

catena-Poly[[[tetraaquaneodymium(III)]-di- μ -isonicotinato] chloride]

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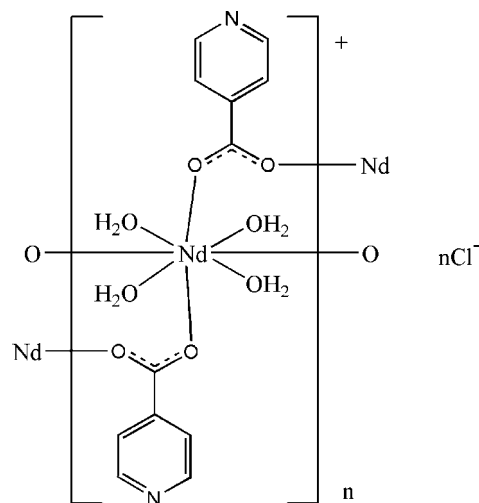
Received 24 October 2011; accepted 25 December 2011

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.012$ Å; R factor = 0.063; wR factor = 0.190; data-to-parameter ratio = 16.9.

In the title complex, $\{[\text{Nd}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}\}_n$, the Nd^{III} cation is located on a twofold rotation axis and coordinated by four isonicotinate anions and four water molecules in a distorted square-antiprismatic geometry. The carboxylate groups of the isonicotinate anions bridge the Nd^{III} cations, forming polymeric chains running along the c axis. The Cl^- anion is located on a twofold rotation axis and is linked to the polymeric chains *via* $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonding. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds are also present in the crystal structure.

Related literature

For some crystal structures of related lanthanide-isonicotinic acid complexes, see: Chen & Fukuzumi (2009); Ma *et al.* (1999); Han *et al.* (2010); Kay *et al.* (1972); Duan *et al.* (2010); Jia *et al.* (2008); Cheng *et al.* (2007); Liu *et al.* (2006); Chai *et al.* (2010).



Experimental

Crystal data

$[\text{Nd}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}$
 $M_r = 495.96$
 Orthorhombic, *Pbcn*
 $a = 8.9223$ (18) Å
 $b = 19.684$ (4) Å
 $c = 10.151$ (2) Å

$V = 1782.9$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.10$ mm⁻¹
 $T = 173$ K
 $0.18 \times 0.17 \times 0.15$ mm

Data collection

Rigaku Saturn724+ CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
 $T_{\text{min}} = 0.49$, $T_{\text{max}} = 0.63$

9085 measured reflections
 2056 independent reflections
 1764 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.190$
 $S = 1.33$
 2056 reflections
 122 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 1.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.06$ e Å⁻³

Table 1

Selected bond lengths (Å).

Nd1—O1 ⁱ	2.425 (6)	Nd1—O3	2.544 (6)
Nd1—O2	2.385 (5)	Nd1—O4	2.480 (6)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H6}\cdots\text{Cl2}^{\text{ii}}$	0.95 (6)	2.29 (6)	3.211 (7)	163 (6)
$\text{O3}-\text{H7}\cdots\text{N1}^{\text{iii}}$	0.97 (4)	1.72 (4)	2.685 (10)	174 (9)
$\text{O4}-\text{H8}\cdots\text{Cl2}^{\text{i}}$	0.96 (4)	2.15 (5)	3.041 (6)	155 (6)
$\text{O4}-\text{H9}\cdots\text{O3}^{\text{iv}}$	0.95 (2)	1.93 (3)	2.841 (8)	160 (8)

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The work was supported financially by the National Natural Science Foundation of China (grant Nos. 50973003 and 21001009), the National High-Tech R&D Program of China (863 Program) and of MOST (No. 2010 A A03A406). Special thanks are due to Dr X. Hao, L. Wang and T.-L. Liang for their assistance in the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5361).

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supplementary materials

Acta Cryst. (2012). E68, m170-m171 [doi:10.1107/S1600536811055619]

***catena*-Poly[[[tetraaquaneodymium(III)]-di- μ -isonicotinato] chloride]**

J.-H. Xue, X.-H. Hua, C.-P. Li, Y.-Z. Xu and J.-G. Wu

Comment

In the synthesis of prepare a lanthanide-isonicotinamide complex, the isonicotinamide changed to isonicotinic acid, resulting in the title complex.

