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Crystal structures of two Sm^{III} complexes with dipicolinate $[DPA]^{2-}$ ligands: comparison of luminescent properties of products obtained at different pH values

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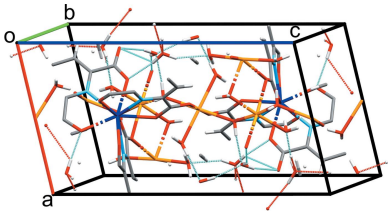
The formation of the two title compounds, $Na_3[Sm(DPA)_3]\cdot14H_2O$ trisodium tris(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)samarate(III) tetradecahydrate, $Na_3[Sm(C_7H_3NO_4)_3]\cdot14H_2O$, and *catena*-poly[[[diaqua(6-carboxypyridine-2-carboxylato-κ^3O^2,N,O^6)samarium(III)]-μ-pyridine-2,6-dicarboxylato-$\kappa^4O^2,N,O^6{:}O^2$] tetrahydrate], $\{[Sm(C_7H_3NO_4)(C_7H_4NO_4)(H_2O)_2]\cdot4H_2O\}_n$, depends on the pH value adjusted with NaOH solution. In both crystal structures, the coordination spheres of the Sm^{III} cations were found to be best described by a tricapped trigonal prism (TTP), with a more regular O_6N_3 donor set for $Na_3[Sm(DPA)_3]\cdot14H_2O$ than that of O_7N_2 for $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$. The supramolecular features of both crystal structures are dominated by O—H···O hydrogen bonds between water molecules and the O atoms of the dipicolinato ligands. Samples were made from solutions at pH = 2, pH = 5, pH = 7, and pH = 10, and the crystals present in each sample were ground to a powder. The powder samples were analyzed with powder X-ray diffraction and luminescence spectroscopy. The splitting of the bands in the luminescence spectra recorded on powders at 77 K was observed to vary with the pH.

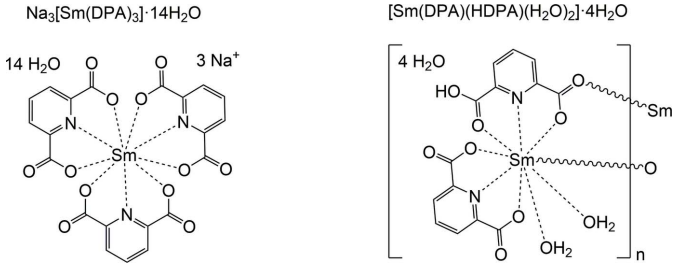
1. Chemical context

The luminescent properties of lanthanide(III) complexes involving the tridentate dipicolinato ligand, $[DPA]^{2-}$, have been studied in great detail (Aebischer *et al.*, 2009; Brayshaw *et al.*, 1995; Chauvin *et al.*, 2004; Kim *et al.*, 1998; Kofod *et al.*, 2020; Mondry & Starynowicz, 1995; Murray *et al.*, 1990; Salaam *et al.*, 2022; Zhou *et al.*, 1994). The luminescent characteristics can be explained by the fact that the formed lanthanide(III) complex with three $[DPA]^{2-}$ ligands coordinating to the central lanthanide(III) cation exhibits an almost perfect tricapped trigonal prism (TTP) coordination environment (Albertsson, 1970; Brayshaw *et al.*, 1995; Kim *et al.*, 1998; Li *et al.*, 2019; Murray *et al.*, 1990; Salaam *et al.*, 2022; Zhou *et al.*, 1994). The luminescence properties have been studied in great depth; however, our knowledge of Sm^{III} with $[DPA]^{2-}$ as the ligand is rather limited (Chuasaard *et al.*, 2017; Kumar *et al.*, 2019; Sharif *et al.*, 2016; Viveros-Andrade *et al.*, 2017).

In the present communication, we report the crystal structures of two compounds with Sm^{III} cations and $[DPA]^{2-}$ ligands, *viz*. salt-like $Na_3[Sm(DPA)_3]\cdot14H_2O$ and polymeric $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$. Both crystallized from mixtures of $Sm(CF_3SO_3)_3$ and H_2DPA solutions at different pH values adjusted with NaOH solution. The amount of the



two compounds crystallized in each sample was found to be controlled by the pH value. This behavior was also monitored by powder X-ray diffraction (PXRD) of the bulk products and their luminescence spectra.



2. Structural commentary

Fig. 1 shows the coordination environment of the central Sm^{III} cation in the crystal structure of $Na_3[Sm(DPA)_3]\cdot14H_2O$ (CCDC number: 2246128). The donor set consists of six oxygen atoms from three chelating $[DPA^{2-}]$ ligands, forming the top and bottom plane of a trigonal prism, and of three capping nitrogen donor atoms placed in the central plane of the trigonal prism. Each of the four Na^{I} cations (two on general positions and two on inversion centers) coordinates by aqua ligands and carboxylate O atoms, thus linking the $[Sm(DPA)_3]^{3-}$ anions into a tri-periodic structure.

Fig. 2 illustrates the coordination environment of the central Sm^{III} cation in the crystal structure of $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$(CCDC number: 2246127). Although the coordination number of 9 is the same as in $Na_3[Sm(DPA)_3]\cdot14H_2O$, here the donor set consists of seven oxygen atoms and two nitrogen atoms. Both $[HDPA]^{-}$ and $[DPA]^{2-}$ ligands *N*,*O*,*O*′-chelate the metal cation. The coordination sphere is completed by two aqua ligands and the carboxylate O atom of another symmetry-related $[DPA]^{2-}$ anion, making it a polymeric structure, with chains of molecules extending parallel to [001].

For both coordination environments of the Sm^{III} cation in the title compounds, a symmetry-deviation analysis was performed to determine the deviation from an ideal coordination environment for coordination number 9. This was achieved by calculating a symmetry-deviation value, σ_{ideal}, using *AlignIt* (Storm Thomsen *et al.*, 2022). More details of this method are described in the supporting information. $Na_3[Sm(DPA)_3]\cdot14H_2O$ was found to be best described as having the shape of a tricapped trigonal prism (TTP), with σ_{ideal} = 1.16, which is in good agreement with what has been reported for other isostructural Ln^{III} complexes (Albertsson, 1970, 1972; Hojnik *et al.*, 2015; Mondry & Starynowicz, 1995; Tancrez *et al.*, 2005; Elahi & Rajasekharan, 2016). The donor set in $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$ is less symmetric compared to $Na_3[Sm(DPA)_3]\cdot14H_2O$, consisting of two nitrogen atoms and seven oxygen atoms. Nevertheless, the Sm^{III} cation in $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$ was also found to have a coordination polyhedron derived from a TTP, with σ_{ideal} = 0.73. This is in good agreement with what was reported for the Eu^{III} analogue (Liu *et al.*, 2014).

3. Supramolecular features

Both $Na_3[Sm(DPA)_3]\cdot14H_2O$ and $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$ contain water molecules, either solely present as solvent molecules for the Na-containing phase (14 per formula unit), or as solvent molecules and as ligands (2 and 4, respectively) for the other phase. Hence, the packing of the structural entities is mainly consolidated by O—H···O hydrogen-bonding networks (Tables 1, 2; Figs. 3, 4). The shortest hydrogen bonds in the two structures are formed between the carboxylate and carboxylic acid groups in

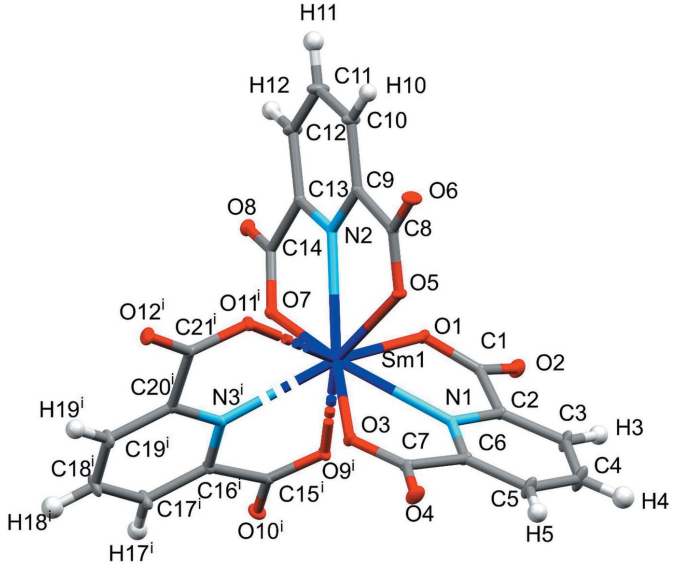


Figure 1
Coordination around the Sm^{III} cation in $Na_3[Sm(DPA)_3]\cdot14H_2O$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) *x*, *y* + 1, *z*.]

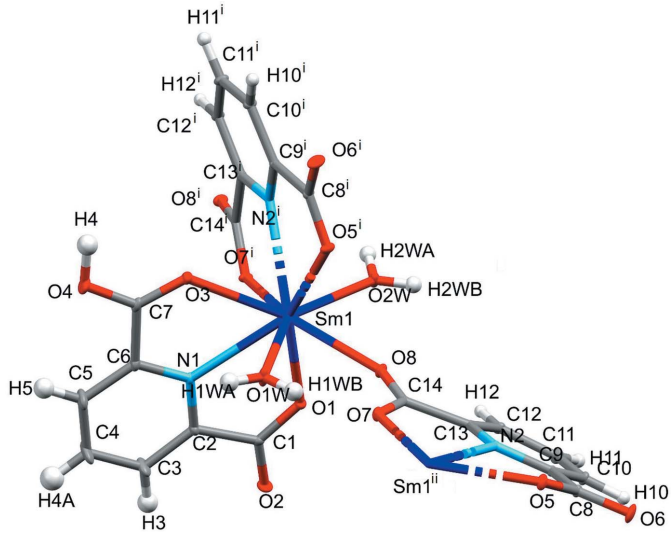


Figure 2
Coordination around the Sm^{III} cation in $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) *x*, $-y+\frac{1}{2}$, $z+\frac{1}{2}$; (ii) *x*, $-y+\frac{1}{2}$, $z-\frac{1}{2}$.]

Table 1
Hydrogen-bond geometry (Å, °) for $Na_3[Sm(DPA)_3]\cdot 14H_2O$.

