Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Reinvestigation of layered poly[aqua-sodium(I) [[aquasamarium(III)]-di-μ-aqua-μ_3-pyridine-2,6-dicarboxylato-μ_2-pyridine-2,6-dicarboxylato] trihydrate]

Kazuya Ikarashi, Zhu Taoyun, Kazuyoshi Uematsu, Kenji Toda and Mineo Sato*

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-no-cho, Niigata City 950-2181, Japan
Correspondence e-mail: msato@eng.niigata-u.ac.jp

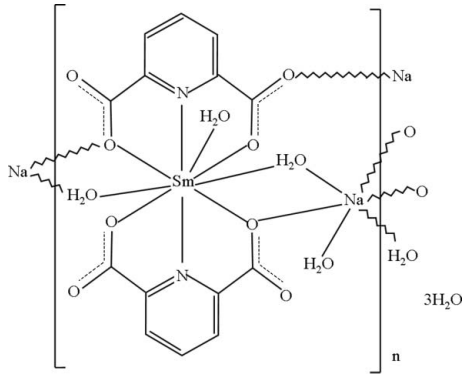
Received 10 May 2007; accepted 12 June 2007

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.081; data-to-parameter ratio = 18.1.

The crystal structure of the title compound, $\{[NaSm(C_7H_3NO_4)_2(H_2O)_4]\cdot 3H_2O\}_n$, was first reported by van Albada, Gorter & Reedijk [(1999), *Polyhedron*, **18**, 1821–1824]. It has now been reinvestigated and confirmed from single-crystal data, giving greater understanding of the role of the water molecules. The two-dimensional layers found in the compound are built up from six-coordinate NaO_6 polyhedra and nine-coordinate SmN_2O_7 polyhedra. The former share edges with each other along the c axis and the latter are bridged by carboxylate groups of pyridine-2,6-dicarboxylate anions along the b axis. Eight-membered rings of water molecules, connected to one another by hydrogen bonding, are formed in the interlayer spaces.

Related literature

For related literature, see: van Albada *et al.* (1999); Benelli & Gatteschi (2002); Brouca-Cabarrecq *et al.* (2002); Duan *et al.* (2004); Ghosh & Bharadwaj (2003).



Experimental

Crystal data

$[NaSm(C_7H_3NO_4)_2(H_2O)_4]\cdot 3H_2O$
M_r = 629.66
Monoclinic, $P2_1/c$
a = 11.2065 (4) Å
b = 17.4485 (3) Å
c = 11.3728 (4) Å
β = 98.163 (1)° [98.163 (1)°
V = 2201.27 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.77 mm^{-1}
T = 296 K
0.30 × 0.18 × 0.04 mm

Data collection

Rigaku R-AXIS-IV diffractometer
Absorption correction: numerical (*ABSCOR*; Higashi, 1999)
T_{min} = 0.558, T_{max} = 0.895
22103 measured reflections
6163 independent reflections
5944 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.081
S = 1.17
6163 reflections
341 parameters
21 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.28 e Å^{-3}

Table 1
Selected bond lengths (Å).

Sm1—O14	2.4144 (19)	Sm1—O2*W*	2.562 (2)
Sm1—O12	2.4213 (19)	Na1—O21	2.392 (2)
Sm1—O23	2.437 (2)	Na1—O5*W*	2.394 (3)
Sm1—O21	2.4460 (19)	Na1—O2*W*	2.434 (3)
Sm1—O3*W*	2.478 (2)	Na1—O24^{i}	2.445 (3)
Sm1—N11	2.533 (2)	Na1—O14^{ii}	2.456 (2)
Sm1—N21	2.540 (2)	Na1—O1*W*^{ii}	2.610 (3)
Sm1—O1*W*	2.547 (2)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*W*···O22^{iii}	0.851	1.931	2.753 (3)	162
O1*W*—H2*W*···O5*W*^{iv}	0.854	1.961	2.794 (3)	165
O2*W*—H3*W*···O11^{iii}	0.848	1.954	2.790 (3)	169
O2*W*—H4*W*···O13^{ii}	0.849	1.884	2.725 (3)	170
O3*W*—H5*W*···O24^{i}	0.851	2.019	2.853 (3)	166
O3*W*—H6*W*···O12^{iii}	0.845	1.885	2.725 (3)	173
O4*W*—H7*W*···O22^{iv}	0.856	2.077	2.907 (4)	163
O4*W*—H8*W*···O23	0.855	1.938	2.779 (3)	168
O5*W*—H9*W*···O4*W*^{ii}	0.848	1.961	2.784 (4)	163
O5*W*—H10*W*···O7*W*	0.852	1.939	2.791 (5)	177
O6*W*—H11*W*···O13^{ii}	0.854	1.947	2.789 (5)	168
O6*W*—H12*W*···O4*W*^{v}	0.854	2.03	2.858 (5)	163
O7*W*—H13*W*···O11^{iii}	0.851	2.22	2.989 (4)	151
O7*W*—H14*W*···O6*W*	0.852	1.96	2.754 (7)	155

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

 doi:10.1107/S160053680702884X

This work was supported by a Grant-in-Aid for Scientific Research (No. 440, Panoscopic Assembling and High Ordered Functions for Rare Earth Materials, and No. 17042012) from the Ministry of Education, Culture, Sports, Science and Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YM2055).

