

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

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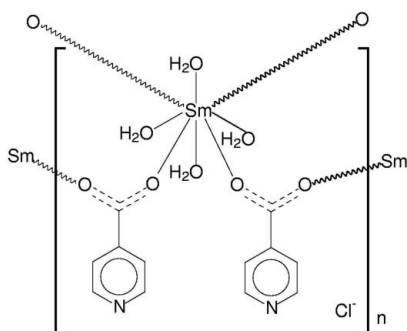
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.072; data-to-parameter ratio = 12.4.

In the structure of the title compound, $\{[\text{Sm}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}\}_n$, 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 coordination 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

$[\text{Sm}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}$
 $M_r = 502.07$

Orthorhombic, $Pbcn$
 $a = 8.9713$ (4) Å

$b = 19.6698$ (9) Å
 $c = 10.1459$ (5) Å
 $V = 1790.38$ (14) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 3.47$ mm⁻¹
 $T = 293$ (2) K
 $0.50 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.216$, $T_{\text{max}} = 0.500$

5176 measured reflections
 1572 independent reflections
 1326 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.072$
 $S = 0.98$
 1572 reflections
 127 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.79$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.84$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{N1}^{\text{i}}$	0.821 (6)	1.895 (7)	2.711 (3)	173 (2)
$\text{O1W}-\text{H1WB}\cdots\text{Cl1}$	0.820 (7)	2.411 (8)	3.2267 (18)	173 (2)
$\text{O2W}-\text{H2WA}\cdots\text{Cl1}^{\text{ii}}$	0.819 (6)	2.233 (6)	3.0465 (16)	172.3 (8)
$\text{O2W}-\text{H2WB}\cdots\text{O1W}^{\text{iii}}$	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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2488).

References

- Cai, L.-Z., Wang, M.-S., Zhou, G.-W., Guo, G.-C., Mao, J.-G. & Huang, J.-S. (2003). *Acta Cryst.* **E59**, m249–m251.
- Cui, Y., Zheng, F.-K. & Huang, J.-S. (1999). *Chem. Lett.* **4**, 281–282.
- Kay, J., Moore, J. W. & Glick, M. D. (1972). *Inorg. Chem.* **11**, 2818–2827.
- Ma, L., Evans, O. R., Foxman, B. M. & Lin, W. B. (1999). *Inorg. Chem.* **38**, 5837–5840.
- Ma, J. F., Hu, N. H. & Ni, J. Z. (1996). *Polyhedron*, **15**, 1797–1799.
- Mao, J. G., Zhang, H. J., Ni, J. Z., Wang, S. B. & Mak, T. C. W. (1998). *J. Chem. Cryst.* **17**, 3999–4009.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, German.
- Siemens (1994). *SAINT* and *SHELXTL*. Siemens X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SHELXTL*. Version 5. Siemens X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART*. Siemens X-ray Instruments Inc., Madison, Wisconsin, USA.
- Starynowicz, P. (1991). *Acta Cryst.* **C47**, 294–297.
- Starynowicz, P. (1993). *Acta Cryst.* **C49**, 1895–1897.
- Zeng, X.-R., Xu, Y., Xiong, R.-G., Zhang, L.-J. & You, X.-Z. (2000). *Acta Cryst.* **C56**, e325–e326.
- Zhang, X., Cui, Y., Zheng, F.-K. & Huang, J.-S. (1999). *Chem. Lett.* pp. 1111–1112.

supplementary materials

Acta Cryst. (2008). E64, m56 [doi:10.1107/S1600536807058230]

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

K.-J. Wu, L.-Z. Cai, G. Xu, G.-W. Zhou and G.-C. Guo

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 $\{[\text{Sm}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}\}_n$.

The structure of the title compound, contains an extended $[\text{Sm}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]^+$ 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 $[\{\text{Eu}(L)_2(\text{H}_2\text{O})_4\}]_n \cdot n\text{H}_2\text{O}$ (*L* = isonicotinic acid N-oxide) (Mao *et al.*, 1998) and $[\text{La}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{NO}_3)$ (Cai *et al.*, 2003), but differs from those found in $\text{Ln}(\text{isonicotinate})_3(\text{H}_2\text{O})_2$ (*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'*-carboxylate 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).

