.6032 (3) | 0.6814 (2) | 0.4951 (8) | 0.0334 (13) |
| H5 | 0.6312 | 0.6491 | 0.4959 | 0.040* |
| C8 | 1.0594 (3) | 0.72707 (18) | 0.4469 (6) | 0.0218 (11) |
| C12 | 1.0174 (3) | 0.67961 (19) | 0.4565 (7) | 0.0279 (12) |
| H12 | 1.0430 | 0.6466 | 0.4493 | 0.033* |
| C14 | 0.0414 (3) | 0.57066 (17) | -0.1642 (7) | 0.0242 (11) |
| C15 | 0.0089 (3) | 0.57587 (18) | 0.0129 (7) | 0.0308 (12) |
| H15 | 0.0389 | 0.5904 | 0.1228 | 0.037* |

supplementary materials

| | | | | |
|-----|--------------|--------------|-------------|-------------|
| C13 | 0.1266 (3) | 0.58696 (18) | -0.1849 (8) | 0.0277 (12) |
| C18 | -0.0059 (3) | 0.54950 (18) | -0.3233 (7) | 0.0291 (12) |
| H18 | 0.0130 | 0.5466 | -0.4469 | 0.035* |
| O6 | 0.1513 (2) | 0.58320 (14) | -0.3490 (5) | 0.0413 (10) |
| C24 | 0.5615 (3) | 0.52881 (19) | 0.2536 (8) | 0.0319 (12) |
| H24 | 0.5514 | 0.5176 | 0.3796 | 0.038* |
| C21 | 0.5267 (3) | 0.57646 (18) | -0.0447 (8) | 0.0299 (12) |
| H21 | 0.4919 | 0.5977 | -0.1263 | 0.036* |
| C16 | -0.0679 (3) | 0.55962 (19) | 0.0274 (8) | 0.0348 (13) |
| H16 | -0.0895 | 0.5645 | 0.1469 | 0.042* |
| C17 | -0.0811 (3) | 0.53274 (19) | -0.2966 (8) | 0.0341 (13) |
| H17 | -0.1117 | 0.5176 | -0.4043 | 0.041* |
| C4 | 0.6027 (3) | 0.77385 (19) | 0.5035 (7) | 0.0316 (12) |
| H4 | 0.6299 | 0.8064 | 0.5080 | 0.038* |
| C11 | 0.9378 (3) | 0.6811 (2) | 0.4766 (7) | 0.0323 (12) |
| H11 | 0.9107 | 0.6487 | 0.4859 | 0.039* |
| O1 | 0.3610 (2) | 0.76974 (13) | 0.5428 (5) | 0.0410 (10) |
| C7 | 1.1467 (3) | 0.72688 (19) | 0.4130 (7) | 0.0249 (11) |
| O3 | 1.17260 (19) | 0.68473 (13) | 0.3448 (5) | 0.0321 (8) |
| O4 | 1.1839 (2) | 0.76939 (14) | 0.4499 (6) | 0.0419 (10) |
| O3W | 0.2587 (2) | 0.57863 (14) | 0.3352 (5) | 0.0308 (8) |
