metal-organic compounds

catena-Poly[[[tetraaquasamarium(III)]-di-μ-isonicotinato-$\kappa^4 O$:O'] chloride]

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In the structure of the title compound, $\{[Sm(C_6H_4NO_2)_2(H_2O)_4]Cl\}_n$, the unique Sm^{III} atom lies on a crystallographic twofold axis and is eight-coordinated by four O atoms from four isonicotinate ligands and four water molecules in a slightly distorted square-antiprismatic coodination environment. The Sm^{III} atoms are bridged by two carboxylate groups of two isonicotinate ligands, forming an extended chain along the *c*-axis direction. These chains are cross-linked through hydrogen bonds, forming a three-dimensional framework, with channels which accommodate the chloride anions.

Related literature

For related literature, see: Cai *et al.* (2003); Cui *et al.* (1999); Kay *et al.* (1972); Ma *et al.* (1996, 1999); Mao *et al.* (1998); Starynowicz (1991, 1993); Zeng *et al.* (2000); Zhang *et al.* (1999).
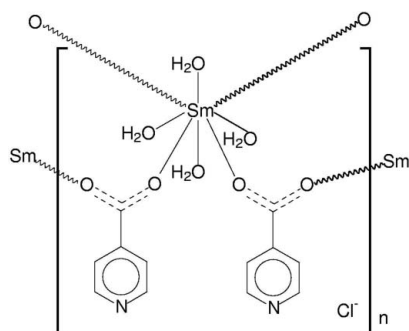
Experimental

Crystal data

$[Sm(C_6H_4NO_2)_2(H_2O)_4]Cl$	Orthorhombic, *Pbcn*
$M_r = 502.07$	$a = 8.9713$ (4) Å
$b = 19.6698$ (9) Å	Mo $K\alpha$ radiation
$c = 10.1459$ (5) Å	$\mu = 3.47$ mm^{-1}
$V = 1790.38$ (14) Å^3	$T = 293$ (2) K
$Z = 4$	$0.50 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer	5176 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1572 independent reflections
$T_{min} = 0.216$, $T_{max} = 0.500$	1326 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	
$S = 0.98$	
1572 reflections	$\Delta\rho_{max} = 0.79$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.84$ e Å^{-3}
6 restraints	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$N1[i]	0.821 (6)	1.895 (7)	2.711 (3)	173 (2)
O1W—H1$WB\cdots$Cl1	0.820 (7)	2.411 (8)	3.2267 (18)	173 (2)
O2W—H2$WA\cdots$Cl1[ii]	0.819 (6)	2.233 (6)	3.0465 (16)	172.3 (8)
O2W—H2$WB\cdots$O1W[iii]	0.817 (6)	2.065 (7)	2.873 (2)	169.8 (12)

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supporting information

catena-Poly[[[tetraaquasamarium(III)]-di-*μ*-isonicotinato-*κ⁴O:O′*] chloride]

Ke-Jun Wu, Li-Zhen Cai, Gang Xu, Guo-Wei Zhou and Guo-Cong Guo

S1. Comment

Much attention has been devoted to the research on lanthanide metal polynuclear compounds because of their magnetic and luminescent properties. Most of these types of compounds were synthesized by the reaction of rare-earth metal ions with bi- or multi-dentate ligands such as nicotinic acid (Starynowicz, 1993; Starynowicz, 1991; Kay *et al.*, 1972; Ma *et al.*, 1996), isonicotinic acid (Ma *et al.*, 1999; Zeng *et al.*, 2000) and isonicotinic acid N-oxide (Mao *et al.*, 1998). In the course of our research in this area, our extended group has reported several such compounds with different bridging ligands (Zhang *et al.*, 1999; Cui *et al.*, 1999; Cai *et al.*, 2003). Herein, we report the synthesis and crystal structure of a new samarium complex with isonicotinic ligand namely {[Sm($C_6H_4NO_2$)$_2$(H_2O)$_4$]Cl}$_n$.