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O13W^{i}	0.85 (1)	1.98 (1)	2.8163 (19)	167 (3)
O2W—H2WA···O11W^{ii}	0.86 (1)	2.10 (1)	2.927 (2)	160 (3)
O2W—H2WA···O12W^{iii}	0.86 (1)	2.76 (3)	3.2317 (19)	116 (2)
O2W—H2WB···O1W	0.86 (1)	1.90 (1)	2.742 (2)	164 (3)
O4W—H4WA···O5W	0.85 (1)	1.91 (1)	2.741 (2)	167 (3)
O4W—H4WB···O5	0.85 (1)	2.02 (1)	2.8534 (17)	169 (3)
O6W—H6WA···O12^{iv}	0.86 (1)	2.00 (1)	2.8435 (19)	168 (3)
O6W—H6WB···O8^{v}	0.87 (1)	2.09 (2)	2.8645 (18)	149 (3)
O7W—H7WA···O6W	0.84 (1)	1.93 (1)	2.7611 (19)	167 (3)
O7W—H7WB···O3^{vi}	0.85 (1)	2.54 (2)	3.1551 (17)	131 (2)
O7W—H7WB···O5^{vi}	0.85 (1)	2.31 (2)	3.0267 (17)	142 (2)
O8W—H8WA···O10^{vii}	0.84 (1)	1.87 (1)	2.7065 (17)	171 (2)
O9W—H9WA···O6^{vi}	0.85 (1)	1.94 (1)	2.7871 (16)	175 (2)
O9W—H9WB···O1^{viii}	0.85 (1)	1.87 (1)	2.7160 (16)	173 (2)
O10W—H10A···O2W^{viii}	0.85 (1)	1.90 (1)	2.7419 (18)	178 (2)
O11W—H11A···O9	0.85 (1)	1.97 (1)	2.8128 (17)	174 (3)
O11W—H11B···O12W	0.85 (1)	2.13 (1)	2.973 (2)	178 (3)
O12W—H12A···O2^{iii}	0.85 (1)	2.11 (1)	2.9542 (18)	173 (3)
O12W—H12B···O8W^{vii}	0.86 (1)	2.03 (2)	2.8057 (18)	149 (3)
O13W—H13A···O12W^{vii}	0.85 (1)	1.99 (1)	2.8235 (18)	170 (2)
O13W—H13B···O7^{viii}	0.85 (1)	2.09 (1)	2.9274 (17)	171 (2)
O13W—H13B···O8^{viii}	0.85 (1)	2.57 (2)	3.1929 (17)	132 (2)

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

$[DPA]^{2-}$ and $[HDPA]^{-}$ to the water molecules, including, for example, O4W—H4WB···O5W, O8W—H8WA···O10^{vii}, and O9W—H9WB···O1^{viii} in the $Na_3[Sm(DPA)_3]\cdot 14H_2O$ structure, and O1W—H1WB···O7, O4W—H4WA···O2^{v}, and O6W—H6WB···O6 in the $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ structure. Notably, in $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ a very strong hydrogen bond [O4···O4W = 2.4703 (19) Å] is established between the carboxy group of the $[HDPA]^{-}$ ligand and a solvent water molecule.

4. Phase formation at different pH values

By combining a solution of $Sm(CF_3SO_3)_3$ and H_2DPA solutions at different pH values, the two title compounds crystallized in each batch. However, the amounts of each compound in a batch were found to be dependent on the pH value of the

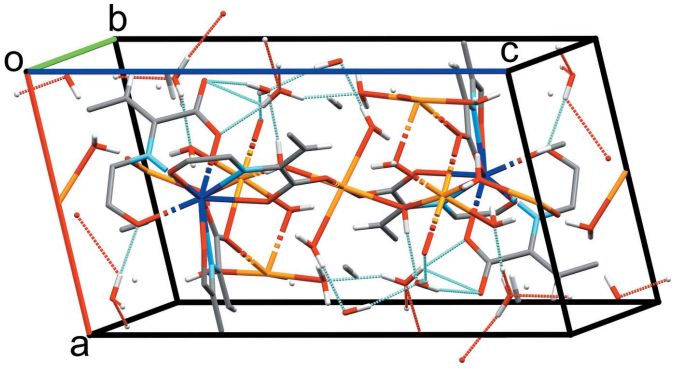


Figure 3
Hydrogen-bonding network in the $Na_3[Sm(DPA)_3]\cdot 14H_2O$ unit cell. Color code: Sm = dark blue, N = light blue, C = gray, H = white, O = red and Na = orange.

Table 2
Hydrogen-bond geometry (Å, °) for $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$.

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O2^{i}	0.85 (1)	1.88 (1)	2.7218 (16)	169 (2)
O1W—H1WB···O7	0.85 (1)	1.91 (1)	2.7103 (15)	157 (2)
O2W—H2WA···O3W	0.85 (1)	1.87 (1)	2.7115 (16)	170 (2)
O2W—H2WB···O6W^{ii}	0.85 (1)	1.90 (1)	2.7193 (16)	163 (2)
O3W—H3WA···O5^{iii}	0.85 (1)	2.04 (1)	2.8679 (15)	164 (2)
O3W—H3WB···O6^{iv}	0.85 (1)	2.01 (1)	2.8568 (16)	173 (2)
O4W—H4WA···O2^{v}	0.85 (1)	1.79 (1)	2.6360 (18)	174 (3)
O4W—H4WB···O5W	0.85 (1)	2.05 (2)	2.773 (2)	143 (3)
O5W—H5WA···O1^{v}	0.85 (1)	2.10 (1)	2.9340 (17)	167 (2)
O5W—H5WB···O6W^{vi}	0.85 (1)	2.14 (1)	2.9579 (19)	162 (2)
O6W—H6WA···O3W^{vii}	0.85 (1)	2.10 (1)	2.8696 (16)	151 (2)
O6W—H6WB···O6	0.85 (1)	1.83 (1)	2.6828 (16)	177 (2)
O4—H4···O4W	1.01 (3)	1.47 (3)	2.4703 (19)	174 (2)

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

H_2DPA solution, which was controlled by addition of NaOH solution. Samples were made at pH = 2, pH = 5, pH = 7, and pH = 10, and the varying amount of the two compounds could be observed from the crystal photographs of each batch (Fig. 5). $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ was the dominating compound at pH = 2 (Fig. 5*a*), while $Na_3[Sm(DPA)_3]\cdot 14H_2O$ was found to dominate at pH = 5, pH = 7, and pH = 10 (Fig. 5*b*,*c*,*d*). This finding is supported by PXRD data recorded from crystals crushed to a powder for all samples (Fig. 6).

5. Analysis of luminescence spectra for samples obtained at different pH values

The crystal field splitting is sensitive to the coordination environment and the donor atoms (Eliseeva & Bünzli, 2010). As Sm^{III} is a luminescent lanthanide(III) cation, the crystal field splitting of the spin-orbit defined $^{S}L_J$ term into the individual electronic states, here double-degenerate Kramers

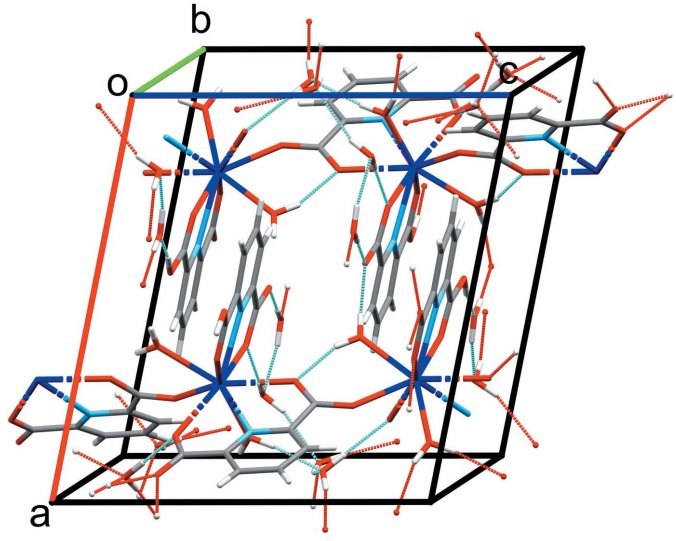


Figure 4
Hydrogen-bonding network in the $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ unit cell. Color code: Sm = dark blue, N = light blue, C = gray, H = white, and O = red.

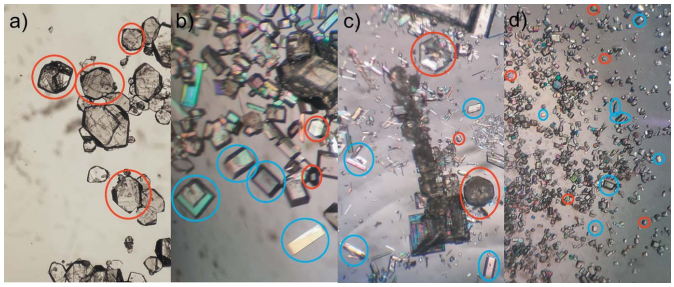


Figure 5
Crystal photographs from selected samples obtained at different pH values; $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ crystals are circled in red and $Na_3[Sm(DPA)_3]\cdot 14H_2O$ in blue. (*a*) Crystals obtained from a solution at pH = 2, where $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ dominates. (*b*) Crystals obtained from a solution at pH = 5, where an almost equal distribution of $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ and $Na_3[Sm(DPA)_3]\cdot 14H_2O$ was found. (*c*) Crystals obtained from a solution at pH = 7, where more $Na_3[Sm(DPA)_3]\cdot 14H_2O$ than $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ crystallized. (*d*) Crystals obtained from a solution at pH = 10, where $Na_3[Sm(DPA)_3]\cdot 14H_2O$ dominates. The images in each panel were selected from three crystallization batches performed at each pH value.

doublets defined by $\pm m_J$ values, can be observed from the luminescence spectra (Cheisson & Schelter, 2019; Wybourne, 2004; Chen *et al.*, 2005; Mortensen *et al.*, 2022; Carnall *et al.*, 1968). Because Sm^{III} is a Kramers cation, it has an uneven number of electrons ($4f^5$) and all states will be double degenerate without the presence of a magnetic field (Eliseeva & Bünzli, 2010). The electronic states in Sm^{III} are a complicated $^6H_{5/2}$ ground state and a $^4G_{5/2}$ emitting state that both have a large multiplicity (Eliseeva & Bünzli, 2010; Chen *et al.*, 2005). The emitting state, $^4G_{5/2}$, can split into maximum Kramers levels. The maximum splitting is calculated as $(2J + 1)/2$ (Eliseeva & Bünzli, 2010). For the states observed from the emission spectra, the maximum splitting is three, four, five, and six for $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$, respectively. To avoid deconvolution of nine bands or more in each transition, the spectra were recorded at 77 K for the polycrystalline material. At 77 K, one of the $\pm m_J$ doublets is predominately populated in $^4G_{5/2}$. Thus, only three bands will be observed for the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition (Lupei *et al.*, 2012; Chen *et al.*, 2005; Skaudzius *et al.*, 2018; Sakirzanovas *et al.*, 2011). The number of observed bands for a $^4G_{5/2} \rightarrow {}^6H_J$ transition should correspond to the maximum splitting of ^6H_J (Eliseeva & Bünzli, 2010; Lupei *et al.*, 2012; Chen *et al.*, 2005; Skaudzius *et al.*, 2018; Sakirzanovas *et al.*, 2011). Additional bands can be an indicator for transitions from the less populated higher-energy $^4G_{5/2}$ states or the presence of more than one emitting species (Chen *et al.*, 2005; Sakirzanovas *et al.*, 2011). Because both $Na_3[Sm(DPA)_3]\cdot 14H_2O$ and $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ are present in the samples, more bands than the maximum splitting are expected (Judd, 1962; Ofelt, 1962).

The luminescent properties of the samples obtained at different pH values were investigated in order to evaluate the effect of having different compounds present in each sample. From the emission spectra it was apparent that there is a change in the luminescenct properties with the change in compound distribution at different pH values (Fig. 7).