| H3B | 0.2294 (19) | 0.578 (2) | 0.429 (4) | 0.046* |
| H3A | 0.3050 (10) | 0.571 (2) | 0.387 (6) | 0.046* |
| O2W | 0.2838 (2) | 0.64789 (16) | -0.2408 (6) | 0.0436 (10) |
| H2A | 0.257 (2) | 0.6245 (15) | -0.310 (7) | 0.065* |
| H2B | 0.251 (2) | 0.6703 (17) | -0.205 (8) | 0.065* |
| N5 | 0.7673 (3) | 0.5865 (2) | 0.3990 (10) | 0.0570 (15) |
| O11 | 0.7991 (3) | 0.5483 (2) | 0.3274 (7) | 0.0789 (15) |
| O9 | 0.7419 (3) | 0.5845 (2) | 0.5614 (7) | 0.094 (2) |
| O10 | 0.7590 (3) | 0.6295 (2) | 0.3006 (8) | 0.0892 (17) |
| N3 | -0.1129 (2) | 0.53684 (16) | -0.1258 (7) | 0.0326 (10) |
| O1W | 0.7704 (3) | 0.65730 (16) | 0.9046 (8) | 0.0724 (14) |
| H1A | 0.769 (5) | 0.644 (2) | 1.019 (4) | 0.109* |
| H1B | 0.763 (5) | 0.6313 (17) | 0.824 (7) | 0.109* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| Nd1 | 0.01421 (13) | 0.02069 (13) | 0.02424 (15) | -0.00081 (11) | 0.00374 (10) | 0.00027 (11) |
| Ag1 | 0.0152 (2) | 0.0632 (3) | 0.0635 (3) | 0.0000 (2) | 0.00745 (19) | -0.0005 (2) |
| Ag2 | 0.0231 (2) | 0.0605 (3) | 0.0700 (4) | 0.0006 (2) | 0.0150 (2) | 0.0039 (2) |
| O7 | 0.028 (2) | 0.037 (2) | 0.037 (2) | 0.0145 (16) | 0.0071 (16) | 0.0030 (16) |
| O2 | 0.0205 (18) | 0.0311 (18) | 0.035 (2) | -0.0041 (15) | 0.0004 (15) | -0.0064 (15) |
| O5 | 0.041 (2) | 0.062 (2) | 0.033 (2) | -0.028 (2) | 0.0013 (18) | -0.0006 (19) |
| C3 | 0.024 (3) | 0.019 (2) | 0.030 (3) | 0.001 (2) | 0.002 (2) | -0.001 (2) |
| C1 | 0.017 (3) | 0.032 (3) | 0.021 (3) | 0.003 (2) | 0.006 (2) | 0.003 (2) |
| C2 | 0.017 (2) | 0.027 (2) | 0.015 (3) | 0.002 (2) | -0.0024 (19) | -0.0007 (19) |
| N2 | 0.021 (2) | 0.040 (3) | 0.042 (3) | 0.005 (2) | 0.0059 (19) | 0.000 (2) |