References

Albada, G. A. van, Gorter, S. & Reedijk, J. (1999). *Polyhedron*, **18**, 1821–1824.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Benelli, C. & Gatteschi, D. (2002). *Chem. Rev.* **102**, 2369–2387.
Brouca-Cabarrecq, C., Fernandes, A., Jaud, J. & Costes, J. P. (2002). *Inorg. Chim. Acta*, **332**, 54–60.
Duan, L., Li, Y., Liu, F., Wang, E., Wang, X., Hu, C. & Xu, L. (2004). *J. Mol. Struct.* **689**, 269–274.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Ghosh, S. K. & Bharadwaj, P. K. (2003). *Inorg. Chem.* **42**, 8250–8254.
Higashi, T. (1999). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E**63**, m2203-m2204 [**doi:10.1107/S160053680702884X**]

Reinvestigation of layered poly[aquasodium(I) [[aquasamarium(III)]-di-μ-aqua-μ_3-pyridine-2,6-dicarboxylato-μ_2-pyridine-2,6-dicarboxylato] trihydrate]

K. Ikarashi, Z. Taoyun, K. Uematsu, K. Toda and M. Sato

Comment

The use of rare earth elements for constructing metal-organic frameworks (MOFs) has been attracted much attention due to their variety of magnetic and optical properties (Benelli & Gatteschi, 2002). Since rare earth ions have a large radius and much affinity for oxygen atoms of ligands, pyridine-2,6-dicarboxylic acid (H_2dipic) is widely studied for constructing MOFs containing rare earth elements (Brouca-Cabarrecq *et al.*, 2002;. Duan *et al.*, 2004; Ghosh & Bharadwaj, 2003). Hydrogen-bonding involving water molecules plays an important role in self-assembly processes for building MOF architectures. The structure of the title compound has already been reported (van Albada *et al.*, 1999), but the role of water molecules was not fully understood. We here report the X-ray crystal structure analysis of the compound, and demonstrate a unique hydogen-bonding cluster of water molecules located in interlayer spaces.

A samarium(III) ion is coordinated by two dipic molecules and three water molecules, forming ninefolded coordination environment with four carboxylic oxygen atoms, two dipic nitrogen atoms, and three oxygen atoms of water molecules (Fig.1). All the bond distances for Sm—O and Na—O are comparable to those reported previously (van Albada *et al.*, 1999). The asymmetric unit involves seven water molecules, which are classified into two groups; one is the molecules coordinating metal ions (O1W, O2W, O3W, and O5W) and the other the molecules isolated as a water of crystallization (O4W, O6W, and O7W) with relatively large thermal vibration ellipsoids. The structure can be described as a layered structure, which consists of metallic coordination polymer layers, separated by an interlamellar region populated by water molecules of crystallization. In the layer block, chains are constructed by the ninefolded samarium polyhedra and the sodium octahedra with edge-sharing fashion, running along the direction parallel to the *c* axis. Each chain is bridged by carboxylate groups of the embedded dipic molecules to adjacent chains, thus forming a two-dimensional network. The interlayer water molecules form unique octamer clusters by hydrogen-bonding, giving eight-membered rings (Fig.2). The atoms O4W, O5W, O6W, and O7W are related to those of the symmetrically equivalent opposite side by the center of symmetry. The rings are tightly fixed to the two-dimensional sheets at the atoms of O5W coordinationg to Na1. In the ring, O4W behaves as hydrogen acceptors while O5W behaves as hydrogen donors, in the hydrogen-bonding scheme. Both the atoms show tetracoordination. On the other hand, the atoms O6W and O7W behave both as hydogen donors and acceptors with tricoordination. The average O···O distance in the ring is 2.796 Å, somewhat longer than that of ice (2.76 Å). The two-dimensional structure of the compound is largely a consequence of hydrogen-bonding interactions among water molecules themselves and the MOF.

Experimental

The title compound was hydrothermally synthesized at 150°C for 72 h in a 40 ml Teflon-lined steel autoclave under autogenous pressure. The starting solution was prepared by mixing $Na_2MoO_4{\cdot}2H_2O$, Sm_2O_3, NaCl, pyridine-2,6-dicarboxylic acid, and deionized water with a molar ratio of 2:1:2:1:555 (total volume, 15 ml), and its pH value was adjusted to 3.05 by hydrochloric acid. After the hydrothermal reaction, the autoclave was slowly cooled to room temperature, and colorless crystals were produced.