Among aromatic carboxylic acids, isonicotinic acid has a conjugated structural motif and can be used to construct extended structures because it is unsymmetrical divergent ligand. Isonicotinic acid with metal ions may have various coordination modes (Chen *et al.*, 2009). The molecular structure of the title compound is shown in Fig. 1. Nd(III) is 8-coordinated to four oxygen atoms from four isonicotinic acid molecules and four water molecules. Each ligand is coordinated to two metal ions as bidentate ligands via two oxygen atoms of carboxyl group. One metal ion is connected to four ligands, thus an extensive network form. Nd(III) is located at the center of a slightly distorted square antiprism. Nd-O distances are from 2.385 to 2.544 Å. The mean Nd-O bond lengths, 2.4585 Å is larger than the mean Sm-O bond lengths (2.426 Å), which is consistent with the lanthanide contraction. The O—H \cdots Cl, O—H \cdots O and O—H \cdots N hydrogen bonds form a three-dimensional network.

For lanthanide-isonicotinate complexes, several structures have been observed. For example, Ln(III) ions can coordinate to six carboxylate oxygen atoms of bridging isonicotinate groups and to two water molecules (Ma *et al.*, 1999); or may coordinate to four carboxylate oxygen atoms of bridging isonicotinate groups, two carboxylate oxygen atoms of the chelating isonicotinate group, and two water molecules (Ma *et al.*, 1999; Han *et al.*, 2010; Kay *et al.*, 1972); or have structure similar to the NdCl₃-isonicotinic acid complex reported here (Chen *et al.*, 2009). Because Cl⁻ or NO₃⁻ does not coordinate to lanthanide ions, so Nd(III) chloride or nitrate ion-isonicotinic acid complexes have the similar coordination sphere (Duan *et al.*, 2010; Jia *et al.*, 2008). When oxalate ligands, chromate ions or other ligands are involved, the coordination situations are a little different (Cheng *et al.*, 2007; Liu *et al.*, 2006; Chai *et al.*, 2010) because oxalate ligand, chromate ions or other ligands also coordinate to metal ions.

Experimental

NdCl₃ (1 mmol) and isonicotinamide (3 mmol) were dissolved in 3ml water and 6 ml ethanol. The solution was put on a water bath, temperature was raised to 80°C. Small aliquots of EtOH were periodically added to the solution during the heating process to prolong the reaction time. The resulting mixtures were filtered and left for crystallization in room temperature, the suitable crystals for X-ray diffraction measurements were obtained in two weeks.

Refinement

The C-bound H-atoms were placed in calculated positions (C—H 0.930 Å) and were included in the refinement in the riding model approximation, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O-bound H atoms were located in a difference Fourier map and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Figures

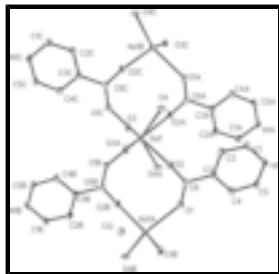


Fig. 1. The molecular structure of the title compound, displacement ellipsoids drawn at 30% probability level. The Hydrogen atoms have been omitted for clarity.

catena-Poly[[[tetraaquaneodymium(III)]-di- μ -isonicotinato] chloride]

Crystal data

[Nd(C₆H₄NO₂)₂(H₂O)₄]Cl

$M_r = 495.96$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 8.9223$ (18) Å

$b = 19.684$ (4) Å

$c = 10.151$ (2) Å

$V = 1782.9$ (6) Å³

$Z = 4$

$F(000) = 972$

$D_x = 1.848$ Mg m⁻³

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

Cell parameters from 4581 reflections

$\theta = 2.0$ – 27.5°

$\mu = 3.10$ mm⁻¹

$T = 173$ K

Block, blue

$0.18 \times 0.17 \times 0.15$ mm

Data collection

Rigaku Saturn724+ CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 28.5714 pixels mm⁻¹

ω scans at fixed $\chi = 45^\circ$

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

$T_{\min} = 0.49$, $T_{\max} = 0.63$

9085 measured reflections

2056 independent reflections

1764 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -11 \rightarrow 6$

$k = -25 \rightarrow 23$

$l = -12 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.063$

$wR(F^2) = 0.190$

$S = 1.33$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 8.5206P]$

2056 reflections
122 parameters
6 restraints

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

$$(\Delta/\sigma)_{\max} = 0.004$$

$$\Delta\rho_{\max} = 1.12 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.06 \text{ e } \text{\AA}^{-3}$$