Five bands are observed for the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition in the emission spectra from all samples. This indicates that more than one species is present in the solid reaction product, as this is one more band than the maximum splitting for $^6H_{7/2}$ would allow per Sm^{III} atom. Hence, Sm^{III} exists in more than one coordination environment in the powdered samples of the bulk material. Thermal populations of more Kramers levels in $^4G_{5/2}$ would result in eight bands (Lupei *et al.*, 2012; Chen *et al.*, 2005; Skaudzius *et al.*, 2018, Sakirzanovas *et al.*, 2011). As this is not the case, the five bands are ascribed as a result of the presence of both $Na_3[Sm(DPA)_3]\cdot 14H_2O$ and $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$, which both have a significant contribution to the emission spectrum of the samples obtained at different pH.

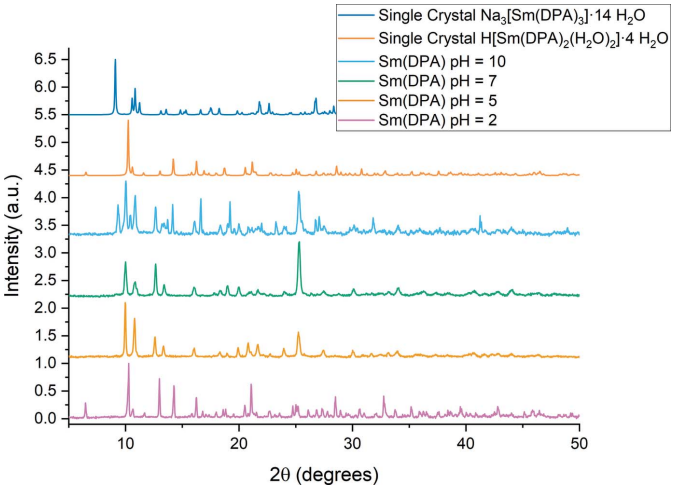


Figure 6
PXRD pattern of the bulk for samples prepared from solution at pH = 2, pH = 5, pH = 7, and pH = 10, as well as simulated PXRD pattern on basis of the current single-crystal data.

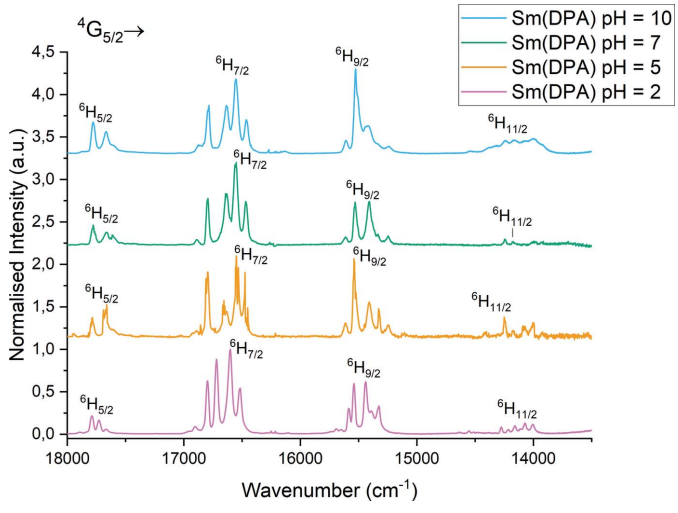


Figure 7
Normalized emission spectra in 2-methyltetrahydrofuran glass at 77 K (excitation at 394 nm) for samples prepared at pH = 2, pH = 5, pH = 7, and pH = 10.

The change in the luminescent properties is apparent in the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, where the splitting patterns clearly varies. Additionally, there is a change in the intensity of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition compared to the the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. At pH = 2, the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is the most intense, whereas at pH = 10, the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition has a higher intensity compared to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. Also, the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition increased in intensity compared to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ band with increasing pH. However, no clear spectral components could be assigned to either $Na_3[Sm(DPA)_3]\cdot 14H_2O$ or $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$. Additional spectra are included in the supporting information.

6. Database survey

$Na_3[Sm(DPA)_3]\cdot 14H_2O$ is isostructural with other $Na_3[Ln(DPA)_3]\cdot 14H_2O$ compounds previously reported for La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Yb^{III}, and Lu^{III} (Albertsson, 1970; Hojnik *et al.*, 2015; Albertsson, 1972; Albertsson *et al.*, 1972; Mondry & Starynowicz, 1995; Tancrez *et al.*, 2005; Elahi & Rajasekharan, 2016). Crystal data of $Na_3[Sm(DPA)_3]\cdot 14H_2O$ have been deposited at the CCDC (CSD code SOPGOT; Hu *et al.*, 1989); however, without atomic coordinates, which motivated us to reinvestigate the crystal structure.

$[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ is isostructural with other $[Ln(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ compounds previously reported for Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, and Er^{III} (Brayshaw *et al.*, 2005; Cheng *et al.*, 2007; Chuasaard *et al.*, 2017; Ghosh & Bharadwaj, 2003; Hou *et al.*, 2011; Kang, 2011; Liu *et al.*, 2005; Moghzi *et al.*, 2020; Najafi *et al.*, 2017; Rafizadeh *et al.*, 2005; Song *et al.*, 2005; Wang *et al.*, 2012; Xu *et al.*, 2009; Kong *et al.*, 2022). The crystal structure of $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$ has been reported previously several times (CSD code FONCUH; best result in terms of reliability factors: FONCUH01; Rafizadeh *et al.*, 2005). For interpretation of the luminescence spectra and a comparison with $Na_3[Sm(DPA)_3]\cdot 14H_2O$, we have also reinvestigated the crystal structure of $[Sm(DPA)(HDPA)(H_2O)_2]\cdot 4H_2O$.

7. Synthesis and crystallization

All chemicals were used as received without further purification. All crystallization experiments were conducted three times.

0.2 *M* $Sm(CF_3SO_3)_3$ stock solution

$Sm(CF_3SO_3)_3$ (2.39 g, 0.400 mmol; 98% from STREM Chemicals) was used to create a 0.20 *M* stock solution by dissolving the salt in water to create a solution with a volume of 20.0±0.04 ml.

0.2 *M* H_2DPA stock solution

H_2DPA (pyridine-2,6-dicarboxylic acid; 0.669 g, 4.01 mmol; Riedel-De Haën) was used to create a 0.2 *M* stock solution by dissolving the acid in water to create a solution with a volume of 20±0.04 ml.

Sm(DPA) at pH = 2 – crystallization

1.0 ml of the 0.2 *M* $Sm(CF_3SO_3)_3$ stock solution was added to a sample vial with 3.0 ml of the 0.2 *M* H_2DPA stock solution. The sample was heated at 353 K for 1 h. The sample vial was closed with a lid and left in a dark place. After 1 d crystals had formed.

Sm(DPA) at pH = 5 – crystallization

NaOH (1.0 *M*) was added to the H_2DPA stock solution to adjust the pH to 5. 0.5 ml of the 0.2 *M* $Sm(CF_3SO_3)_3$ solution were added to a sample vial with 1.5 ml of the 0.2 *M* H_2DPA stock solution. The sample was heated at 353 K for 1 h. The sample vial was placed in a container with acetone, placing a lid on top of the container and left for acetone diffusion. After 3 d crystals had formed.

Sm(DPA) at pH = 7 – crystallization

NaOH (1.0 *M*) was added to the H_2DPA stock solution to adjust the pH to 7. 0.5 ml of the 0.2 *M* $Sm(CF_3SO_3)_3$ solution were added to a sample vial with 1.5 ml of the 0.2 *M* H_2DPA stock solution. The sample was heated at 353 K for 1 h. The sample was then filtered through a Q-Max RR syringe filter from Frisinette and transferred to a vial. The latter was placed in a container with acetone, placing a lid on top of the container and left for an acetone diffusion. After 1 d crystals had formed.

Sm(DPA) at pH = 10 – crystallization

NaOH (1.0 *M*) was added to the H_2DPA stock solution to adjust the pH to 10. 0.5 ml of the 0.2 *M* $Sm(CF_3SO_3)_3$ solution were added to a sample vial with 1.5 ml of the 0.2 *M* H_2DPA stock solution. The sample was heated at 353 K for 1 h. The sample was then filtered through a Q-Max RR syringe filter from Frisinette and transferred to a vial. The later was placed in a container with acetone, placing a lid on top of the container and left for an acetone diffusion. After 1 d crystals had formed.

8. Other experimental procedures

For both PXRD and optical spectroscopy measurements, the crystals, which had precipitated in each sample, were collected by suction filtration with a vacuum pump. The crystals were removed from the filter, dried in air and ground to a powder.

Powder X-ray Diffraction

PXRD diffractograms were recorded for all samples prepared at different pH values. Data were collected using a Bruker D8 Advance diffractometer using a Cu *Kα* source (λ = 1.5406 Å). Samples were measured using a low-background silica sample holder at 293 K.

Optical Spectroscopy

Crystal powders from all samples prepared at different pH were added to a 5.0 mm diameter NMR silica cylinder (Bruker) together with 2-methyltetrahydrofuran glass. The samples were cooled using liquid nitrogen and were measured using a cold-finger setup. This setup was used for both the emission and excitation spectra and for determination of luminescent lifetimes.

Emission and excitation spectra were measured with a xenon arc lamp as the excitation source on a PTI QuantaMaster8075 from Horiba Scientific.

Table 3
Experimental details.

	$Na_3[Sm(C_7H_3NO_4)_3]\cdot14H_2O$	$[Sm(C_7H_3NO_4)(C_7H_4NO_4)(H_2O)_2]\cdot4H_2O$
Crystal data		
M_r	966.85	589.66
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	10.2674 (10), 10.9688 (10), 17.1570 (16)	13.9292 (8), 11.1969 (7), 12.8086 (7)
α, β, γ (°)	73.835 (3), 77.573 (3), 72.894 (3)	90, 103.049 (2), 90
V (Å^3)	1754.9 (3)	1946.1 (2)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.81	3.10
Crystal size (mm)	0.78 × 0.58 × 0.26	0.48 × 0.40 × 0.15
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2019)	Multi-scan (*SADABS*; Bruker, 2019)
T_{min}, T_{max}	0.615, 0.747	0.575, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	107477, 13465, 12700	74345, 7424, 6679
R_{int}	0.045	0.044
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.771	0.769
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.058, 1.11	0.018, 0.042, 1.08
No. of reflections	13465	7424
No. of parameters	574	319
No. of restraints	28	12
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.32, −1.15	0.73, −1.09

Computer programs: *APEX2* and *SAINT* (Bruker, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

For emission spectroscopy, an excitation wavelength at 401 nm (24938 cm^{-1}) was used. Emission was detected from 550 nm (18182 cm^{-1}) to 760 nm (13158 cm^{-1}). The emission slits were kept at 1.0 nm for the two outermost slits and 5.0 nm or the middle slit for all samples, and the excitation slits were all kept at 8.0 nm. The voltage bias was kept at 3.2 V for the reference detector.

For excitation spectroscopy, an emission wavelength at 598 nm (16722 cm^{-1}) was used. Excitation was detected from 250 nm (40000 cm^{-1}) to 590 nm (16949 cm^{-1}). Emission slits were all kept at 8.0 nm and excitation slits were kept at 1.0 nm for the two outermost slits and 5.0 nm for the middle slit for all samples. The voltage bias was kept at 6.8 V for the reference detector.