Refinement

The H atoms bonded to a C atom were positioned geometrically after each cycle in idealized locations and refined as riding on their parent C atoms with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{iso}(C atom). All the hydrogen atoms bonded to an O atom of water molecules were located in a difference Fourier map, and isotropically refined with distance restraints of O—H = 0.85 Å and H—H = 0.93 Å, and with U_{iso}(H) = 1.5U_{iso}(O atom). The maximum and minimum electron-density peaks are located at 1.23 and 0.82 Å, respectively, from Sm1.

Figures

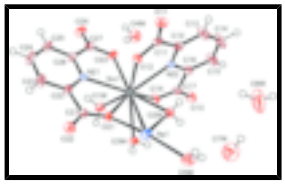


Fig. 1. The asymmetric unit of the compound with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for H atoms).

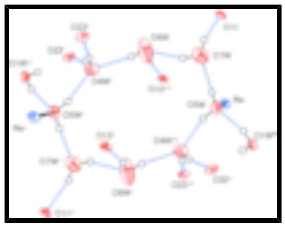


Fig. 2. The hydrogen-bondings between water molecules in an eight-membered ring. [Symmetry codes: (i) *x* + 1, *y*, *z*; (ii) −*x* + 1, *y* + 1/2, −*z* + 3/2; (iii) −*x* + 1, *y* + 1/2, −*z* + 1/2; (iv) −*x*, *y* + 1/2, −*z* + 3/2; (v) −*x* + 1, −*y* + 1, −*z* + 1; (vi) −*x*, −*y* + 1, −*z* + 1; (vii) *x* + 1, −*y* − 1/2, *z* − 3/2; (viii) *x*, −*y* − 1/2, *z* − 3/2;].

poly[aquasodium(I) [[aquasamarium(III)]- di-μ-aqua-μ$_3$-pyridine-2,6-dicarboxylato-μ$_2$-pyridine-2,6-dicarboxylato] trihydrate]

Crystal data

$[NaSm(C_7H_3NO_4)_2(H_2O)_4]\cdot 3H_2O$	F_{000} = 1244
M_r = 629.66	D_x = 1.9 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.7107 Å
Hall symbol: -P 2ybc	Cell parameters from 19188 reflections
a = 11.2065 (4) Å	θ = 2.2–30.0º
b = 17.4485 (3) Å	μ = 2.77 mm^{-1}
c = 11.3728 (4) Å	*T* = 296 K
β = 98.1630 (10)º	Plate, colourless
V = 2201.27 (12) Å^3	0.30 × 0.18 × 0.04 mm
Z = 4	

Data collection

Rigaku R-AXIS-IV diffractometer	5944 reflections with $I > 2\sigma(I)$
Detector resolution: 10.00 pixels mm^{-1}	R_{int} = 0.046
T = 296 K	θ_{max} = 30.0º

ω scans	θ_{min} = 1.8º
Absorption correction: numerical (ABSCOR; Higashi, 1999)	h = −15→15
T_{min} = 0.558, T_{max} = 0.895	k = −22→22
22103 measured reflections	l = −15→15
6163 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.032	H-atom parameters constrained
$wR(F^2)$ = 0.081	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 2.6934P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.17	$(\Delta/\sigma)_{max} < 0.001$
6163 reflections	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
341 parameters	$\Delta\rho_{min}$ = −1.28 e Å^{-3}
21 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00064 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Sm1	0.102796 (11)	0.181254 (7)	0.774431 (10)	0.01333 (6)
Na1	0.08028 (12)	0.37858 (7)	0.61494 (11)	0.0256 (2)
N11	0.3268 (2)	0.15540 (13)	0.78946 (18)	0.0169 (4)
O11	0.3317 (2)	0.14824 (14)	0.48054 (17)	0.0274 (5)
O12	0.18328 (19)	0.16788 (12)	0.58886 (17)	0.0198 (4)
O13	0.3800 (2)	0.17141 (15)	1.10109 (19)	0.0303 (5)
O14	0.21058 (18)	0.16585 (13)	0.97242 (17)	0.0210 (4)
C11	0.2934 (3)	0.15591 (16)	0.5767 (2)	0.0185 (5)
C12	0.3796 (2)	0.15293 (17)	0.6910 (2)	0.0197 (5)
C13	0.5037 (3)	0.1523 (2)	0.6958 (3)	0.0342 (7)