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Nd1	0.5000	0.51140 (3)	0.2500	0.0166 (3)
Cl2	0.0000	0.55946 (19)	0.7500	0.0334 (8)
O4	0.6995 (7)	0.4591 (3)	0.1133 (5)	0.0263 (13)
H8	0.802 (4)	0.448 (5)	0.131 (7)	0.032*
H9	0.694 (9)	0.459 (5)	0.020 (2)	0.032*
O1	0.5450 (7)	0.3957 (3)	0.5981 (6)	0.0250 (13)
O2	0.6051 (7)	0.4301 (3)	0.3977 (5)	0.0225 (12)
O3	0.2471 (7)	0.5501 (3)	0.1620 (6)	0.0242 (13)
H6	0.163 (6)	0.526 (3)	0.195 (10)	0.029*
H7	0.211 (8)	0.5964 (15)	0.157 (9)	0.029*
C6	0.5817 (8)	0.3855 (4)	0.4827 (8)	0.0164 (15)
C3	0.6021 (10)	0.3129 (4)	0.4415 (8)	0.0217 (17)
C2	0.6744 (10)	0.2956 (4)	0.3247 (8)	0.0261 (19)
H2	0.7100	0.3295	0.2691	0.031*
C4	0.5480 (12)	0.2591 (4)	0.5189 (10)	0.030 (2)
H4	0.4971	0.2678	0.5970	0.035*
N1	0.6459 (9)	0.1776 (4)	0.3683 (7)	0.0286 (17)
C5	0.5713 (12)	0.1933 (4)	0.4775 (9)	0.030 (2)
H5	0.5329	0.1581	0.5285	0.036*
C1	0.6936 (11)	0.2279 (4)	0.2911 (10)	0.030 (2)
H1	0.7412	0.2173	0.2123	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nd1	0.0210 (4)	0.0139 (4)	0.0148 (4)	0.000	-0.0010 (2)	0.000
Cl2	0.0240 (15)	0.0327 (18)	0.043 (2)	0.000	-0.0092 (13)	0.000
O4	0.025 (3)	0.040 (4)	0.014 (3)	0.008 (3)	0.001 (2)	-0.002 (3)

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O1	0.034 (3)	0.019 (3)	0.022 (3)	-0.002 (3)	0.007 (3)	-0.005 (2)
O2	0.025 (3)	0.016 (3)	0.026 (3)	-0.001 (2)	-0.006 (3)	0.007 (2)
O3	0.022 (3)	0.015 (3)	0.035 (3)	0.005 (2)	0.005 (3)	0.005 (2)
C6	0.006 (4)	0.018 (4)	0.025 (4)	0.000 (3)	-0.008 (3)	0.000 (3)
C3	0.023 (4)	0.022 (4)	0.021 (4)	0.000 (3)	0.002 (3)	0.001 (3)
C2	0.026 (5)	0.026 (4)	0.027 (4)	-0.003 (4)	0.006 (4)	0.002 (4)
C4	0.037 (5)	0.020 (4)	0.032 (5)	-0.005 (4)	0.003 (4)	0.002 (4)
N1	0.040 (4)	0.021 (4)	0.025 (4)	0.002 (3)	-0.009 (3)	-0.009 (3)
C5	0.040 (6)	0.015 (4)	0.035 (5)	0.000 (4)	0.006 (4)	0.004 (3)
C1	0.035 (5)	0.023 (5)	0.031 (5)	0.005 (4)	-0.003 (4)	-0.008 (4)

Geometric parameters (\AA , $^\circ$)