   The structure of the title compound, contains an extended [Sm($C_6H_4NO_2$)$_2$(H_2O)$_4$]$^+$ cationic chains and Cl$^-$ anions. The Sm^{III} ion is eight-coordinated by four O atoms belonging to four different isonicotinic ligands (Sm—O, average 2.363 (2) Å) and four water molecules (Sm—O, average 2.489 (2) Å) (Fig. 1). The coordination geometry of the Sm^{III} cation is best described in terms of its position at the center of a slightly distorted square antiprism. One of the square faces is comprised by O1, O1A, O2W and O2WA atoms with a mean deviation of 0.272 Å and the other one is defined by atoms O2, O2A, O1W and O1WA atoms with a mean deviation of 0.506 Å. The Sm atoms are bridged each other by two *syn-syn μ-O,O′*-carboxylate groups of isonicotinic ligands to form an extended chain along the *c* axis. This geometry is similar to that found in [{Eu(*L*)$_2$(H_2O)$_4$}]$_n$.nH_2O (*L* = isonicotinic acid N-oxide) (Mao *et al.*, 1998) and [La($C_6H_4NO_2$)$_2$(H_2O)$_4$](NO$_3$) (Cai *et al.*, 2003), but differs from those found in Ln(isonicotinate)$_3$(H_2O)$_2$ (Ln = Ce, Pr, Nd, Sm, Eu, Tb) (Ma *et al.*, 1999) in which the Ln^{III} atoms are bridged by four *syn-syn μ-O,O′*-carboxylate groups of isonicotinic ligands (Ln = Ce, Pr, Nd) or coordinated by both two *syn-syn μ-O,O′*-carboxySmte groups and chelating carboxylate groups of isonicotinic ligands (Ln = Sm, Eu, Tb). To the best of our knowledge, the arrangement in present complex is rare in the lanthanide analogs.

   The inter-chain hydrogen bonds, which are created by the uncoordinated nitrogen atoms of isonicotinic ligands and coordinated water molecules between neighboring chains link the cationic chains into a three-dimensional network with channels along the *c* axis in which the chloride anions are located, as shown in Fig. 2. The other intermolecular hydrogen bonds are formed by the chloride anions and coordinated water molecules (see hydrogen bond geometry table).

S2. Experimental

The title complex was prepared by mixing a 1:1 molar ratio of SmCl$_3$.6(H_2O) (37 mg, 0.1 mmol) and C_5H_4NCOOH (12 mg, 0.1 mmol) in 10 ml mixed solvent of H_2O/EtOH (v:v = 1:1). The pH value of the solution was adjusted to 5.8 with NH$_3$. H_2O. The reaction mixture was filtered and colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

S3. Refinement

Water H atoms were located in a difference Fourier map and refined as riding in their as-found positions, with $U_{iso}(H)$ =1.5$U_{eq}(O)$. H atoms bonded to C atoms were placed in calclulated positions with C—H = 0.93Å and $U_{iso}(H)$ = 1.2$U_{eq}(C)$.
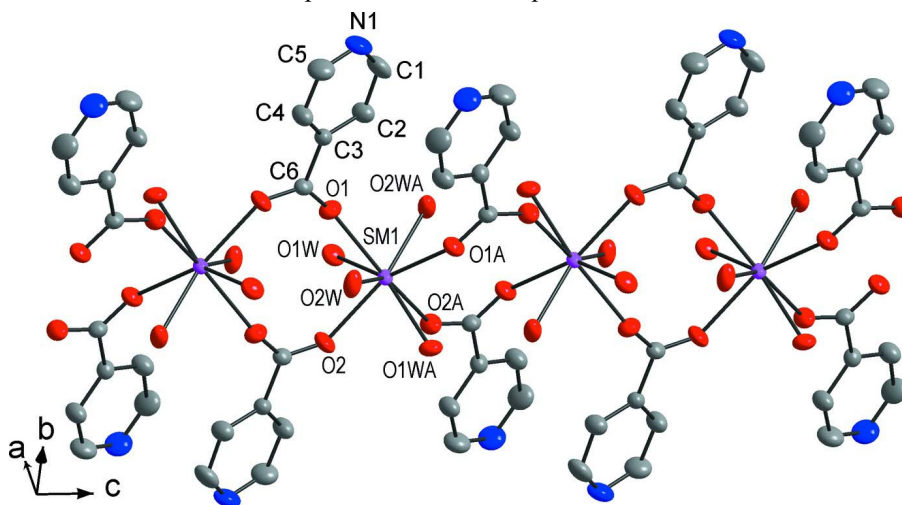