| | | | | | | |
|-----|-------------|-----------|-----------|--------------|-------------|--------------|
| N1 | 0.022 (2) | 0.036 (3) | 0.040 (3) | 0.003 (2) | 0.0046 (19) | 0.002 (2) |
| C6 | 0.020 (3) | 0.025 (3) | 0.029 (3) | -0.003 (2) | 0.004 (2) | -0.003 (2) |
| C10 | 0.025 (3) | 0.028 (3) | 0.039 (3) | 0.006 (2) | 0.000 (2) | -0.001 (2) |
| C9 | 0.027 (3) | 0.023 (3) | 0.033 (3) | -0.002 (2) | 0.003 (2) | -0.002 (2) |
| C20 | 0.025 (3) | 0.018 (2) | 0.034 (3) | 0.000 (2) | 0.001 (2) | -0.002 (2) |
| C19 | 0.024 (3) | 0.020 (2) | 0.034 (3) | 0.003 (2) | 0.003 (2) | -0.005 (2) |
| O8 | 0.035 (2) | 0.046 (2) | 0.032 (2) | 0.0109 (18) | 0.0120 (17) | 0.0124 (18) |
| N4 | 0.024 (2) | 0.028 (2) | 0.044 (3) | -0.0003 (19) | 0.007 (2) | -0.004 (2) |
| C22 | 0.031 (3) | 0.030 (3) | 0.042 (4) | 0.003 (2) | 0.010 (2) | 0.005 (2) |
| C23 | 0.023 (3) | 0.034 (3) | 0.045 (4) | 0.005 (2) | -0.001 (2) | 0.002 (3) |
| C5 | 0.024 (3) | 0.031 (3) | 0.044 (4) | 0.012 (2) | 0.003 (2) | 0.000 (2) |
| C8 | 0.019 (3) | 0.029 (3) | 0.017 (3) | -0.001 (2) | 0.0016 (19) | -0.003 (2) |
| C12 | 0.022 (3) | 0.025 (3) | 0.037 (3) | 0.002 (2) | 0.003 (2) | -0.001 (2) |
| C14 | 0.024 (3) | 0.019 (2) | 0.029 (3) | -0.004 (2) | 0.000 (2) | 0.000 (2) |
| C15 | 0.035 (3) | 0.028 (3) | 0.029 (3) | -0.005 (2) | 0.003 (2) | -0.006 (2) |
| C13 | 0.028 (3) | 0.023 (3) | 0.031 (3) | -0.008 (2) | 0.000 (2) | -0.002 (2) |
| C18 | 0.029 (3) | 0.030 (3) | 0.029 (3) | -0.003 (2) | 0.006 (2) | -0.002 (2) |
| O6 | 0.035 (2) | 0.057 (3) | 0.033 (2) | -0.0149 (19) | 0.0110 (17) | -0.0100 (18) |
| C24 | 0.029 (3) | 0.033 (3) | 0.034 (3) | -0.001 (2) | 0.001 (2) | 0.001 (2) |
| C21 | 0.032 (3) | 0.025 (3) | 0.033 (3) | 0.002 (2) | 0.003 (2) | 0.002 (2) |
| C16 | 0.032 (3) | 0.038 (3) | 0.035 (3) | 0.006 (3) | 0.012 (2) | -0.001 (2) |
| C17 | 0.030 (3) | 0.035 (3) | 0.036 (3) | -0.009 (2) | -0.005 (3) | 0.003 (2) |
| C4 | 0.027 (3) | 0.028 (3) | 0.040 (3) | -0.007 (2) | 0.002 (2) | 0.000 (2) |
| C11 | 0.026 (3) | 0.032 (3) | 0.040 (3) | -0.006 (2) | 0.004 (2) | 0.004 (2) |
| O1 | 0.022 (2) | 0.034 (2) | 0.067 (3) | 0.0073 (16) | 0.0020 (17) | -0.0206 (19) |
| C7 | 0.020 (3) | 0.032 (3) | 0.022 (3) | 0.001 (2) | 0.000 (2) | 0.003 (2) |
| O3 | 0.0211 (19) | 0.037 (2) | 0.040 (2) | 0.0038 (16) | 0.0118 (15) | -0.0043 (17) |
| O4 | 0.022 (2) | 0.043 (2) | 0.061 (3) | -0.0105 (17) | 0.0040 (17) | -0.0183 (19) |
| O3W | 0.026 (2) | 0.034 (2) | 0.033 (2) | 0.0006 (17) | 0.0093 (15) | 0.0029 (16) |
| O2W | 0.043 (2) | 0.058 (3) | 0.030 (2) | -0.010 (2) | 0.0055 (18) | -0.0101 (18) |
| N5 | 0.033 (3) | 0.068 (4) | 0.066 (5) | 0.011 (3) | -0.011 (3) | -0.016 (4) |
| O11 | 0.052 (3) | 0.109 (4) | 0.073 (4) | 0.026 (3) | -0.003 (2) | -0.027 (3) |
| O9 | 0.082 (4) | 0.167 (6) | 0.035 (3) | 0.062 (4) | 0.013 (3) | 0.004 (3) |
| O10 | 0.096 (5) | 0.084 (4) | 0.090 (4) | -0.013 (3) | 0.021 (3) | -0.014 (3) |
| N3 | 0.027 (2) | 0.030 (2) | 0.041 (3) | -0.0025 (19) | 0.006 (2) | 0.002 (2) |
| O1W | 0.071 (3) | 0.041 (3) | 0.106 (4) | -0.009 (3) | 0.010 (3) | 0.001 (2) |