Experimental

The title complex was prepared by mixing a 1:1 molar ratio of $\text{SmCl}_3 \cdot 6(\text{H}_2\text{O})$ (37 mg, 0.1 mmol) and $\text{C}_5\text{H}_4\text{NCOOH}$ (12 mg, 0.1 mmol) in 10 ml mixed solvent of $\text{H}_2\text{O}/\text{EtOH}$ (*v:v* = 1:1). The pH value of the solution was adjusted to 5.8 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. The reaction mixture was filtered and colorless single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Refinement

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

Figures

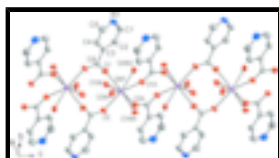


Fig. 1. View of part of the one-dimensional cationic chain of the title compound. The Cl anions are not shown. Displacement ellipsoids are shown at the 30% probability level {symmetry code: (A) 1 - x, y, 0.5 - z}.

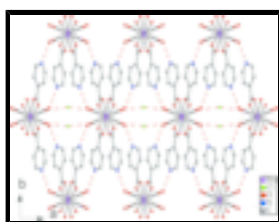


Fig. 2. Packing of the title compound. Dashed lines represent the donor-acceptor relationships of the hydrogen bonds but H atoms are not shown.

catena-Poly[[[tetraaquasamarium(III)]-di- μ -isoniconitinato- $\kappa^4\text{O}^1$] chloride]

Crystal data

$[\text{Sm}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_4]\text{Cl}$

$M_r = 502.07$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 8.9713(4)\text{Å}$

$b = 19.6698(9)\text{Å}$

$c = 10.1459(5)\text{Å}$

$V = 1790.38(14)\text{Å}^3$

$Z = 4$

$F_{000} = 980$

$D_x = 1.863\text{ Mg m}^{-3}$

Melting point: not measured K

Mo $K\alpha$ radiation

$\lambda = 0.71073\text{Å}$

Cell parameters from 3359 reflections

$\theta = 2.1\text{--}25.1^\circ$

$\mu = 3.47\text{ mm}^{-1}$

$T = 293(2)\text{ K}$

Block, green

$0.50 \times 0.20 \times 0.20\text{ mm}$

Data collection

Siemens SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)\text{ K}$

ω scans

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

$T_{\text{min}} = 0.216$, $T_{\text{max}} = 0.500$

1572 independent reflections

1326 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 25.1^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -10 \rightarrow 10$

$k = -23 \rightarrow 11$

5176 measured reflections

$l = -10 \rightarrow 12$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.026$

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.072$

$$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 4.3692P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 0.98$

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

1572 reflections

$\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$

127 parameters

$\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$

6 restraints

Extinction correction: SHELXL,

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.0199 (3)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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

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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 (\AA , $^\circ$)

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—O2 ⁱⁱⁱ	82.65 (8)	Sm1—O2W—H2WA	121.3 (9)
O1 ⁱ —Sm1—O2W ⁱⁱⁱ	69.61 (6)	Sm1—O2W—H2WB	126.9 (13)
O1 ⁱⁱ —Sm1—O2W ⁱⁱⁱ	78.16 (6)	H2WA—O2W—H2WB	108.9 (10)
O2—Sm1—O2W ⁱⁱⁱ	80.75 (6)	C5—N1—C1	117.2 (2)
O2 ⁱⁱⁱ —Sm1—O2W ⁱⁱⁱ	141.67 (6)	N1—C1—C2	123.9 (3)
O1 ⁱ —Sm1—O2W	78.16 (6)	N1—C1—H1A	118.1
O1 ⁱⁱ —Sm1—O2W	69.61 (6)	C2—C1—H1A	118.1
O2—Sm1—O2W	141.67 (6)	N1—C5—C4	123.4 (2)
O2 ⁱⁱⁱ —Sm1—O2W	80.75 (6)	N1—C5—H2A	118.3
O2W ⁱⁱⁱ —Sm1—O2W	130.93 (9)	C4—C5—H2A	118.3
O1 ⁱ —Sm1—O1W ⁱⁱⁱ	68.82 (5)	C5—C4—C3	118.9 (2)