Figure 1

View of part of the one-dimensional cationic chain of the title compound. The Cl anions are not shown. Displacement ellipsoids are shown at the 30% probability level {symmetry code: (A) 1 - *x*,*y*,0.5 - *z*].
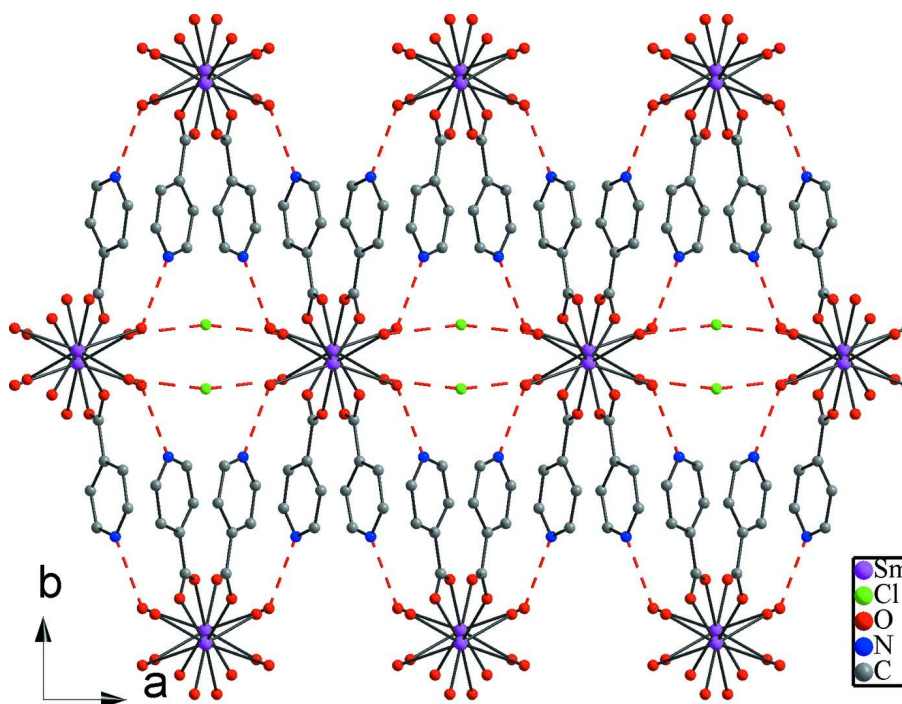

Figure 2

Packing of the title compound. Dashed lines represent the donor-acceptor relatioships of the hydrogen bonds but H atoms are not shown.

catena-Poly[[[tetraaquasamarium(III)]-di-μ-isoniconitinato-κ⁴O:O′] chloride]

Crystal data

[Sm($C_6H_4NO_2$)$_2$(H_2O)$_4$]Cl	$D_x = 1.863$ Mg m^{-3}
$M_r = 502.07$	Melting point: not measured K
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 3359 reflections
$a = 8.9713$ (4) Å	$\theta = 2.1–25.1°$
$b = 19.6698$ (9) Å	$\mu = 3.47$ mm^{-1}
$c = 10.1459$ (5) Å	$T = 293$ K
$V = 1790.38$ (14) Å^3	Block, green
$Z = 4$	$0.50 \times 0.20 \times 0.20$ mm
$F(000) = 980$	