Geometric parameters (Å, °)

| | | | |
|-----------------------|-----------|---------|-----------|
| Nd1—O1 ⁱ | 2.381 (3) | N4—C23 | 1.341 (6) |
| Nd1—O2 | 2.502 (3) | N4—C22 | 1.342 (6) |
| Nd1—O3 ⁱⁱ | 2.426 (3) | C22—C21 | 1.370 (7) |
| Nd1—O4 ⁱⁱⁱ | 2.432 (3) | C22—H22 | 0.9300 |
| Nd1—O5 | 2.416 (3) | C23—C24 | 1.366 (7) |
| Nd1—O7 | 2.406 (3) | C23—H23 | 0.9300 |
| Nd1—O2W | 2.492 (4) | C5—H5 | 0.9300 |
| Nd1—O3W | 2.564 (3) | C8—C12 | 1.381 (6) |
| Ag1—N1 | 2.155 (4) | C8—C7 | 1.521 (6) |

supplementary materials

| | | | |
|---|-------------|-------------|-----------|
| Ag1—N2 | 2.155 (4) | C12—C11 | 1.372 (6) |
| Ag1—O1W ⁱ | 2.888 (4) | C12—H12 | 0.9300 |
| Ag1—O10 | 2.771 (5) | C14—C15 | 1.377 (7) |
| Ag2—N3 ^{iv} | 2.200 (4) | C14—C18 | 1.380 (6) |
| Ag2—N4 | 2.184 (4) | C14—C13 | 1.521 (7) |
| Ag2—O3W ^v | 2.741 (4) | C15—C16 | 1.378 (7) |
| Ag2—O9 ^{vi} | 2.950 (5) | C15—H15 | 0.9300 |
| O7—C19 | 1.272 (5) | C13—O6 | 1.232 (6) |
| O2—C1 | 1.246 (5) | C18—C17 | 1.372 (7) |
| O5—C13 | 1.271 (5) | C18—H18 | 0.9300 |
| C3—C4 | 1.361 (6) | C24—H24 | 0.9300 |
| C3—C2 | 1.387 (6) | C21—H21 | 0.9300 |
| C3—H3 | 0.9300 | C16—N3 | 1.348 (6) |
| C1—O1 | 1.253 (5) | C16—H16 | 0.9300 |
| C1—C2 | 1.505 (6) | C17—N3 | 1.330 (7) |
| C2—C6 | 1.378 (6) | C17—H17 | 0.9300 |
| N2—C11 | 1.348 (6) | C4—H4 | 0.9300 |
| N2—C10 | 1.349 (6) | C11—H11 | 0.9300 |
| N1—C5 | 1.342 (6) | C7—O4 | 1.241 (5) |
| N1—C4 | 1.343 (6) | C7—O3 | 1.241 (5) |
| C6—C5 | 1.369 (6) | O3W—H3B | 0.85 (3) |
| C6—H6 | 0.9300 | O3W—H3A | 0.85 (3) |
| C10—C9 | 1.365 (7) | O2W—H2A | 0.85 (4) |
| C10—H10 | 0.9300 | O2W—H2B | 0.84 (4) |
| C9—C8 | 1.381 (6) | N5—O11 | 1.215 (6) |
| C9—H9 | 0.9300 | N5—O9 | 1.223 (7) |
| C20—C24 | 1.390 (6) | N5—O10 | 1.260 (7) |
| C20—C21 | 1.392 (7) | O1W—H1A | 0.85 (3) |
| C20—C19 | 1.507 (7) | O1W—H1B | 0.85 (4) |
| C19—O8 | 1.234 (6) | | |
| O1 ⁱ —Nd1—O7 | 81.12 (12) | O8—C19—C20 | 118.6 (4) |
| O1 ⁱ —Nd1—O5 | 143.84 (12) | O7—C19—C20 | 115.6 (5) |
| O7—Nd1—O5 | 101.23 (13) | C23—N4—C22 | 117.1 (5) |
| O1 ⁱ —Nd1—O3 ⁱⁱ | 118.20 (12) | C23—N4—Ag2 | 121.5 (3) |
| O7—Nd1—O3 ⁱⁱ | 139.85 (11) | C22—N4—Ag2 | 121.2 (4) |
| O5—Nd1—O3 ⁱⁱ | 83.25 (12) | N4—C22—C21 | 122.8 (5) |
| O1 ⁱ —Nd1—O4 ⁱⁱⁱ | 77.33 (11) | N4—C22—H22 | 118.6 |
| O7—Nd1—O4 ⁱⁱⁱ | 145.83 (12) | C21—C22—H22 | 118.6 |
| O5—Nd1—O4 ⁱⁱⁱ | 81.87 (13) | N4—C23—C24 | 123.2 (5) |
| O3 ⁱⁱ —Nd1—O4 ⁱⁱⁱ | 74.25 (12) | N4—C23—H23 | 118.4 |
| O1 ⁱ —Nd1—O2W | 76.30 (13) | C24—C23—H23 | 118.4 |
| O7—Nd1—O2W | 73.28 (12) | N1—C5—C6 | 123.1 (4) |
| O5—Nd1—O2W | 70.13 (12) | N1—C5—H5 | 118.4 |
| O3 ⁱⁱ —Nd1—O2W | 142.39 (11) | C6—C5—H5 | 118.4 |
| O4 ⁱⁱⁱ —Nd1—O2W | 76.03 (13) | C9—C8—C12 | 117.4 (4) |