H13	0.5387	0.1488	0.6267	0.041*
C14	0.5747 (3)	0.1570 (3)	0.8057 (3)	0.0437 (9)
H14	0.6583	0.1569	0.8112	0.052*
C15	0.5201 (3)	0.1618 (3)	0.9069 (3)	0.0360 (8)
H15	0.5661	0.1665	0.9813	0.043*
C16	0.3956 (3)	0.15934 (18)	0.8955 (2)	0.0210 (5)
C17	0.3240 (3)	0.16562 (17)	0.9990 (2)	0.0196 (5)
N21	−0.0648 (2)	0.11795 (13)	0.63391 (19)	0.0173 (4)
O21	−0.03307 (18)	0.26630 (11)	0.64738 (17)	0.0212 (4)
O22	−0.2002 (2)	0.28990 (13)	0.5209 (2)	0.0285 (5)
O23	0.10578 (18)	0.04169 (13)	0.76633 (17)	0.0238 (4)
O24	0.0160 (2)	−0.07055 (12)	0.7216 (2)	0.0291 (5)
C21	−0.1269 (2)	0.24589 (16)	0.5790 (2)	0.0188 (5)
C22	−0.1463 (2)	0.16042 (17)	0.5652 (2)	0.0187 (5)
C23	−0.2356 (3)	0.12771 (19)	0.4838 (3)	0.0280 (6)
H23	−0.2919	0.1581	0.4373	0.034*
C24	−0.2390 (3)	0.0490 (2)	0.4735 (3)	0.0345 (7)
H24	−0.2972	0.0256	0.4187	0.041*
C25	−0.1552 (3)	0.00475 (18)	0.5450 (3)	0.0280 (6)
H25	−0.1564	−0.0484	0.5395	0.034*
C26	−0.0693 (2)	0.04196 (16)	0.6252 (2)	0.0190 (5)
C27	0.0243 (3)	−0.00019 (15)	0.7095 (2)	0.0195 (5)
O1W	−0.0451 (2)	0.12687 (13)	0.9033 (2)	0.0277 (4)
H1W	−0.094	0.1591	0.927	0.042*
H2W	−0.084	0.0863	0.880	0.042*
O2W	0.21951 (19)	0.30604 (12)	0.75680 (18)	0.0214 (4)
H3W	0.248	0.326	0.8231	0.032*
H4W	0.272	0.308	0.710	0.032*
O3W	0.03015 (19)	0.28534 (12)	0.89442 (16)	0.0199 (4)
H5W	0.006	0.3247	0.854	0.03*
H6W	0.083	0.2981	0.952	0.03*
O4W	0.2530 (3)	−0.05242 (17)	0.9220 (2)	0.0394 (6)
H7W	0.231	−0.0993	0.924	0.059*
H8W	0.205	−0.029	0.868	0.059*
O5W	0.1904 (2)	0.49655 (15)	0.6342 (2)	0.0356 (5)
H9W	0.220	0.506	0.571	0.053*
H10W	0.247	0.492	0.692	0.053*
O6W	0.5694 (4)	0.4115 (4)	0.7266 (4)	0.110 (2)
H11W	0.517	0.387	0.680	0.165*
H12W	0.619	0.432	0.686	0.165*
O7W	0.3811 (4)	0.4793 (2)	0.8188 (3)	0.0625 (9)
H13W	0.390	0.450	0.879	0.094*
H14W	0.438	0.471	0.778	0.094*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sm1	0.01602 (8)	0.01226 (9)	0.01101 (7)	−0.00069 (4)	−0.00049 (5)	0.00020 (3)