O1 ⁱⁱ —Sm1—O1W ⁱⁱⁱ	140.43 (5)	C5—C4—H3A	120.6
O2—Sm1—O1W ⁱⁱⁱ	72.03 (6)	C3—C4—H3A	120.6
O2 ⁱⁱⁱ —Sm1—O1W ⁱⁱⁱ	81.20 (6)	C1—C2—C3	118.4 (2)
O2W ⁱⁱⁱ —Sm1—O1W ⁱⁱⁱ	124.99 (5)	C1—C2—H4A	120.8
O2W—Sm1—O1W ⁱⁱⁱ	71.44 (5)	C3—C2—H4A	120.8
O1 ⁱ —Sm1—O1W	140.43 (5)	C2—C3—C4	118.2 (2)
O1 ⁱⁱ —Sm1—O1W	68.82 (5)	C2—C3—C6	121.0 (2)
O2—Sm1—O1W	81.20 (6)	C4—C3—C6	120.8 (2)
O2 ⁱⁱⁱ —Sm1—O1W	72.03 (6)	O1—C6—O2	125.2 (2)
O2W ⁱⁱⁱ —Sm1—O1W	71.44 (5)	O1—C6—C3	117.68 (19)
O2W—Sm1—O1W	124.99 (5)	O2—C6—C3	117.10 (18)
O1W ⁱⁱⁱ —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 ($\text{\AA}, ^\circ$)

<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>
O1W—H1WA \cdots N1 ^{iv}	0.821 (6)	1.895 (7)	2.711 (3)	173 (2)
O1W—H1WB \cdots C11	0.820 (7)	2.411 (8)	3.2267 (18)	173 (2)
O2W—H2WA \cdots C11 ^v	0.819 (6)	2.233 (6)	3.0465 (16)	172.3 (8)
O2W—H2WB \cdots O1W ^{vi}	0.817 (6)	2.065 (7)	2.873 (2)	169.8 (12)

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

Fig. 1

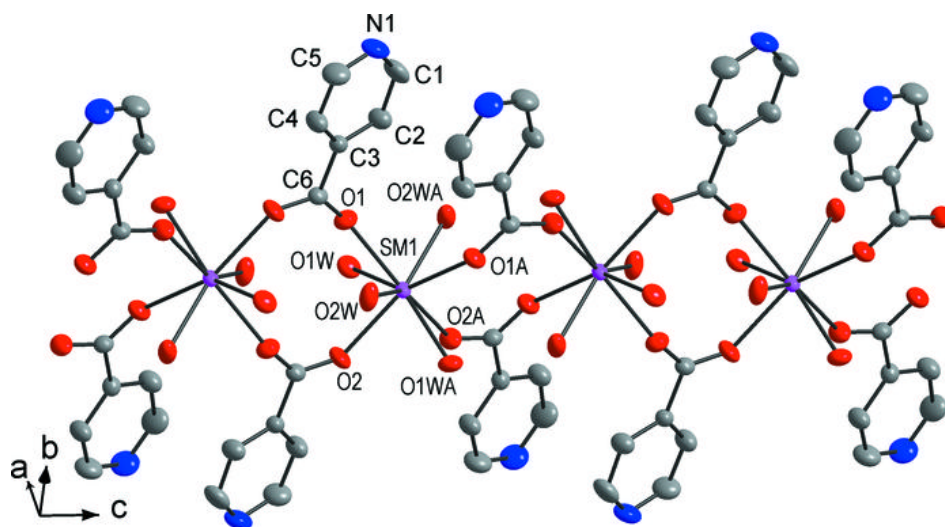


Fig. 2