Luminescence Lifetimes

The luminescence lifetimes were determined for all powder samples using a TCSPC FluoTime300 from PicoQuant. The excitation wavelength was 405 nm (24691 cm^{-1}), and the emission wavelength 600 nm (16667 cm^{-1}). The effective sync rate was kept at 1 kHz, with 5000 pulses, a period length of 1.0 ms, a burst length of 625 µs, and a time/channel at 80 ns. The temperature was kept at 298 K. The luminescence lifetimes were fitted using a mono-exponential decay function using the software *EasyTau 2* (PicoQuant, 2018).

9. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms attached to aromatic carbon atoms were added automatically using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. All hydrogen atoms of water molecules were discernible in difference-Fourier maps. They were refined with a distance restraint of 0.85 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$. The H atom of the carboxylate group (H4) in $[Sm(DPA)(HDPA)(H_2O)_2]\cdot4H_2O$ was found in difference-Fourier maps and was refined freely. The comparatively high residual positive electron density in $Na_3[Sm(DPA)_3]\cdot14H_2O$ is located at distances of ≃1.4 Å from atoms H6*WA* and H6*WB*. Contributions of additional atoms and/or disorder did not result in other reasonable models.

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supporting information

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Crystal structures of two Sm^{III} complexes with dipicolinate $[DPA]^{2-}$ ligands: comparison of luminescent properties of products obtained at different pH values

Sabina Svava Mortensen and Thomas Just Sørensen

Computing details

For both structures, data collection: *APEX2* (Bruker, 2019); cell refinement: *SAINT* (Bruker, 2019); data reduction: *SAINT* (Bruker, 2019); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Trisodium tris(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)samarate(III) tetradecahydrate (I)

Crystal data

$Na_3[Sm(C_7H_3NO_4)_3]\cdot 14H_2O$
$M_r = 966.85$
Triclinic, $P\overline{1}$
$a = 10.2674$ (10) Å
$b = 10.9688$ (10) Å
$c = 17.1570$ (16) Å
$\alpha = 73.835$ (3)°
$\beta = 77.573$ (3)°
$\gamma = 72.894$ (3)°
$V = 1754.9$ (3) Å^3
$Z = 2$
$F(000) = 974$
$D_x = 1.830$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9982 reflections
$\theta = 2.4$–$33.2°$
$\mu = 1.81$ mm^{-1}
$T = 100$ K
Prism, colourless
0.78 × 0.58 × 0.26 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2019)
$T_{min} = 0.615$, $T_{max} = 0.747$
107477 measured reflections
13465 independent reflections
12700 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 33.2°$, $\theta_{min} = 2.0°$
$h = -15\rightarrow15$
$k = -16\rightarrow16$
$l = -26\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.058$
$S = 1.11$
13465 reflections
574 parameters
28 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 2.2772P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 3.32$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sm1	0.48815 (2)	0.74844 (2)	0.75088 (2)	0.00321 (2)
Na1	0.500000	0.500000	0.500000	0.00980 (16)
Na2	0.50358 (6)	0.25158 (6)	0.75459 (4)	0.00837 (11)
Na3	0.14568 (7)	1.30026 (7)	0.74024 (5)	0.01388 (13)
Na4	0.500000	0.000000	1.000000	0.00854 (16)
O1	0.32228 (11)	0.96519 (11)	0.72600 (7)	0.00735 (19)
O2	0.10717 (12)	1.09223 (11)	0.74353 (8)	0.0111 (2)
O3	0.42909 (11)	0.53805 (11)	0.78804 (7)	0.00775 (19)
O4	0.29239 (12)	0.41204 (11)	0.78682 (8)	0.0117 (2)
O5	0.47032 (11)	0.71148 (11)	0.62035 (7)	0.00748 (19)
O6	0.55858 (13)	0.70498 (12)	0.49004 (7)	0.0109 (2)
O7	0.60619 (11)	0.90222 (11)	0.77079 (7)	0.00738 (19)
O8	0.69830 (11)	1.07466 (11)	0.72233 (7)	0.00862 (19)
O9	0.39263 (11)	−0.21216 (11)	0.88660 (7)	0.00830 (19)
O10	0.43084 (12)	−0.19347 (12)	1.00559 (7)	0.0103 (2)
O11	0.70788 (11)	−0.41510 (11)	0.71542 (7)	0.00843 (19)
O12	0.89428 (11)	−0.57662 (11)	0.74960 (7)	0.0100 (2)
N1	0.23451 (12)	0.75259 (12)	0.76118 (8)	0.0053 (2)
N2	0.60933 (13)	0.87570 (12)	0.62274 (8)	0.0055 (2)
N3	0.63346 (13)	−0.37902 (12)	0.86490 (8)	0.0059 (2)
C1	0.19098 (15)	0.98546 (14)	0.73974 (9)	0.0061 (2)
C2	0.13830 (14)	0.86619 (14)	0.75074 (9)	0.0065 (2)
C3	0.00166 (16)	0.87325 (16)	0.74916 (11)	0.0123 (3)
H3	−0.063565	0.953392	0.742608	0.015*
C4	−0.03531 (17)	0.75749 (17)	0.75761 (13)	0.0169 (3)
H4	−0.125743	0.759170	0.755871	0.020*
C5	0.06437 (16)	0.63935 (16)	0.76868 (12)	0.0132 (3)
H5	0.042040	0.560674	0.774643	0.016*
C6	0.19804 (14)	0.64151 (14)	0.77064 (9)	0.0065 (2)
C7	0.31407 (15)	0.51924 (14)	0.78274 (9)	0.0066 (2)
C8	0.54421 (15)	0.74740 (14)	0.55205 (9)	0.0065 (2)
C9	0.61918 (15)	0.84837 (14)	0.55005 (9)	0.0063 (2)
C10	0.69509 (17)	0.90667 (16)	0.47973 (10)	0.0110 (3)
H10	0.702967	0.884285	0.430172	0.013*
C11	0.75889 (19)	0.99887 (18)	0.48485 (10)	0.0141 (3)
H11	0.809417	1.039876	0.438477	0.017*
C12	0.74666 (17)	1.02945 (16)	0.55983 (10)	0.0114 (3)
H12	0.787242	1.092062	0.564500	0.014*
C13	0.67220 (15)	0.96399 (14)	0.62765 (9)	0.0062 (2)

C14	0.65829 (14)	0.98425 (14)	0.71282 (9)	0.0059 (2)
C15	0.46267 (15)	−0.24388 (14)	0.94523 (9)	0.0068 (2)
C16	0.59566 (15)	−0.34874 (15)	0.93826 (9)	0.0072 (2)
C17	0.67366 (17)	−0.40708 (17)	1.00180 (10)	0.0134 (3)
H17	0.646641	−0.382103	1.051571	0.016*
C18	0.79362 (18)	−0.50416 (19)	0.98895 (11)	0.0167 (3)
H18	0.847093	−0.546644	1.030714	0.020*
C19	0.83254 (16)	−0.53684 (17)	0.91333 (10)	0.0122 (3)
H19	0.911577	−0.602159	0.903756	0.015*
C20	0.75090 (15)	−0.46988 (14)	0.85216 (9)	0.0066 (2)
C21	0.78861 (15)	−0.49090 (14)	0.76585 (9)	0.0068 (2)
O1W	0.04883 (15)	1.24786 (15)	1.03199 (9)	0.0206 (3)
H1WA	−0.008 (2)	1.201 (2)	1.0422 (18)	0.031*
H1WB	0.1197 (19)	1.203 (2)	1.0544 (16)	0.031*
O2W	0.14195 (14)	1.18981 (14)	0.88110 (9)	0.0173 (2)
H2WA	0.122 (3)	1.1150 (15)	0.8944 (17)	0.026*
H2WB	0.114 (3)	1.223 (3)	0.9238 (11)	0.026*
O3W	0.13440 (13)	1.42018 (13)	0.60105 (9)	0.0175 (3)
H3WA	0.190 (2)	1.467 (2)	0.5968 (17)	0.026*
H3WB	0.0554 (15)	1.470 (2)	0.5944 (17)	0.026*
O4W	0.28586 (13)	0.60772 (13)	0.57011 (8)	0.0153 (2)
H4WA	0.221 (2)	0.665 (2)	0.5476 (15)	0.023*
H4WB	0.331 (2)	0.644 (2)	0.5892 (15)	0.023*
O5W	0.05492 (16)	0.76417 (16)	0.50456 (10)	0.0248 (3)
H5WA	−0.011 (2)	0.728 (3)	0.5275 (18)	0.037*
H5WB	0.078 (3)	0.751 (3)	0.4552 (9)	0.037*
O6W	0.16147 (15)	0.72091 (14)	0.34836 (9)	0.0194 (3)
H6WA	0.133 (3)	0.686 (3)	0.3180 (15)	0.029*
H6WB	0.179 (3)	0.7923 (17)	0.3158 (14)	0.029*
O7W	0.42934 (13)	0.58120 (12)	0.36593 (8)	0.0119 (2)
H7WA	0.3439 (11)	0.614 (2)	0.3659 (16)	0.018*
H7WB	0.444 (3)	0.5135 (17)	0.3476 (15)	0.018*
O8W	0.62364 (12)	0.31062 (11)	0.83406 (7)	0.0097 (2)
H8WA	0.597 (2)	0.276 (2)	0.8833 (7)	0.015*
H8WB	0.569 (2)	0.3851 (13)	0.8228 (15)	0.015*
O9W	0.37670 (12)	0.20510 (11)	0.67876 (7)	0.00911 (19)
H9WA	0.391 (2)	0.233 (2)	0.6273 (6)	0.014*
H9WB	0.365 (2)	0.1282 (13)	0.6909 (15)	0.014*
O10W	0.42198 (12)	0.09077 (12)	0.86809 (7)	0.0103 (2)
H10A	0.3359 (10)	0.122 (2)	0.8710 (15)	0.016*
H10B	0.442 (3)	0.0245 (17)	0.8480 (14)	0.016*
O11W	0.12847 (13)	−0.08265 (14)	0.95098 (9)	0.0170 (2)
H11A	0.2100 (14)	−0.117 (3)	0.9312 (16)	0.025*
H11B	0.132 (3)	−0.091 (3)	1.0010 (7)	0.025*
O12W	0.13612 (13)	−0.11638 (14)	1.12813 (9)	0.0168 (2)
H12A	0.0624 (18)	−0.111 (3)	1.1623 (13)	0.025*
H12B	0.187 (2)	−0.1918 (15)	1.1490 (16)	0.025*
O13W	0.71107 (12)	−0.07398 (12)	0.91019 (7)	0.0118 (2)