Na1	0.0319 (6)	0.0210 (6)	0.0238 (6)	−0.0002 (5)	0.0037 (5)	0.0002 (4)
N11	0.0193 (10)	0.0185 (11)	0.0118 (9)	0.0019 (8)	−0.0016 (7)	0.0002 (7)
O11	0.0312 (11)	0.0386 (13)	0.0126 (8)	0.0042 (9)	0.0038 (8)	−0.0025 (8)
O12	0.0197 (9)	0.0253 (10)	0.0138 (8)	−0.0002 (7)	0.0004 (7)	−0.0016 (7)
O13	0.0259 (11)	0.0509 (15)	0.0127 (9)	0.0062 (9)	−0.0026 (8)	−0.0020 (8)
O14	0.0193 (9)	0.0286 (10)	0.0147 (8)	0.0002 (8)	0.0015 (7)	0.0014 (7)
C11	0.0245 (13)	0.0156 (13)	0.0146 (11)	0.0025 (9)	−0.0002 (9)	−0.0010 (8)
C12	0.0210 (12)	0.0242 (14)	0.0140 (10)	0.0012 (10)	0.0031 (9)	−0.0004 (9)
C13	0.0211 (14)	0.060 (2)	0.0218 (14)	0.0070 (14)	0.0054 (11)	0.0024 (14)
C14	0.0154 (14)	0.088 (3)	0.0279 (16)	0.0085 (16)	0.0023 (12)	−0.0003 (18)
C15	0.0208 (14)	0.065 (2)	0.0206 (14)	0.0042 (14)	−0.0029 (11)	−0.0033 (14)
C16	0.0209 (12)	0.0282 (14)	0.0129 (11)	0.0044 (10)	−0.0010 (9)	0.0009 (9)
C17	0.0236 (13)	0.0201 (13)	0.0143 (11)	0.0043 (10)	0.0000 (9)	0.0007 (9)
N21	0.0206 (10)	0.0140 (11)	0.0166 (9)	−0.0019 (8)	0.0002 (8)	0.0002 (7)
O21	0.0221 (10)	0.0172 (10)	0.0221 (9)	−0.0009 (7)	−0.0038 (7)	0.0009 (7)
O22	0.0259 (11)	0.0232 (12)	0.0339 (11)	0.0036 (8)	−0.0048 (9)	0.0076 (8)
O23	0.0278 (11)	0.0148 (11)	0.0264 (10)	0.0013 (7)	−0.0044 (8)	−0.0002 (7)
O24	0.0401 (13)	0.0142 (10)	0.0322 (11)	−0.0027 (8)	0.0026 (9)	0.0016 (7)
C21	0.0206 (12)	0.0170 (13)	0.0179 (11)	0.0002 (9)	−0.0003 (9)	0.0017 (8)
C22	0.0191 (12)	0.0182 (13)	0.0175 (11)	−0.0025 (9)	−0.0020 (9)	0.0026 (9)
C23	0.0269 (14)	0.0286 (16)	0.0249 (13)	−0.0031 (11)	−0.0082 (11)	0.0030 (11)
C24	0.0350 (17)	0.0297 (18)	0.0338 (16)	−0.0102 (13)	−0.0128 (13)	−0.0042 (12)
C25	0.0348 (16)	0.0182 (15)	0.0287 (14)	−0.0070 (11)	−0.0030 (12)	−0.0040 (10)
C26	0.0233 (12)	0.0159 (12)	0.0171 (11)	−0.0041 (9)	0.0008 (9)	−0.0017 (8)
C27	0.0283 (13)	0.0134 (12)	0.0174 (11)	0.0006 (9)	0.0051 (9)	0.0007 (8)
O1W	0.0303 (11)	0.0241 (11)	0.0311 (11)	−0.0060 (8)	0.0124 (9)	−0.0066 (8)
O2W	0.0251 (10)	0.0217 (10)	0.0175 (9)	−0.0034 (8)	0.0031 (7)	−0.0020 (7)
O3W	0.0260 (10)	0.0184 (10)	0.0144 (8)	0.0001 (7)	−0.0004 (7)	−0.0009 (6)
O4W	0.0395 (14)	0.0407 (16)	0.0358 (13)	0.0055 (11)	−0.0021 (10)	0.0070 (11)
O5W	0.0414 (14)	0.0278 (13)	0.0396 (13)	0.0008 (10)	0.0124 (11)	0.0022 (10)
O6W	0.055 (2)	0.204 (6)	0.077 (3)	−0.058 (3)	0.026 (2)	−0.071 (4)
O7W	0.071 (2)	0.065 (2)	0.054 (2)	−0.0094 (18)	0.0177 (17)	0.0094 (16)

Geometric parameters (Å, °)

Sm1—O14	2.4144 (19)	C15—H15	0.93
Sm1—O12	2.4213 (19)	C16—C17	1.520 (4)
Sm1—O23	2.437 (2)	N21—C26	1.330 (3)
Sm1—O21	2.4460 (19)	N21—C22	1.338 (3)
Sm1—O3W	2.478 (2)	O21—C21	1.267 (3)
Sm1—N11	2.533 (2)	O22—C21	1.243 (3)
Sm1—N21	2.540 (2)	O23—C27	1.272 (3)
Sm1—O1W	2.547 (2)	O24—C27	1.240 (3)
Sm1—O2W	2.562 (2)	O24—Na1^{iv}	2.445 (3)
Sm1—Na1	3.8831 (12)	C21—C22	1.512 (4)
Sm1—Na1^{i}	4.0532 (12)	C22—C23	1.386 (4)
Na1—O21	2.392 (2)	C23—C24	1.379 (5)
Na1—O5W	2.394 (3)	C23—H23	0.93
Na1—O2W	2.434 (3)	C24—C25	1.387 (5)