Nd1—O1 ⁱ	2.425 (6)	O3—H6	0.95 (2)
Nd1—O1 ⁱⁱ	2.425 (6)	O3—H7	0.97 (2)
Nd1—O2 ⁱⁱⁱ	2.385 (5)	C6—C3	1.501 (10)
Nd1—O2	2.385 (5)	C3—C2	1.392 (11)
Nd1—O3 ⁱⁱⁱ	2.544 (6)	C3—C4	1.404 (12)
Nd1—O3	2.544 (6)	C2—C1	1.385 (12)
Nd1—O4 ⁱⁱⁱ	2.480 (6)	C2—H2	0.9300
Nd1—O4	2.480 (6)	C4—C5	1.377 (12)
O4—H8	0.96 (2)	C4—H4	0.9300
O4—H9	0.95 (2)	N1—C5	1.330 (12)
O1—C6	1.234 (9)	N1—C1	1.332 (12)
O1—Nd1 ⁱ	2.425 (6)	C5—H5	0.9300
O2—C6	1.248 (9)	C1—H1	0.9300
O2 ⁱⁱⁱ —Nd1—O2	95.7 (3)	Nd1—O4—H8	132 (5)
O2 ⁱⁱⁱ —Nd1—O1 ⁱ	147.2 (2)	Nd1—O4—H9	121 (5)
O2—Nd1—O1 ⁱ	99.8 (2)	H8—O4—H9	104 (3)
O2 ⁱⁱⁱ —Nd1—O1 ⁱⁱ	99.8 (2)	C6—O1—Nd1 ⁱ	140.4 (5)
O2—Nd1—O1 ⁱⁱ	147.2 (2)	C6—O2—Nd1	147.2 (5)
O1 ⁱ —Nd1—O1 ⁱⁱ	82.1 (3)	Nd1—O3—H6	115 (5)
O2 ⁱⁱⁱ —Nd1—O4 ⁱⁱⁱ	78.0 (2)	Nd1—O3—H7	127 (5)
O2—Nd1—O4 ⁱⁱⁱ	69.63 (19)	H6—O3—H7	103 (3)
O1 ⁱ —Nd1—O4 ⁱⁱⁱ	80.7 (2)	O1—C6—O2	125.9 (7)
O1 ⁱⁱ —Nd1—O4 ⁱⁱⁱ	141.9 (2)	O1—C6—C3	116.9 (7)
O2 ⁱⁱⁱ —Nd1—O4	69.63 (19)	O2—C6—C3	117.2 (7)
O2—Nd1—O4	78.0 (2)	C2—C3—C4	116.8 (8)
O1 ⁱ —Nd1—O4	141.9 (2)	C2—C3—C6	121.8 (7)
O1 ⁱⁱ —Nd1—O4	80.7 (2)	C4—C3—C6	121.4 (7)
O4 ⁱⁱⁱ —Nd1—O4	131.0 (3)	C1—C2—C3	120.2 (8)
O2 ⁱⁱⁱ —Nd1—O3 ⁱⁱⁱ	140.41 (19)	C1—C2—H2	119.9
O2—Nd1—O3 ⁱⁱⁱ	68.36 (19)	C3—C2—H2	119.9
O1 ⁱ —Nd1—O3 ⁱⁱⁱ	72.4 (2)	C5—C4—C3	119.1 (9)

O1 ⁱⁱ —Nd1—O3 ⁱⁱⁱ	81.4 (2)	C5—C4—H4	120.4
O4 ⁱⁱⁱ —Nd1—O3 ⁱⁱⁱ	124.35 (18)	C3—C4—H4	120.4
O4—Nd1—O3 ⁱⁱⁱ	71.60 (19)	C5—N1—C1	118.5 (7)
O2 ⁱⁱⁱ —Nd1—O3	68.36 (19)	N1—C5—C4	123.2 (8)
O2—Nd1—O3	140.41 (19)	N1—C5—H5	118.4
O1 ⁱ —Nd1—O3	81.4 (2)	C4—C5—H5	118.4
O1 ⁱⁱ —Nd1—O3	72.4 (2)	N1—C1—C2	122.0 (9)
O4 ⁱⁱⁱ —Nd1—O3	71.60 (19)	N1—C1—H1	119.0
O4—Nd1—O3	124.35 (18)	C2—C1—H1	119.0
O3 ⁱⁱⁱ —Nd1—O3	145.1 (3)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O3—H6 \cdots Cl2 ^{iv}	0.95 (6)	2.29 (6)	3.211 (7)	163 (6)
O3—H7 \cdots N1 ^v	0.97 (4)	1.72 (4)	2.685 (10)	174 (9)
O4—H8 \cdots Cl2 ⁱ	0.96 (4)	2.15 (5)	3.041 (6)	155 (6)
O4—H9 \cdots O3 ^{vi}	0.95 (2)	1.93 (3)	2.841 (8)	160 (8)

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

Fig. 1