H13A	0.751 (2)	−0.0124 (18)	0.8938 (15)	0.018*
H13B	0.688 (3)	−0.077 (2)	0.8664 (10)	0.018*
O14W	0.87868 (14)	−0.40551 (14)	0.56379 (8)	0.0173 (2)
H14A	0.820 (2)	−0.413 (3)	0.6072 (11)	0.026*
H14B	0.849 (3)	−0.412 (3)	0.5230 (12)	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sm1	0.00305 (3)	0.00300 (3)	0.00357 (3)	−0.00045 (2)	−0.00041 (2)	−0.00111 (2)
Na1	0.0114 (4)	0.0097 (4)	0.0094 (4)	−0.0041 (3)	−0.0013 (3)	−0.0026 (3)
Na2	0.0084 (3)	0.0083 (3)	0.0095 (3)	−0.0017 (2)	−0.0021 (2)	−0.0035 (2)
Na3	0.0141 (3)	0.0118 (3)	0.0153 (3)	−0.0031 (2)	−0.0016 (3)	−0.0031 (3)
Na4	0.0096 (4)	0.0086 (4)	0.0074 (4)	−0.0014 (3)	−0.0015 (3)	−0.0024 (3)
O1	0.0053 (4)	0.0053 (4)	0.0107 (5)	−0.0013 (3)	−0.0009 (4)	−0.0009 (4)
O2	0.0087 (5)	0.0051 (5)	0.0181 (6)	0.0005 (4)	−0.0007 (4)	−0.0038 (4)
O3	0.0057 (4)	0.0051 (4)	0.0116 (5)	−0.0010 (3)	−0.0013 (4)	−0.0008 (4)
O4	0.0104 (5)	0.0048 (5)	0.0199 (6)	−0.0029 (4)	0.0004 (4)	−0.0039 (4)
O5	0.0089 (4)	0.0099 (5)	0.0054 (4)	−0.0053 (4)	0.0004 (4)	−0.0025 (4)
O6	0.0172 (5)	0.0126 (5)	0.0061 (5)	−0.0080 (4)	0.0004 (4)	−0.0041 (4)
O7	0.0092 (5)	0.0075 (5)	0.0064 (5)	−0.0036 (4)	−0.0016 (4)	−0.0013 (4)
O8	0.0089 (5)	0.0072 (5)	0.0121 (5)	−0.0031 (4)	−0.0019 (4)	−0.0044 (4)
O9	0.0072 (4)	0.0106 (5)	0.0060 (5)	0.0009 (4)	−0.0017 (4)	−0.0031 (4)
O10	0.0138 (5)	0.0098 (5)	0.0069 (5)	−0.0004 (4)	−0.0012 (4)	−0.0043 (4)
O11	0.0069 (4)	0.0097 (5)	0.0071 (5)	0.0006 (4)	−0.0012 (4)	−0.0020 (4)
O12	0.0064 (4)	0.0098 (5)	0.0127 (5)	0.0014 (4)	−0.0005 (4)	−0.0052 (4)
N1	0.0051 (5)	0.0045 (5)	0.0060 (5)	−0.0007 (4)	−0.0003 (4)	−0.0014 (4)
N2	0.0059 (5)	0.0047 (5)	0.0061 (5)	−0.0016 (4)	−0.0009 (4)	−0.0015 (4)
N3	0.0060 (5)	0.0049 (5)	0.0064 (5)	−0.0010 (4)	−0.0007 (4)	−0.0014 (4)
C1	0.0065 (6)	0.0045 (6)	0.0070 (6)	−0.0012 (4)	−0.0011 (4)	−0.0008 (5)
C2	0.0053 (5)	0.0054 (6)	0.0085 (6)	−0.0009 (4)	−0.0007 (4)	−0.0017 (5)
C3	0.0053 (6)	0.0076 (6)	0.0239 (8)	0.0002 (5)	−0.0031 (5)	−0.0048 (6)
C4	0.0070 (6)	0.0100 (7)	0.0358 (10)	−0.0024 (5)	−0.0046 (6)	−0.0071 (7)
C5	0.0068 (6)	0.0081 (7)	0.0260 (9)	−0.0025 (5)	−0.0019 (6)	−0.0057 (6)
C6	0.0054 (5)	0.0050 (6)	0.0092 (6)	−0.0015 (4)	0.0006 (4)	−0.0028 (5)
C7	0.0059 (5)	0.0052 (6)	0.0079 (6)	−0.0008 (4)	0.0006 (4)	−0.0018 (5)
C8	0.0075 (6)	0.0065 (6)	0.0060 (6)	−0.0022 (5)	−0.0012 (4)	−0.0015 (5)
C9	0.0074 (6)	0.0062 (6)	0.0056 (6)	−0.0023 (5)	−0.0011 (4)	−0.0010 (5)
C10	0.0148 (7)	0.0134 (7)	0.0070 (6)	−0.0086 (6)	0.0001 (5)	−0.0018 (5)
C11	0.0204 (8)	0.0174 (8)	0.0077 (7)	−0.0131 (6)	0.0019 (6)	−0.0017 (6)
C12	0.0151 (7)	0.0125 (7)	0.0093 (6)	−0.0099 (6)	0.0002 (5)	−0.0016 (5)
C13	0.0067 (5)	0.0054 (6)	0.0070 (6)	−0.0022 (4)	−0.0013 (4)	−0.0011 (5)
C14	0.0037 (5)	0.0055 (6)	0.0091 (6)	−0.0001 (4)	−0.0022 (4)	−0.0026 (5)
C15	0.0079 (6)	0.0062 (6)	0.0054 (6)	−0.0018 (5)	0.0003 (4)	−0.0010 (5)
C16	0.0074 (6)	0.0071 (6)	0.0067 (6)	−0.0004 (5)	−0.0022 (5)	−0.0014 (5)
C17	0.0128 (7)	0.0162 (7)	0.0085 (7)	0.0035 (6)	−0.0050 (5)	−0.0033 (6)
C18	0.0136 (7)	0.0210 (8)	0.0108 (7)	0.0062 (6)	−0.0072 (6)	−0.0033 (6)
C19	0.0091 (6)	0.0129 (7)	0.0110 (7)	0.0038 (5)	−0.0041 (5)	−0.0023 (5)

C20	0.0061 (5)	0.0057 (6)	0.0073 (6)	−0.0007 (4)	−0.0015 (4)	−0.0011 (5)
C21	0.0051 (5)	0.0067 (6)	0.0087 (6)	−0.0016 (4)	0.0003 (5)	−0.0029 (5)
O1W	0.0154 (6)	0.0214 (7)	0.0224 (7)	0.0007 (5)	−0.0086 (5)	−0.0020 (5)
O2W	0.0145 (6)	0.0194 (6)	0.0200 (6)	−0.0046 (5)	−0.0026 (5)	−0.0076 (5)
O3W	0.0104 (5)	0.0145 (6)	0.0238 (7)	−0.0024 (4)	0.0002 (5)	−0.0012 (5)
O4W	0.0120 (5)	0.0174 (6)	0.0193 (6)	−0.0056 (5)	−0.0020 (4)	−0.0070 (5)
O5W	0.0208 (7)	0.0254 (8)	0.0269 (8)	−0.0074 (6)	−0.0052 (6)	−0.0008 (6)
O6W	0.0188 (6)	0.0178 (6)	0.0235 (7)	−0.0049 (5)	−0.0067 (5)	−0.0045 (5)
O7W	0.0143 (5)	0.0099 (5)	0.0121 (5)	−0.0025 (4)	−0.0024 (4)	−0.0040 (4)
O8W	0.0101 (5)	0.0073 (5)	0.0109 (5)	−0.0004 (4)	−0.0035 (4)	−0.0010 (4)
O9W	0.0127 (5)	0.0082 (5)	0.0078 (5)	−0.0047 (4)	−0.0021 (4)	−0.0014 (4)
O10W	0.0105 (5)	0.0090 (5)	0.0102 (5)	0.0008 (4)	−0.0025 (4)	−0.0027 (4)
O11W	0.0093 (5)	0.0195 (6)	0.0188 (6)	0.0020 (5)	−0.0015 (5)	−0.0056 (5)
O12W	0.0098 (5)	0.0183 (6)	0.0216 (7)	−0.0027 (5)	0.0017 (5)	−0.0076 (5)
O13W	0.0107 (5)	0.0146 (6)	0.0096 (5)	−0.0023 (4)	−0.0026 (4)	−0.0023 (4)
O14W	0.0132 (6)	0.0215 (6)	0.0118 (6)	−0.0012 (5)	−0.0001 (4)	−0.0002 (5)

Geometric parameters (Å, º)

Sm1—O1	2.4700 (11)	N3—C20	1.3400 (19)
Sm1—O3	2.4367 (11)	C1—C2	1.508 (2)
Sm1—O5	2.4371 (11)	C2—C3	1.388 (2)
Sm1—O7	2.4764 (11)	C3—H3	0.9300
Sm1—O9^{i}	2.4288 (11)	C3—C4	1.391 (2)
Sm1—O11^{i}	2.5128 (11)	C4—H4	0.9300
Sm1—N1	2.5597 (12)	C4—C5	1.389 (2)
Sm1—N2	2.5428 (12)	C5—H5	0.9300
Sm1—N3^{i}	2.5522 (13)	C5—C6	1.387 (2)
Na1—O6^{ii}	2.4461 (12)	C6—C7	1.507 (2)
Na1—O6	2.4461 (12)	C8—C9	1.513 (2)
Na1—O4W	2.4087 (13)	C9—C10	1.389 (2)
Na1—O4W^{ii}	2.4087 (13)	C10—H10	0.9300
Na1—H4WB	2.54 (3)	C10—C11	1.387 (2)
Na1—O7W^{ii}	2.4100 (13)	C11—H11	0.9300
Na1—O7W	2.4100 (13)	C11—C12	1.389 (2)
Na2—Na3^{iii}	3.6071 (10)	C12—H12	0.9300
Na2—O4	2.4261 (13)	C12—C13	1.389 (2)
Na2—O8^{iii}	2.4308 (13)	C13—C14	1.509 (2)
Na2—C7	3.1086 (16)	C15—C16	1.511 (2)
Na2—C14^{iii}	3.0944 (16)	C16—C17	1.387 (2)
Na2—O7W^{ii}	2.4764 (14)	C17—H17	0.9300
Na2—O8W	2.3415 (13)	C17—C18	1.393 (2)
Na2—H8WB	2.41 (2)	C18—H18	0.9300
Na2—O9W	2.2670 (13)	C18—C19	1.387 (2)
Na2—O10W	2.4208 (14)	C19—H19	0.9300
Na3—O2	2.4117 (14)	C19—C20	1.389 (2)
Na3—O4^{i}	2.5614 (14)	C20—C21	1.512 (2)
Na3—O12^{iv}	2.5306 (13)	O1W—H1WA	0.852 (10)