Na1—O24^{ii}	2.445 (3)	C24—H24	0.93
Na1—O14^{iii}	2.456 (2)	C25—C26	1.389 (4)
Na1—O1W^{iii}	2.610 (3)	C25—H25	0.93
Na1—Sm1^{iii}	4.0532 (12)	C26—C27	1.509 (4)
Na1—H4W	2.58	O1W—Na1^{i}	2.610 (3)
N11—C16	1.338 (3)	O1W—H1W	0.851
N11—C12	1.339 (3)	O1W—H2W	0.854
O11—C11	1.238 (3)	O2W—H3W	0.848
O12—C11	1.278 (3)	O2W—H4W	0.849
O13—C17	1.243 (3)	O3W—H5W	0.851
O14—C17	1.264 (3)	O3W—H6W	0.845
O14—Na1^{i}	2.456 (2)	O4W—H7W	0.856
C11—C12	1.506 (4)	O4W—H8W	0.855
C12—C13	1.384 (4)	O5W—H9W	0.848
C13—C14	1.385 (5)	O5W—H10W	0.852
C13—H13	0.93	O6W—H11W	0.854
C14—C15	1.380 (5)	O6W—H12W	0.854
C14—H14	0.93	O7W—H13W	0.851
C15—C16	1.383 (4)	O7W—H14W	0.852
O14—Sm1—O12	127.10 (7)	O2W—Na1—H4W	19.2
O14—Sm1—O23	85.20 (7)	O24^{ii}—Na1—H4W	106.6
O12—Sm1—O23	82.06 (7)	O14^{iii}—Na1—H4W	65.6
O14—Sm1—O21	143.66 (7)	O1W^{iii}—Na1—H4W	132.6
O12—Sm1—O21	79.70 (7)	Sm1—Na1—H4W	52.0
O23—Sm1—O21	126.48 (6)	Sm1^{iii}—Na1—H4W	96.7
O14—Sm1—O3W	74.21 (7)	C16—N11—C12	119.3 (2)
O12—Sm1—O3W	137.98 (7)	C16—N11—Sm1	119.38 (17)
O23—Sm1—O3W	139.51 (7)	C12—N11—Sm1	120.03 (17)
O21—Sm1—O3W	69.82 (7)	C11—O12—Sm1	126.48 (17)
O14—Sm1—N11	63.73 (7)	C17—O14—Sm1	125.19 (17)
O12—Sm1—N11	63.47 (7)	C17—O14—Na1^{i}	120.86 (17)
O23—Sm1—N11	78.80 (7)	Sm1—O14—Na1^{i}	112.64 (9)
O21—Sm1—N11	132.52 (7)	O11—C11—O12	125.1 (2)
O3W—Sm1—N11	119.57 (7)	O11—C11—C12	119.9 (3)
O14—Sm1—N21	139.98 (7)	O12—C11—C12	115.0 (2)
O12—Sm1—N21	75.13 (7)	N11—C12—C13	121.8 (3)
O23—Sm1—N21	63.55 (7)	N11—C12—C11	114.5 (2)
O21—Sm1—N21	63.22 (7)	C13—C12—C11	123.5 (2)
O3W—Sm1—N21	113.19 (7)	C12—C13—C14	118.8 (3)
N11—Sm1—N21	127.06 (7)	C12—C13—H13	120.6
O14—Sm1—O1W	72.65 (7)	C14—C13—H13	120.6
O12—Sm1—O1W	145.01 (7)	C15—C14—C13	119.3 (3)
O23—Sm1—O1W	70.31 (7)	C15—C14—H14	120.4
O21—Sm1—O1W	99.49 (8)	C13—C14—H14	120.4
O3W—Sm1—O1W	70.40 (7)	C14—C15—C16	118.7 (3)
N11—Sm1—O1W	127.92 (8)	C14—C15—H15	120.6

N21—Sm1—O1W	73.54 (7)	C16—C15—H15	120.6
O14—Sm1—O2W	88.52 (7)	N11—C16—C15	122.0 (3)
O12—Sm1—O2W	75.89 (7)	N11—C16—C17	113.7 (2)
O23—Sm1—O2W	146.73 (7)	C15—C16—C17	124.2 (3)
O21—Sm1—O2W	73.75 (7)	O13—C17—O14	125.4 (3)
O3W—Sm1—O2W	68.38 (7)	O13—C17—C16	118.5 (3)
N11—Sm1—O2W	69.18 (7)	O14—C17—C16	116.0 (2)
N21—Sm1—O2W	131.34 (7)	C26—N21—C22	119.5 (2)
O1W—Sm1—O2W	137.96 (7)	C26—N21—Sm1	119.82 (18)
O14—Sm1—Na1	121.67 (6)	C22—N21—Sm1	120.60 (18)
O12—Sm1—Na1	71.69 (5)	C21—O21—Na1	123.25 (17)
O23—Sm1—Na1	150.29 (5)	C21—O21—Sm1	125.80 (18)
O21—Sm1—Na1	36.14 (5)	Na1—O21—Sm1	106.76 (8)
O3W—Sm1—Na1	66.59 (5)	C27—O23—Sm1	125.49 (18)
N11—Sm1—Na1	100.81 (6)	C27—O24—Na1^{iv}	119.5 (2)
N21—Sm1—Na1	95.65 (5)	O22—C21—O21	125.5 (3)
O1W—Sm1—Na1	126.50 (6)	O22—C21—C22	118.7 (2)
O2W—Sm1—Na1	37.82 (5)	O21—C21—C22	115.8 (2)
O14—Sm1—Na1^{i}	34.01 (5)	N21—C22—C23	122.0 (3)
O12—Sm1—Na1^{i}	152.80 (5)	N21—C22—C21	114.2 (2)
O23—Sm1—Na1^{i}	77.40 (5)	C23—C22—C21	123.7 (3)
O21—Sm1—Na1^{i}	127.06 (5)	C24—C23—C22	118.4 (3)
O3W—Sm1—Na1^{i}	65.96 (5)	C24—C23—H23	120.8
N11—Sm1—Na1^{i}	94.89 (5)	C22—C23—H23	120.8
N21—Sm1—Na1^{i}	110.38 (5)	C23—C24—C25	119.8 (3)
O1W—Sm1—Na1^{i}	38.75 (6)	C23—C24—H24	120.1
O2W—Sm1—Na1^{i}	113.29 (5)	C25—C24—H24	120.1
Na1—Sm1—Na1^{i}	131.76 (2)	C24—C25—C26	118.3 (3)
O21—Na1—O5W	165.54 (10)	C24—C25—H25	120.9
O21—Na1—O2W	77.07 (8)	C26—C25—H25	120.9
O5W—Na1—O2W	96.48 (9)	N21—C26—C25	122.0 (3)
O21—Na1—O24^{ii}	83.03 (8)	N21—C26—C27	115.0 (2)
O5W—Na1—O24^{ii}	84.01 (9)	C25—C26—C27	122.9 (3)
O2W—Na1—O24^{ii}	89.74 (8)	O24—C27—O23	124.9 (3)
O21—Na1—O14^{iii}	102.81 (8)	O24—C27—C26	119.8 (3)
O5W—Na1—O14^{iii}	89.13 (9)	O23—C27—C26	115.3 (2)
O2W—Na1—O14^{iii}	83.57 (8)	Sm1—O1W—Na1^{i}	103.62 (8)
O24^{ii}—Na1—O14^{iii}	169.83 (10)	Sm1—O1W—H1W	115
O21—Na1—O1W^{iii}	83.36 (8)	Na1^{i}—O1W—H1W	91
O5W—Na1—O1W^{iii}	108.58 (9)	Sm1—O1W—H2W	118
O2W—Na1—O1W^{iii}	143.37 (9)	Na1^{i}—O1W—H2W	116
O24^{ii}—Na1—O1W^{iii}	118.45 (9)	H1W—O1W—H2W	108.8
O14^{iii}—Na1—O1W^{iii}	70.89 (7)	Na1—O2W—Sm1	101.97 (8)
O21—Na1—Sm1	37.10 (5)	Na1—O2W—H3W	120