Data collection

Siemens SMART CCD diffractometer	5176 measured reflections
Radiation source: fine-focus sealed tube	1572 independent reflections
Graphite monochromator	1326 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.1°$, $\theta_{min} = 2.1°$
	$h = -10 \rightarrow 10$
	$k = -23 \rightarrow 11$
$T_{min} = 0.216$, $T_{max} = 0.500$	$l = -10 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.026$	
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 4.3692P]$
$S = 0.98$	where $P = (F_o^2 + 2F_c^2)/3$
1572 reflections	$(\Delta/\sigma)_{max} = 0.001$
127 parameters	$\Delta\rho_{max} = 0.79$ e Å^{-3}
6 restraints	$\Delta\rho_{min} = -0.84$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: *SHELXL*, Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0199 (3)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Sm1	0.0000	0.488380 (7)	0.2500	0.02081 (5)
Cl1	0.5000	0.55724 (6)	0.2500	0.0505 (3)
O1W	0.24788 (18)	0.44913 (8)	0.16326 (16)	0.0356 (4)
O1	0.10167 (18)	0.43193 (8)	0.60241 (16)	0.0345 (4)
O2	0.0437 (2)	0.39771 (8)	0.39964 (16)	0.0366 (4)
O2W	−0.19848 (17)	0.54040 (10)	0.11577 (15)	0.0394 (5)
N1	0.1463 (3)	0.17887 (11)	0.6303 (2)	0.0474 (6)
C1	0.1948 (3)	0.22974 (14)	0.7048 (3)	0.0468 (7)
H1A	0.2448	0.2191	0.7824	0.056*
C5	0.0741 (4)	0.19498 (12)	0.5206 (3)	0.0472 (8)
H2A	0.0387	0.1599	0.4676	0.057*
C4	0.0487 (3)	0.26104 (12)	0.4810 (2)	0.0359 (6)

H3A	−0.0040	0.2701	0.4040	0.043*
C2	0.1755 (3)	0.29747 (13)	0.6739 (2)	0.0368 (7)
H4A	0.2106	0.3314	0.7297	0.044*
C3	0.1028 (2)	0.31367 (11)	0.5579 (2)	0.0260 (5)
C6	0.0799 (3)	0.38691 (10)	0.5173 (2)	0.0266 (5)
H2WA	−0.2831 (6)	0.5451 (13)	0.1446 (8)	0.039 (7)*
H1WA	0.2846 (14)	0.4110 (2)	0.159 (2)	0.053 (8)*
H1WB	0.3149 (9)	0.4764 (3)	0.178 (3)	0.077 (11)*
H2WB	−0.2009 (14)	0.5434 (16)	0.0355 (5)	0.066 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sm1	0.02907 (9)	0.01576 (9)	0.01760 (9)	0.000	0.00088 (6)	0.000
Cl1	0.0344 (5)	0.0528 (6)	0.0644 (6)	0.000	0.0134 (4)	0.000
O1W	0.0404 (8)	0.0241 (7)	0.0422 (8)	0.0090 (7)	0.0000 (8)	−0.0053 (7)
O1	0.0422 (8)	0.0235 (7)	0.0379 (8)	0.0010 (7)	0.0021 (8)	−0.0083 (7)
O2	0.0557 (9)	0.0238 (7)	0.0304 (8)	−0.0003 (8)	−0.0067 (8)	0.0085 (7)
O2W	0.0336 (8)	0.0587 (11)	0.0260 (8)	0.0099 (8)	0.0036 (7)	0.0054 (8)
N1	0.0580 (13)	0.0274 (10)	0.0568 (13)	0.0088 (10)	−0.0028 (12)	0.0109 (10)
C1	0.0543 (15)	0.0429 (15)	0.0431 (13)	0.0059 (13)	−0.0134 (14)	0.0158 (12)
C5	0.0631 (18)	0.0236 (11)	0.0550 (15)	−0.0010 (13)	−0.0030 (15)	−0.0041 (12)
C4	0.0522 (13)	0.0260 (11)	0.0297 (12)	−0.0010 (11)	−0.0093 (12)	0.0000 (10)
C2	0.0469 (14)	0.0283 (12)	0.0353 (12)	0.0018 (11)	−0.0082 (11)	−0.0013 (11)
C3	0.0312 (11)	0.0226 (10)	0.0242 (10)	0.0035 (9)	0.0014 (9)	0.0010 (8)
C6	0.0311 (12)	0.0188 (9)	0.0298 (11)	−0.0001 (9)	0.0035 (10)	0.0017 (9)

Geometric parameters (Å, º)