Na3—O2W	2.3805 (16)	O1W—H1WB	0.850 (10)
Na3—O3W	2.3931 (16)	O2W—H2WA	0.861 (10)
Na3—H3WA	2.66 (3)	O2W—H2WB	0.862 (10)
Na3—O9W^{i}	2.4307 (14)	O3W—H3WA	0.847 (10)
Na4—O10	2.4001 (12)	O3W—H3WB	0.846 (10)
Na4—O10^{v}	2.4001 (12)	O4W—H4WA	0.849 (10)
Na4—O10W^{v}	2.4107 (12)	O4W—H4WB	0.847 (10)
Na4—O10W	2.4107 (12)	O5W—H5WA	0.852 (10)
Na4—O13W^{v}	2.4400 (12)	O5W—H5WB	0.871 (10)
Na4—O13W	2.4400 (12)	O6W—H6WA	0.862 (10)
O1—C1	1.2800 (17)	O6W—H6WB	0.867 (10)
O2—C1	1.2416 (18)	O7W—H7WA	0.844 (10)
O3—C7	1.2828 (17)	O7W—H7WB	0.847 (10)
O4—C7	1.2404 (18)	O8W—H8WA	0.844 (9)
O5—C8	1.2806 (18)	O8W—H8WB	0.844 (9)
O6—C8	1.2401 (18)	O9W—H9WA	0.846 (9)
O7—C14	1.2810 (18)	O9W—H9WB	0.848 (9)
O8—C14	1.2399 (17)	O10W—H10A	0.845 (10)
O9—C15	1.2724 (18)	O10W—H10B	0.843 (10)
O10—C15	1.2458 (18)	O11W—H11A	0.848 (10)
O11—C21	1.2766 (18)	O11W—H11B	0.846 (10)
O12—C21	1.2468 (18)	O12W—H12A	0.849 (10)
N1—C2	1.3372 (19)	O12W—H12B	0.862 (10)
N1—C6	1.3354 (18)	O13W—H13A	0.845 (10)
N2—C9	1.3386 (19)	O13W—H13B	0.846 (10)
N2—C13	1.3409 (18)	O14W—H14A	0.852 (10)
N3—C16	1.3387 (19)	O14W—H14B	0.846 (10)

O1—Sm1—O7	74.91 (4)	O10—Na4—O13W^{v}	90.20 (4)
O1—Sm1—O11^{i}	153.30 (4)	O10W^{v}—Na4—O10W	180.0
O1—Sm1—N1	62.60 (4)	O10W—Na4—O13W	79.58 (4)
O1—Sm1—N2	77.31 (4)	O10W—Na4—O13W^{v}	100.42 (4)
O1—Sm1—N3^{i}	133.62 (4)	O10W^{v}—Na4—O13W^{v}	79.58 (4)
O3—Sm1—O1	125.28 (4)	O10W^{v}—Na4—O13W	100.42 (4)
O3—Sm1—O5	75.87 (4)	O13W^{v}—Na4—O13W	180.0
O3—Sm1—O7	152.08 (4)	C1—O1—Sm1	125.52 (9)
O3—Sm1—O11^{i}	74.52 (4)	C1—O2—Na3	130.03 (10)
O3—Sm1—N1	62.70 (4)	C7—O3—Sm1	126.16 (9)
O3—Sm1—N2	134.63 (4)	Na2—O4—Na3^{iii}	92.60 (5)
O3—Sm1—N3^{i}	78.41 (4)	C7—O4—Na2	111.84 (10)
O5—Sm1—O1	92.07 (4)	C7—O4—Na3^{iii}	144.16 (11)
O5—Sm1—O7	126.55 (4)	C8—O5—Sm1	124.80 (9)
O5—Sm1—O11^{i}	74.58 (4)	C8—O6—Na1	120.67 (10)
O5—Sm1—N1	75.42 (4)	C14—O7—Sm1	124.81 (9)
O5—Sm1—N2	63.44 (4)	C14—O8—Na2^{i}	110.69 (9)
O5—Sm1—N3^{i}	134.19 (4)	C15—O9—Sm1^{iii}	123.86 (10)
O7—Sm1—O11^{i}	94.32 (4)	C15—O10—Na4	120.46 (10)
O7—Sm1—N1	133.37 (4)	C21—O11—Sm1^{iii}	125.58 (10)

O7—Sm1—N2	63.14 (4)	C21—O12—Na3^{vi}	157.96 (10)
O7—Sm1—N3^{i}	73.78 (4)	C2—N1—Sm1	120.78 (9)
O9^{i}—Sm1—O1	75.25 (4)	C6—N1—Sm1	120.08 (9)
O9^{i}—Sm1—O3	91.81 (4)	C6—N1—C2	118.93 (12)
O9^{i}—Sm1—O5	152.88 (4)	C9—N2—Sm1	119.93 (9)
O9^{i}—Sm1—O7	73.85 (4)	C9—N2—C13	119.10 (13)
O9^{i}—Sm1—O11^{i}	125.88 (4)	C13—N2—Sm1	120.81 (10)
O9^{i}—Sm1—N1	77.46 (4)	C16—N3—Sm1^{iii}	118.99 (10)
O9^{i}—Sm1—N2	133.52 (4)	C16—N3—C20	118.90 (13)
O9^{i}—Sm1—N3^{i}	63.72 (4)	C20—N3—Sm1^{iii}	121.98 (10)
O11^{i}—Sm1—N1	132.31 (4)	O1—C1—C2	114.80 (13)
O11^{i}—Sm1—N2	76.04 (4)	O2—C1—O1	125.97 (14)
O11^{i}—Sm1—N3^{i}	62.28 (4)	O2—C1—C2	119.22 (13)
N2—Sm1—N1	120.44 (4)	N1—C2—C1	114.50 (12)
N2—Sm1—N3^{i}	116.16 (4)	N1—C2—C3	122.49 (14)
N3^{i}—Sm1—N1	123.40 (4)	C3—C2—C1	123.00 (13)
O6^{ii}—Na1—O6	180.00 (5)	C2—C3—H3	120.8
O6^{ii}—Na1—H4WB	113.8 (4)	C2—C3—C4	118.35 (14)
O6—Na1—H4WB	66.2 (4)	C4—C3—H3	120.8
O4W^{ii}—Na1—O6	97.97 (4)	C3—C4—H4	120.4
O4W—Na1—O6^{ii}	97.97 (4)	C5—C4—C3	119.25 (15)
O4W^{ii}—Na1—O6^{ii}	82.03 (4)	C5—C4—H4	120.4
O4W—Na1—O6	82.03 (4)	C4—C5—H5	120.8
O4W—Na1—O4W^{ii}	180.0	C6—C5—C4	118.42 (14)
O4W—Na1—H4WB	19.5 (3)	C6—C5—H5	120.8
O4W^{ii}—Na1—H4WB	160.5 (3)	N1—C6—C5	122.55 (14)
O4W^{ii}—Na1—O7W	85.01 (4)	N1—C6—C7	114.55 (12)
O4W—Na1—O7W^{ii}	85.01 (4)	C5—C6—C7	122.90 (13)
O4W—Na1—O7W	94.99 (4)	O3—C7—Na2	81.93 (8)
O4W^{ii}—Na1—O7W^{ii}	94.99 (4)	O3—C7—C6	114.75 (12)
O7W^{ii}—Na1—O6^{ii}	91.13 (4)	O4—C7—Na2	46.42 (8)
O7W^{ii}—Na1—O6	88.87 (4)	O4—C7—O3	125.91 (14)
O7W—Na1—O6	91.13 (4)	O4—C7—C6	119.34 (13)
O7W—Na1—O6^{ii}	88.87 (4)	C6—C7—Na2	157.60 (10)
O7W^{ii}—Na1—H4WB	74.3 (5)	O5—C8—C9	115.43 (13)
O7W—Na1—H4WB	105.7 (5)	O6—C8—O5	125.08 (14)
O7W—Na1—O7W^{ii}	180.0	O6—C8—C9	119.48 (13)
Na3^{iii}—Na2—H8WB	119.8 (4)	N2—C9—C8	114.36 (12)
O4—Na2—Na3^{iii}	45.18 (3)	N2—C9—C10	121.99 (13)
O4—Na2—O8^{iii}	173.35 (5)	C10—C9—C8	123.64 (13)
O4—Na2—C7	21.74 (4)	C9—C10—H10	120.6
O4—Na2—C14^{iii}	151.35 (4)	C11—C10—C9	118.75 (15)
O4—Na2—O7W^{ii}	89.10 (5)	C11—C10—H10	120.6
O4—Na2—H8WB	75.0 (4)	C10—C11—H11	120.3
O8^{iii}—Na2—Na3^{iii}	128.45 (4)	C10—C11—C12	119.43 (15)
O8^{iii}—Na2—C7	164.79 (4)	C12—C11—H11	120.3
O8^{iii}—Na2—C14^{iii}	22.02 (4)	C11—C12—H12	120.9
O8^{iii}—Na2—O7W^{ii}	94.67 (5)	C13—C12—C11	118.19 (14)

O8^{iii}—Na2—H8WB	111.1 (4)	C13—C12—H12	120.9
C7—Na2—Na3^{iii}	65.15 (3)	N2—C13—C12	122.50 (14)
C7—Na2—H8WB	57.5 (3)	N2—C13—C14	114.75 (12)
C14^{iii}—Na2—Na3^{iii}	106.82 (3)	C12—C13—C14	122.74 (13)
C14^{iii}—Na2—C7	171.39 (4)	O7—C14—Na2^{i}	103.23 (9)
C14^{iii}—Na2—H8WB	131.1 (3)	O7—C14—C13	115.40 (12)
O7W^{ii}—Na2—Na3^{iii}	101.31 (4)	O8—C14—Na2^{i}	47.30 (7)
O7W^{ii}—Na2—C7	74.28 (4)	O8—C14—O7	125.03 (14)
O7W^{ii}—Na2—C14^{iii}	105.37 (5)	O8—C14—C13	119.55 (13)
O7W^{ii}—Na2—H8WB	80.2 (5)	C13—C14—Na2^{i}	121.13 (9)
O8W—Na2—Na3^{iii}	135.37 (4)	O9—C15—C16	116.08 (13)
O8W—Na2—O4	92.78 (5)	O10—C15—O9	124.98 (14)
O8W—Na2—O8^{iii}	92.68 (5)	O10—C15—C16	118.92 (13)
O8W—Na2—C7	77.19 (4)	N3—C16—C15	114.28 (13)
O8W—Na2—C14^{iii}	111.41 (4)	N3—C16—C17	122.66 (14)
O8W—Na2—O7W^{ii}	90.09 (5)	C17—C16—C15	123.05 (14)
O8W—Na2—H8WB	20.4 (3)	C16—C17—H17	120.9
O8W—Na2—O10W	93.71 (5)	C16—C17—C18	118.15 (15)
O9W—Na2—Na3^{iii}	41.54 (3)	C18—C17—H17	120.9
O9W—Na2—O4	83.79 (5)	C17—C18—H18	120.3
O9W—Na2—O8^{iii}	90.77 (5)	C19—C18—C17	119.40 (15)
O9W—Na2—C7	99.36 (5)	C19—C18—H18	120.3
O9W—Na2—C14^{iii}	72.04 (4)	C18—C19—H19	120.7
O9W—Na2—O7W^{ii}	89.31 (5)	C18—C19—C20	118.56 (15)
O9W—Na2—O8W	176.53 (5)	C20—C19—H19	120.7
O9W—Na2—H8WB	156.3 (3)	N3—C20—C19	122.26 (14)
O9W—Na2—O10W	86.76 (5)	N3—C20—C21	114.72 (12)
O10W—Na2—Na3^{iii}	74.40 (3)	C19—C20—C21	123.01 (13)
O10W—Na2—O4	88.49 (5)	O11—C21—C20	115.27 (13)
O10W—Na2—O8^{iii}	87.38 (4)	O12—C21—O11	126.00 (14)
O10W—Na2—C7	104.39 (4)	O12—C21—C20	118.71 (13)
O10W—Na2—C14^{iii}	75.29 (4)	H1WA—O1W—H1WB	109 (3)
O10W—Na2—O7W^{ii}	175.59 (5)	Na3—O2W—H2WA	116.0 (19)
O10W—Na2—H8WB	102.7 (5)	Na3—O2W—H2WB	128.6 (19)
Na2^{i}—Na3—H3WA	86.7 (4)	H2WA—O2W—H2WB	107 (3)
O2—Na3—Na2^{i}	108.54 (4)	Na3—O3W—H3WA	99.2 (19)
O2—Na3—O4^{i}	144.68 (5)	Na3—O3W—H3WB	112.4 (19)
O2—Na3—O12^{iv}	95.66 (5)	H3WA—O3W—H3WB	109 (3)
O2—Na3—H3WA	119.8 (4)	Na1—O4W—H4WA	126.1 (18)
O2—Na3—O9W^{i}	83.28 (4)	Na1—O4W—H4WB	88.8 (18)
O4^{i}—Na3—Na2^{i}	42.21 (3)	H4WA—O4W—H4WB	110 (3)
O4^{i}—Na3—H3WA	83.5 (3)	H5WA—O5W—H5WB	107 (3)
O12^{iv}—Na3—Na2^{i}	154.56 (4)	H6WA—O6W—H6WB	104 (3)
O12^{iv}—Na3—O4^{i}	112.43 (5)	Na1—O7W—Na2^{ii}	131.75 (5)
O12^{iv}—Na3—H3WA	88.0 (6)	Na1—O7W—H7WA	114.8 (18)
O2W—Na3—Na2^{i}	81.53 (4)	Na1—O7W—H7WB	104.9 (18)
O2W—Na3—O2	76.69 (5)	Na2^{ii}—O7W—H7WA	94.6 (18)
O2W—Na3—O4^{i}	78.94 (5)	Na2^{ii}—O7W—H7WB	104.5 (18)