| | | | |
|----------------------------|-------------|---------------------------|------------|
| O1 ⁱ —Nd1—O2 | 71.79 (11) | C9—C8—C7 | 121.2 (4) |
| O7—Nd1—O2 | 76.91 (11) | C12—C8—C7 | 121.3 (4) |
| O5—Nd1—O2 | 144.23 (11) | C11—C12—C8 | 120.0 (4) |
| O3 ⁱⁱ —Nd1—O2 | 76.96 (11) | C11—C12—H12 | 120.0 |
| O4 ⁱⁱⁱ —Nd1—O2 | 119.84 (11) | C8—C12—H12 | 120.0 |
| O2W—Nd1—O2 | 138.99 (12) | C15—C14—C18 | 117.7 (5) |
| O1 ⁱ —Nd1—O3W | 141.28 (11) | C15—C14—C13 | 121.5 (4) |
| O7—Nd1—O3W | 70.39 (11) | C18—C14—C13 | 120.7 (5) |
| O5—Nd1—O3W | 69.53 (11) | C14—C15—C16 | 120.0 (5) |
| O3 ⁱⁱ —Nd1—O3W | 74.22 (11) | C14—C15—H15 | 120.0 |
| O4 ⁱⁱⁱ —Nd1—O3W | 139.34 (12) | C16—C15—H15 | 120.0 |
| O2W—Nd1—O3W | 117.61 (12) | O6—C13—O5 | 126.3 (5) |
| O2—Nd1—O3W | 76.51 (10) | O6—C13—C14 | 118.5 (4) |
| O1 ⁱ —Nd1—H2B | 75.9 (13) | O5—C13—C14 | 115.2 (5) |
| O7—Nd1—H2B | 92.3 (10) | C17—C18—C14 | 119.1 (5) |
| O5—Nd1—H2B | 68.0 (13) | C17—C18—H18 | 120.4 |
| O3 ⁱⁱ —Nd1—H2B | 125.2 (6) | C14—C18—H18 | 120.4 |
| O4 ⁱⁱⁱ —Nd1—H2B | 56.7 (5) | C23—C24—C20 | 120.2 (5) |
| O2W—Nd1—H2B | 19.3 (10) | C23—C24—H24 | 119.9 |
| O2—Nd1—H2B | 147.1 (13) | C20—C24—H24 | 119.9 |
| O3W—Nd1—H2B | 129.5 (12) | C22—C21—C20 | 120.3 (5) |
| N2—Ag1—N1 | 178.82 (16) | C22—C21—H21 | 119.9 |
| N4—Ag2—N3 ^{iv} | 147.86 (15) | C20—C21—H21 | 119.9 |
| C19—O7—Nd1 | 138.6 (3) | N3—C16—C15 | 122.2 (5) |
| C1—O2—Nd1 | 132.5 (3) | N3—C16—H16 | 118.9 |
| C13—O5—Nd1 | 146.1 (3) | C15—C16—H16 | 118.9 |
| C4—C3—C2 | 119.9 (4) | N3—C17—C18 | 123.8 (5) |
| C4—C3—H3 | 120.0 | N3—C17—H17 | 118.1 |
| C2—C3—H3 | 120.0 | C18—C17—H17 | 118.1 |
| O2—C1—O1 | 125.1 (4) | N1—C4—C3 | 122.5 (4) |
| O2—C1—C2 | 118.9 (4) | N1—C4—H4 | 118.7 |
| O1—C1—C2 | 115.9 (4) | C3—C4—H4 | 118.7 |
| C6—C2—C3 | 117.7 (4) | N2—C11—C12 | 122.4 (5) |
| C6—C2—C1 | 121.9 (4) | N2—C11—H11 | 118.8 |
| C3—C2—C1 | 120.4 (4) | C12—C11—H11 | 118.8 |
| C11—N2—C10 | 117.4 (4) | C1—O1—Nd1 ^{vii} | 163.4 (3) |
| C11—N2—Ag1 | 121.4 (3) | O4—C7—O3 | 126.7 (5) |
| C10—N2—Ag1 | 121.1 (3) | O4—C7—C8 | 116.7 (4) |
| C5—N1—C4 | 117.4 (4) | O3—C7—C8 | 116.5 (4) |
| C5—N1—Ag1 | 121.4 (3) | C7—O3—Nd1 ^{iv} | 135.8 (3) |
| C4—N1—Ag1 | 121.2 (3) | C7—O4—Nd1 ^{viii} | 162.1 (3) |
| C5—C6—C2 | 119.3 (4) | Nd1—O3W—H3B | 122 (3) |
| C5—C6—H6 | 120.4 | Nd1—O3W—H3A | 108 (3) |
| C2—C6—H6 | 120.4 | H3B—O3W—H3A | 105.7 (17) |
| N2—C10—C9 | 122.5 (4) | Nd1—O2W—H2A | 122 (4) |
| N2—C10—H10 | 118.8 | Nd1—O2W—H2B | 59 (4) |