O5W—Na1—Sm1	136.15 (8)	Sm1—O2W—H3W	114
O2W—Na1—Sm1	40.21 (5)	Na1—O2W—H4W	90
O24^{ii}—Na1—Sm1	88.46 (6)	Sm1—O2W—H4W	119
O14^{iii}—Na1—Sm1	91.32 (6)	H3W—O2W—H4W	109.6
O1W^{iii}—Na1—Sm1	112.90 (6)	Sm1—O3W—H5W	113
O21—Na1—Sm1^{iii}	92.45 (6)	Sm1—O3W—H6W	112
O5W—Na1—Sm1^{iii}	101.99 (7)	H5W—O3W—H6W	110.0
O2W—Na1—Sm1^{iii}	112.23 (6)	H7W—O4W—H8W	108.0
O24^{ii}—Na1—Sm1^{iii}	156.07 (7)	Na1—O5W—H9W	111
O14^{iii}—Na1—Sm1^{iii}	33.35 (5)	Na1—O5W—H10W	108
O1W^{iii}—Na1—Sm1^{iii}	37.64 (5)	H9W—O5W—H10W	109.3
Sm1—Na1—Sm1^{iii}	102.07 (3)	H11W—O6W—H12W	108.7
O21—Na1—H4W	88.4	H13W—O7W—H14W	109.1
O5W—Na1—H4W	89.1		

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*, *y*+1/2, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*−1/2; (iv) −*x*, *y*−1/2, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W···O22^{i}	0.851	1.931	2.753 (3)	162
O1W—H2W···O5W^{iv}	0.854	1.961	2.794 (3)	165
O2W—H3W···O11^{i}	0.848	1.954	2.790 (3)	169
O2W—H4W···O13^{iii}	0.849	1.884	2.725 (3)	170
O3W—H5W···O24^{ii}	0.851	2.019	2.853 (3)	166
O3W—H6W···O12^{i}	0.845	1.885	2.725 (3)	173
O4W—H7W···O22^{iv}	0.856	2.077	2.907 (4)	163
O4W—H8W···O23	0.855	1.938	2.779 (3)	168
O5W—H9W···O4W^{iii}	0.848	1.961	2.784 (4)	163
O5W—H10W···O7W	0.852	1.939	2.791 (5)	177
O6W—H11W···O13^{iii}	0.854	1.947	2.789 (5)	168
O6W—H12W···O4W^{v}	0.854	2.03	2.858 (5)	163
O7W—H13W···O11^{i}	0.851	2.22	2.989 (4)	151
O7W—H14W···O6W	0.852	1.96	2.754 (7)	155

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (iv) −*x*, *y*−1/2, −*z*+3/2; (iii) *x*, −*y*+1/2, *z*−1/2; (ii) −*x*, *y*+1/2, −*z*+3/2; (v) −*x*+1, *y*+1/2, −*z*+3/2.