O2W—Na3—O12^{iv}	97.00 (5)	H7WA—O7W—H7WB	103 (2)
O2W—Na3—O3W	176.16 (6)	Na2—O8W—H8WA	106.0 (17)
O2W—Na3—H3WA	162.4 (4)	Na2—O8W—H8WB	84.7 (17)
O2W—Na3—O9W^{i}	103.12 (5)	H8WA—O8W—H8WB	106 (2)
O3W—Na3—Na2^{i}	101.53 (4)	Na2—O9W—Na3^{iii}	100.26 (5)
O3W—Na3—O2	104.30 (5)	Na2—O9W—H9WA	117.2 (17)
O3W—Na3—O4^{i}	101.73 (5)	Na2—O9W—H9WB	118.1 (17)
O3W—Na3—O12^{iv}	79.24 (5)	Na3^{iii}—O9W—H9WA	113.2 (17)
O3W—Na3—H3WA	18.3 (3)	Na3^{iii}—O9W—H9WB	94.1 (17)
O3W—Na3—O9W^{i}	80.70 (5)	H9WA—O9W—H9WB	111 (2)
O9W^{i}—Na3—Na2^{i}	38.20 (3)	Na2—O10W—H10A	101.1 (17)
O9W^{i}—Na3—O4^{i}	77.79 (4)	Na2—O10W—H10B	102.4 (17)
O9W^{i}—Na3—O12^{iv}	158.99 (5)	Na4—O10W—Na2	128.07 (5)
O9W^{i}—Na3—H3WA	74.6 (6)	Na4—O10W—H10A	113.7 (17)
O10^{v}—Na4—O10	180.00 (6)	Na4—O10W—H10B	102.6 (17)
O10—Na4—O10W^{v}	92.22 (4)	H10A—O10W—H10B	107 (2)
O10—Na4—O10W	87.78 (4)	H11A—O11W—H11B	105 (3)
O10^{v}—Na4—O10W	92.22 (4)	H12A—O12W—H12B	103 (3)
O10^{v}—Na4—O10W^{v}	87.78 (4)	Na4—O13W—H13A	107.4 (17)
O10^{v}—Na4—O13W^{v}	89.80 (4)	Na4—O13W—H13B	107.5 (17)
O10—Na4—O13W	89.80 (4)	H13A—O13W—H13B	102 (2)
O10^{v}—Na4—O13W	90.20 (4)	H14A—O14W—H14B	112 (3)

Sm1—O1—C1—O2	164.44 (12)	O9—C15—C16—C17	−170.69 (15)
Sm1—O1—C1—C2	−16.46 (18)	O10—C15—C16—N3	−168.08 (13)
Sm1—O3—C7—Na2	149.87 (9)	O10—C15—C16—C17	10.7 (2)
Sm1—O3—C7—O4	165.65 (12)	N1—C2—C3—C4	−0.9 (3)
Sm1—O3—C7—C6	−14.47 (18)	N1—C6—C7—Na2	−130.8 (2)
Sm1—O5—C8—O6	162.94 (12)	N1—C6—C7—O3	4.68 (19)
Sm1—O5—C8—C9	−16.30 (18)	N1—C6—C7—O4	−175.43 (14)
Sm1—O7—C14—Na2^{i}	121.58 (8)	N2—C9—C10—C11	−2.0 (2)
Sm1—O7—C14—O8	168.27 (11)	N2—C13—C14—Na2^{i}	−115.99 (12)
Sm1—O7—C14—C13	−12.81 (17)	N2—C13—C14—O7	9.65 (19)
Sm1^{iii}—O9—C15—O10	157.66 (12)	N2—C13—C14—O8	−171.36 (13)
Sm1^{iii}—O9—C15—C16	−20.84 (17)	N3—C16—C17—C18	−2.2 (3)
Sm1^{iii}—O11—C21—O12	176.34 (11)	N3—C20—C21—O11	3.42 (19)
Sm1^{iii}—O11—C21—C20	−5.05 (17)	N3—C20—C21—O12	−177.86 (13)
Sm1—N1—C2—C1	−4.62 (17)	C1—C2—C3—C4	178.19 (16)
Sm1—N1—C2—C3	174.58 (12)	C2—N1—C6—C5	1.1 (2)
Sm1—N1—C6—C5	−173.65 (12)	C2—N1—C6—C7	−179.45 (13)
Sm1—N1—C6—C7	5.79 (17)	C2—C3—C4—C5	1.1 (3)
Sm1—N2—C9—C8	4.58 (16)	C3—C4—C5—C6	−0.2 (3)
Sm1—N2—C9—C10	−174.00 (12)	C4—C5—C6—N1	−0.9 (3)
Sm1—N2—C13—C12	175.90 (12)	C4—C5—C6—C7	179.67 (16)
Sm1—N2—C13—C14	−2.79 (16)	C5—C6—C7—Na2	48.6 (3)
Sm1^{iii}—N3—C16—C15	3.18 (16)	C5—C6—C7—O3	−175.88 (15)
Sm1^{iii}—N3—C16—C17	−175.62 (12)	C5—C6—C7—O4	4.0 (2)
Sm1^{iii}—N3—C20—C19	178.06 (12)	C6—N1—C2—C1	−179.35 (13)

Sm1^{iii}—N3—C20—C21	−0.53 (16)	C6—N1—C2—C3	−0.1 (2)
Na1—O6—C8—O5	−17.7 (2)	C8—C9—C10—C11	179.54 (15)
Na1—O6—C8—C9	161.50 (10)	C9—N2—C13—C12	0.5 (2)
Na2—O4—C7—O3	−21.8 (2)	C9—N2—C13—C14	−178.15 (13)
Na2—O4—C7—C6	158.31 (11)	C9—C10—C11—C12	0.7 (3)
Na2^{i}—O8—C14—O7	−74.53 (16)	C10—C11—C12—C13	1.1 (3)
Na2^{i}—O8—C14—C13	106.58 (12)	C11—C12—C13—N2	−1.8 (2)
Na3—O2—C1—O1	−6.3 (2)	C11—C12—C13—C14	176.80 (15)
Na3—O2—C1—C2	174.60 (10)	C12—C13—C14—Na2^{i}	65.32 (17)
Na3^{iii}—O4—C7—Na2	−129.7 (2)	C12—C13—C14—O7	−169.04 (14)
Na3^{iii}—O4—C7—O3	−151.47 (13)	C12—C13—C14—O8	10.0 (2)
Na3^{iii}—O4—C7—C6	28.6 (3)	C13—N2—C9—C8	179.98 (13)
Na3^{vi}—O12—C21—O11	125.3 (3)	C13—N2—C9—C10	1.4 (2)
Na3^{vi}—O12—C21—C20	−53.3 (3)	C15—C16—C17—C18	179.08 (16)
Na4—O10—C15—O9	−87.53 (17)	C16—N3—C20—C19	2.1 (2)
Na4—O10—C15—C16	90.94 (14)	C16—N3—C20—C21	−176.44 (13)
O1—C1—C2—N1	12.93 (19)	C16—C17—C18—C19	1.5 (3)
O1—C1—C2—C3	−166.27 (15)	C17—C18—C19—C20	0.9 (3)
O2—C1—C2—N1	−167.90 (14)	C18—C19—C20—N3	−2.8 (2)
O2—C1—C2—C3	12.9 (2)	C18—C19—C20—C21	175.69 (15)
O5—C8—C9—N2	6.77 (19)	C19—C20—C21—O11	−175.16 (14)
O5—C8—C9—C10	−174.68 (15)	C19—C20—C21—O12	3.6 (2)
O6—C8—C9—N2	−172.51 (14)	C20—N3—C16—C15	179.22 (12)
O6—C8—C9—C10	6.0 (2)	C20—N3—C16—C17	0.4 (2)
O9—C15—C16—N3	10.52 (19)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···O13*W*^{vii}	0.85 (1)	1.98 (1)	2.8163 (19)	167 (3)
O2*W*—H2*WA*···O11*W*^{i}	0.86 (1)	2.10 (1)	2.927 (2)	160 (3)
O2*W*—H2*WA*···O12*W*^{viii}	0.86 (1)	2.76 (3)	3.2317 (19)	116 (2)
O2*W*—H2*WB*···O1*W*	0.86 (1)	1.90 (1)	2.742 (2)	164 (3)
O4*W*—H4*WA*···O5*W*	0.85 (1)	1.91 (1)	2.741 (2)	167 (3)
O4*W*—H4*WB*···O5	0.85 (1)	2.02 (1)	2.8534 (17)	169 (3)
O6*W*—H6*WA*···O12^{ix}	0.86 (1)	2.00 (1)	2.8435 (19)	168 (3)
O6*W*—H6*WB*···O8^{x}	0.87 (1)	2.09 (2)	2.8645 (18)	149 (3)
O7*W*—H7*WA*···O6*W*	0.84 (1)	1.93 (1)	2.7611 (19)	167 (3)
O7*W*—H7*WB*···O3^{ii}	0.85 (1)	2.54 (2)	3.1551 (17)	131 (2)
O7*W*—H7*WB*···O5^{ii}	0.85 (1)	2.31 (2)	3.0267 (17)	142 (2)
O8*W*—H8*WA*···O10^{v}	0.84 (1)	1.87 (1)	2.7065 (17)	171 (2)
O9*W*—H9*WA*···O6^{ii}	0.85 (1)	1.94 (1)	2.7871 (16)	175 (2)
O9*W*—H9*WB*···O1^{iii}	0.85 (1)	1.87 (1)	2.7160 (16)	173 (2)
O10*W*—H10*A*···O2*W*^{iii}	0.85 (1)	1.90 (1)	2.7419 (18)	178 (2)
O11*W*—H11*A*···O9	0.85 (1)	1.97 (1)	2.8128 (17)	174 (3)
O11*W*—H11*B*···O12*W*	0.85 (1)	2.13 (1)	2.973 (2)	178 (3)