supplementary materials

| | | | |
|-------------|-----------|--------------------------|-----------|
| C9—C10—H10 | 118.8 | H2A—O2W—H2B | 106 (4) |
| C10—C9—C8 | 120.3 (4) | O11—N5—O9 | 122.7 (7) |
| C10—C9—H9 | 119.9 | O11—N5—O10 | 118.7 (7) |
| C8—C9—H9 | 119.9 | O9—N5—O10 | 118.6 (6) |
| C24—C20—C21 | 116.4 (5) | C17—N3—C16 | 117.0 (5) |
| C24—C20—C19 | 121.2 (5) | C17—N3—Ag ²ⁱⁱ | 121.6 (3) |
| C21—C20—C19 | 122.3 (4) | C16—N3—Ag ²ⁱⁱ | 121.4 (4) |
| O8—C19—O7 | 125.8 (5) | H1A—O1W—H1B | 106 (5) |

Symmetry codes: (i) $x, -y+3/2, z-1/2$; (ii) $x-1, y, z$; (iii) $x-1, -y+3/2, z-1/2$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y, z-1$; (vii) $x, -y+3/2, z+1/2$; (viii) $x+1, -y+3/2, z+1/2$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O1W—H1A \cdots O10 ^{ix} | 0.85 (3) | 1.96 (2) | 2.796 (8) | 167 (7) |
| O1W—H1B \cdots O9 | 0.85 (4) | 2.12 (5) | 2.945 (8) | 164 (6) |
| O2W—H2A \cdots O6 | 0.85 (4) | 2.06 (3) | 2.799 (5) | 145 (5) |
| O2W—H2B \cdots O4 ⁱⁱⁱ | 0.84 (4) | 2.21 (4) | 3.033 (5) | 166 (5) |
| O3W—H3A \cdots O8 | 0.85 (3) | 1.87 (2) | 2.653 (5) | 153 (4) |
| O3W—H3B \cdots O6 ^{ix} | 0.85 (3) | 2.11 (3) | 2.951 (5) | 174 (5) |

Symmetry codes: (ix) $x, y, z+1$; (iii) $x-1, -y+3/2, z-1/2$.

Fig. 1

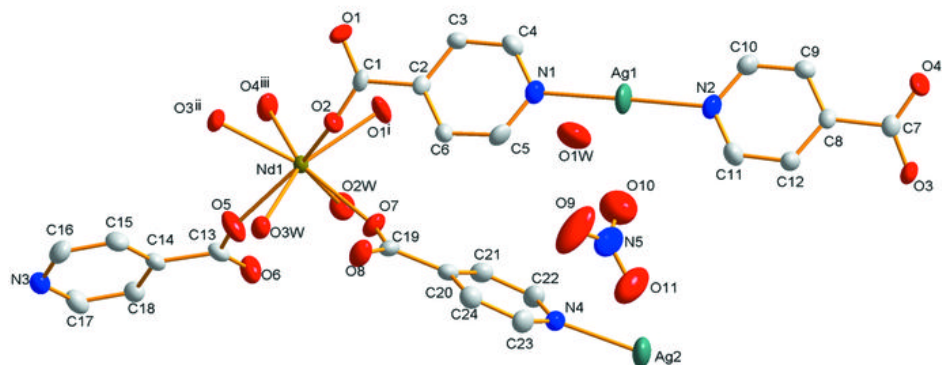


Fig. 2