Sm1—O1^i	2.3519 (15)	O2W—H2WA	0.819 (6)
Sm1—O1^{ii}	2.3519 (16)	O2W—H2WB	0.817 (6)
Sm1—O2	2.3747 (16)	N1—C5	1.326 (4)
Sm1—O2^{iii}	2.3747 (16)	N1—C1	1.327 (4)
Sm1—O2W^{iii}	2.4642 (16)	C1—C2	1.379 (4)
Sm1—O2W	2.4642 (16)	C1—H1A	0.9300
Sm1—O1W^{iii}	2.5132 (16)	C5—C4	1.379 (3)
Sm1—O1W	2.5132 (16)	C5—H2A	0.9300
O1W—H1WA	0.821 (6)	C4—C3	1.384 (3)
O1W—H1WB	0.820 (7)	C4—H3A	0.9300
O1—C6	1.252 (3)	C2—C3	1.383 (3)
O1—Sm1^i	2.3519 (15)	C2—H4A	0.9300
O2—C6	1.255 (3)	C3—C6	1.512 (3)
O1^i—Sm1—O1^{ii}	96.41 (8)	Sm1—O1W—H1WA	131.0 (10)
O1^i—Sm1—O2	99.06 (6)	Sm1—O1W—H1WB	112.5 (10)
O1^{ii}—Sm1—O2	147.52 (6)	H1WA—O1W—H1WB	108.2 (10)
O1^i—Sm1—O2^{iii}	147.52 (6)	C6—O1—Sm1^i	148.18 (15)
O1^{ii}—Sm1—O2^{iii}	99.06 (6)	C6—O2—Sm1	141.07 (14)

O2—Sm1—O2iii	82.65 (8)	Sm1—O2W—H2WA	121.3 (9)
O1i—Sm1—O2Wiii	69.61 (6)	Sm1—O2W—H2WB	126.9 (13)
O1ii—Sm1—O2Wiii	78.16 (6)	H2WA—O2W—H2WB	108.9 (10)
O2—Sm1—O2Wiii	80.75 (6)	C5—N1—C1	117.2 (2)
O2iii—Sm1—O2Wiii	141.67 (6)	N1—C1—C2	123.9 (3)
O1i—Sm1—O2W	78.16 (6)	N1—C1—H1A	118.1
O1ii—Sm1—O2W	69.61 (6)	C2—C1—H1A	118.1
O2—Sm1—O2W	141.67 (6)	N1—C5—C4	123.4 (2)
O2iii—Sm1—O2W	80.75 (6)	N1—C5—H2A	118.3
O2Wiii—Sm1—O2W	130.93 (9)	C4—C5—H2A	118.3
O1i—Sm1—O1Wiii	68.82 (5)	C5—C4—C3	118.9 (2)
O1ii—Sm1—O1Wiii	140.43 (5)	C5—C4—H3A	120.6
O2—Sm1—O1Wiii	72.03 (6)	C3—C4—H3A	120.6
O2iii—Sm1—O1Wiii	81.20 (6)	C1—C2—C3	118.4 (2)
O2Wiii—Sm1—O1Wiii	124.99 (5)	C1—C2—H4A	120.8
O2W—Sm1—O1Wiii	71.44 (5)	C3—C2—H4A	120.8
O1i—Sm1—O1W	140.43 (5)	C2—C3—C4	118.2 (2)
O1ii—Sm1—O1W	68.82 (5)	C2—C3—C6	121.0 (2)
O2—Sm1—O1W	81.20 (6)	C4—C3—C6	120.8 (2)
O2iii—Sm1—O1W	72.03 (6)	O1—C6—O2	125.2 (2)
O2Wiii—Sm1—O1W	71.44 (5)	O1—C6—C3	117.68 (19)
O2W—Sm1—O1W	124.99 (5)	O2—C6—C3	117.10 (18)
O1Wiii—Sm1—O1W	144.22 (7)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*WA*⋯N1iv	0.82 (1)	1.90 (1)	2.711 (3)	173 (2)
O1*W*—H1*WB*⋯Cl1	0.82 (1)	2.41 (1)	3.2267 (18)	173 (2)
O2*W*—H2*WA*⋯Cl1v	0.82 (1)	2.23 (1)	3.0465 (16)	172 (1)
O2*W*—H2*WB*⋯O1*W*vi	0.82 (1)	2.07 (1)	2.873 (2)	170 (1)

Symmetry codes: (iv) −*x*+1/2, −*y*+1/2, *z*−1/2; (v) *x*−1, *y*, *z*; (vi) −*x*, −*y*+1, −*z*.