Fig. 1

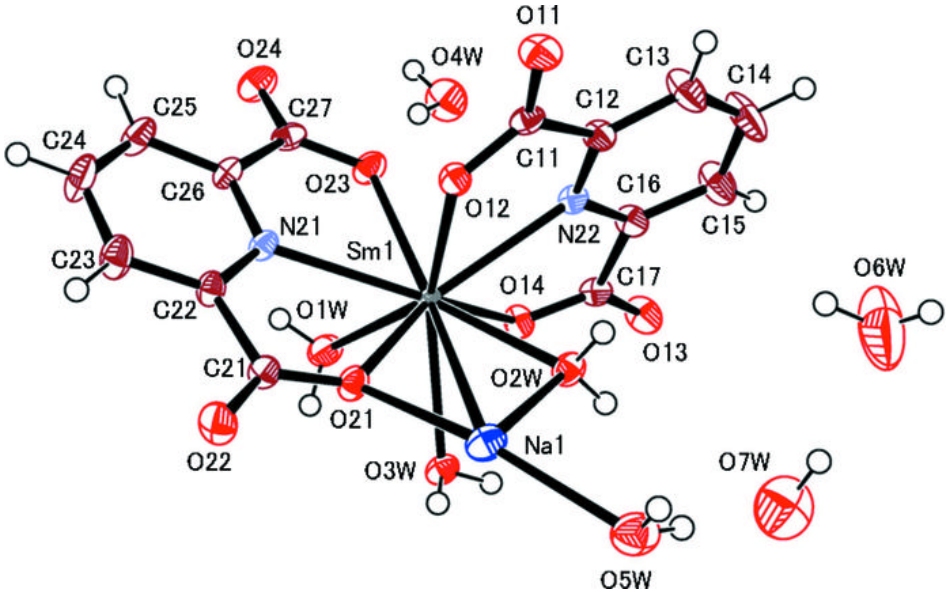
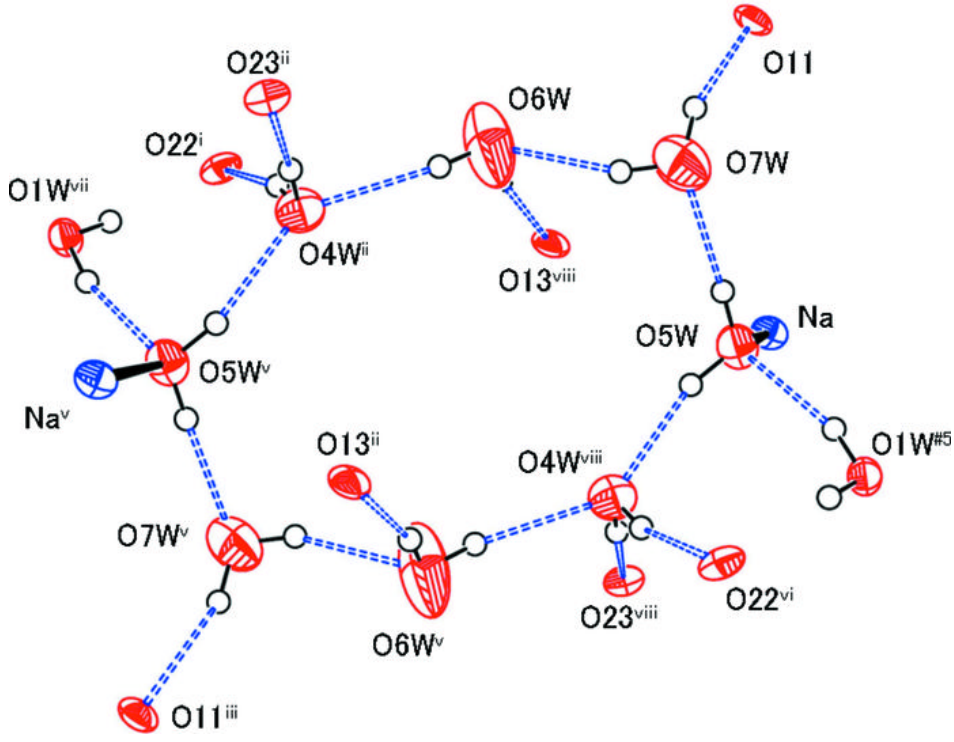

O11
O24
O4W
C13
C14
C25
C27
C12
C24
C11
C26
O23
O12
C16
N21
Sm1
N22
C15
C23
O14
C17
O6W
C22
O1W
O13
C21
O2W
O21
Na1
O22
O3W
O7W
O5W

Fig. 2


O23ii
O22i
O1Wvii
O4Wii
O6W
O13viii
O11
O7W
Na
O5W
O5Wv
Nav
O13ii
O4Wviii
O1W#5
O7Wv
O6Wv
O23viii
O22vi
O11iii