O12*W*—H12*A*···O2^{viii}	0.85 (1)	2.11 (1)	2.9542 (18)	173 (3)
O12*W*—H12*B*···O8*W*^{v}	0.86 (1)	2.03 (2)	2.8057 (18)	149 (3)
O13*W*—H13*A*···O12*W*^{v}	0.85 (1)	1.99 (1)	2.8235 (18)	170 (2)
O13*W*—H13*B*···O7^{iii}	0.85 (1)	2.09 (1)	2.9274 (17)	171 (2)
O13*W*—H13*B*···O8^{iii}	0.85 (1)	2.57 (2)	3.1929 (17)	132 (2)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*, *y*−1, *z*; (v) −*x*+1, −*y*, −*z*+2; (vii) −*x*+1, −*y*+1, −*z*+2; (viii) −*x*, −*y*+1, −*z*+2; (ix) −*x*+1, −*y*, −*z*+1; (x) −*x*+1, −*y*+2, −*z*+1.

catena-Poly[[[diaqua(6-carboxypyridine-2-carboxylato-κ^3O^2,N,O^6)samarium(III)]-μ-pyridine-2,6-dicarboxylato-$\kappa^4O^2,N,O^6:O^2$] tetrahydrate] (II)

Crystal data

$[Sm(C_7H_3NO_4)(C_7H_4NO_4)(H_2O)_2]\cdot 4H_2O$
M_r = 589.66
Monoclinic, $P2_1/c$
a = 13.9292 (8) Å
b = 11.1969 (7) Å
c = 12.8086 (7) Å
β = 103.049 (2)°
V = 1946.1 (2) Å^3
Z = 4
$F(000)$ = 1164
D_x = 2.013 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9554 reflections
θ = 2.4–35.1°
μ = 3.10 mm^{-1}
T = 100 K
Plate, colourless
0.48 × 0.40 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2019)
T_{min} = 0.575, T_{max} = 0.747
74345 measured reflections
7424 independent reflections
6679 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 33.1°, θ_{min} = 2.4°
h = −21→21
k = −17→17
l = −17→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.042
S = 1.08
7424 reflections
319 parameters
12 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.012P)^2 + 2.2391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −1.09 e Å^{-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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Sm1	0.73193 (2)	0.29610 (2)	0.84878 (2)	0.00303 (2)
O1	0.65850 (8)	0.10076 (9)	0.86514 (9)	0.00783 (19)

O2	0.53228 (8)	−0.01891 (10)	0.87649 (10)	0.0123 (2)
O3	0.64950 (8)	0.49371 (9)	0.85969 (9)	0.00847 (19)
O4	0.51949 (9)	0.60513 (11)	0.87239 (10)	0.0145 (2)
H4	0.5646 (18)	0.676 (2)	0.875 (2)	0.022*
O5	0.84574 (8)	0.07310 (10)	0.27878 (9)	0.00810 (19)
O6	0.92027 (9)	−0.10506 (10)	0.28114 (9)	0.0106 (2)
O7	0.72787 (8)	0.22062 (9)	0.54309 (8)	0.00693 (18)
O8	0.78295 (8)	0.16945 (10)	0.71580 (8)	0.00725 (18)
C1	0.56995 (11)	0.08151 (13)	0.86995 (12)	0.0074 (2)
C2	0.50502 (11)	0.18986 (13)	0.86725 (12)	0.0083 (2)
C3	0.40535 (12)	0.18312 (16)	0.86702 (17)	0.0177 (3)
H3	0.374223	0.108078	0.869860	0.021*
C4	0.35229 (13)	0.28896 (17)	0.8625 (2)	0.0240 (4)
H4A	0.283664	0.286989	0.860236	0.029*
C5	0.40023 (12)	0.39746 (16)	0.86144 (16)	0.0176 (3)
H5	0.365676	0.470880	0.859381	0.021*
C6	0.50027 (11)	0.39530 (14)	0.86343 (12)	0.0091 (2)
C7	0.56268 (11)	0.50434 (13)	0.86471 (12)	0.0083 (3)
C8	0.88073 (10)	−0.02353 (13)	0.32337 (11)	0.0061 (2)
C9	0.87488 (10)	−0.03865 (12)	0.43907 (11)	0.0052 (2)
C10	0.90835 (11)	−0.13997 (13)	0.49895 (12)	0.0073 (2)
H10	0.934576	−0.205672	0.467574	0.009*
C11	0.90257 (11)	−0.14290 (13)	0.60575 (12)	0.0084 (2)
H11	0.925058	−0.210990	0.648565	0.010*
C12	0.86374 (10)	−0.04573 (13)	0.64965 (11)	0.0066 (2)
H12	0.861422	−0.044590	0.723200	0.008*
C13	0.82835 (10)	0.04988 (12)	0.58257 (11)	0.0049 (2)
C14	0.77620 (10)	0.15538 (12)	0.61763 (11)	0.0049 (2)
N1	0.55123 (9)	0.29383 (11)	0.86438 (10)	0.0063 (2)
N2	0.83414 (9)	0.05330 (11)	0.47961 (9)	0.0046 (2)
O1W	0.63395 (9)	0.34532 (11)	0.67167 (9)	0.0117 (2)
H1WA	0.5864 (10)	0.3940 (15)	0.6529 (18)	0.018*
H1WB	0.6530 (15)	0.3178 (19)	0.6179 (11)	0.018*
O2W	0.87579 (8)	0.18700 (10)	0.93554 (9)	0.0091 (2)
H2WA	0.8967 (16)	0.1939 (19)	1.0029 (3)	0.014*
H2WB	0.9169 (11)	0.1431 (15)	0.9135 (16)	0.014*
O3W	0.95920 (8)	0.19105 (10)	1.14835 (9)	0.00890 (19)
H3WA	0.9230 (12)	0.1699 (19)	1.1904 (13)	0.013*
H3WB	0.9949 (13)	0.2501 (12)	1.1748 (16)	0.013*
O4W	0.63135 (11)	0.77889 (12)	0.89098 (16)	0.0307 (4)
H4WA	0.6029 (18)	0.8463 (11)	0.888 (2)	0.046*
H4WB	0.6931 (4)	0.785 (3)	0.896 (3)	0.046*
O5W	0.80409 (10)	0.90705 (12)	0.90443 (12)	0.0217 (3)
H5WA	0.7688 (15)	0.9695 (12)	0.900 (2)	0.033*
H5WB	0.8408 (15)	0.919 (2)	0.9662 (9)	0.033*
O6W	0.96769 (9)	−0.05672 (10)	0.09389 (9)	0.0116 (2)
H6WA	0.9816 (16)	0.0173 (5)	0.0980 (18)	0.017*
H6WB	0.9508 (15)	−0.072 (2)	0.1523 (9)	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sm1	0.00394 (3)	0.00300 (3)	0.00234 (3)	−0.00019 (2)	0.00113 (2)	−0.00035 (2)
O1	0.0069 (4)	0.0056 (4)	0.0115 (5)	−0.0009 (4)	0.0033 (4)	0.0000 (4)
O2	0.0093 (5)	0.0066 (5)	0.0214 (6)	−0.0034 (4)	0.0040 (4)	0.0004 (4)
O3	0.0085 (5)	0.0062 (4)	0.0105 (5)	0.0012 (4)	0.0017 (4)	−0.0005 (4)
O4	0.0147 (5)	0.0075 (5)	0.0220 (6)	0.0043 (4)	0.0055 (5)	−0.0020 (4)
O5	0.0116 (5)	0.0074 (4)	0.0064 (4)	0.0034 (4)	0.0044 (4)	0.0019 (4)
O6	0.0176 (5)	0.0080 (5)	0.0085 (5)	0.0054 (4)	0.0075 (4)	0.0001 (4)
O7	0.0088 (4)	0.0078 (5)	0.0043 (4)	0.0032 (4)	0.0018 (4)	0.0014 (3)
O8	0.0109 (5)	0.0079 (4)	0.0035 (4)	0.0020 (4)	0.0025 (4)	−0.0006 (4)
C1	0.0078 (6)	0.0066 (6)	0.0074 (6)	−0.0014 (5)	0.0010 (5)	−0.0009 (5)
C2	0.0064 (6)	0.0084 (6)	0.0109 (6)	0.0005 (5)	0.0032 (5)	0.0002 (5)
C3	0.0078 (6)	0.0134 (7)	0.0341 (10)	−0.0006 (5)	0.0090 (6)	0.0023 (7)
C4	0.0089 (7)	0.0171 (8)	0.0493 (13)	0.0024 (6)	0.0136 (8)	0.0039 (8)
C5	0.0113 (7)	0.0137 (7)	0.0301 (9)	0.0049 (6)	0.0095 (6)	0.0018 (7)
C6	0.0092 (6)	0.0083 (6)	0.0106 (6)	0.0025 (5)	0.0036 (5)	0.0005 (5)
C7	0.0112 (6)	0.0071 (6)	0.0070 (6)	0.0033 (5)	0.0025 (5)	−0.0001 (5)
C8	0.0080 (6)	0.0061 (6)	0.0053 (6)	0.0007 (4)	0.0034 (5)	−0.0003 (5)
C9	0.0060 (5)	0.0052 (5)	0.0049 (5)	0.0004 (4)	0.0022 (4)	0.0000 (4)
C10	0.0095 (6)	0.0058 (6)	0.0067 (6)	0.0021 (5)	0.0024 (5)	0.0000 (5)
C11	0.0117 (6)	0.0069 (6)	0.0066 (6)	0.0021 (5)	0.0017 (5)	0.0022 (5)
C12	0.0087 (6)	0.0064 (6)	0.0042 (6)	0.0004 (5)	0.0006 (5)	0.0002 (4)
C13	0.0060 (5)	0.0055 (5)	0.0033 (5)	−0.0003 (4)	0.0014 (4)	0.0001 (4)
C14	0.0057 (5)	0.0041 (5)	0.0051 (5)	−0.0007 (4)	0.0018 (4)	−0.0006 (4)
N1	0.0066 (5)	0.0069 (5)	0.0059 (5)	0.0008 (4)	0.0023 (4)	−0.0001 (4)
N2	0.0057 (5)	0.0044 (5)	0.0041 (5)	−0.0002 (4)	0.0023 (4)	−0.0003 (4)
O1W	0.0127 (5)	0.0169 (6)	0.0049 (5)	0.0090 (4)	0.0012 (4)	−0.0004 (4)
O2W	0.0088 (5)	0.0123 (5)	0.0055 (4)	0.0047 (4)	0.0003 (4)	−0.0017 (4)
O3W	0.0100 (5)	0.0109 (5)	0.0065 (5)	−0.0018 (4)	0.0032 (4)	−0.0005 (4)
O4W	0.0192 (7)	0.0093 (6)	0.0653 (12)	0.0012 (5)	0.0129 (7)	−0.0009 (6)
O5W	0.0188 (6)	0.0118 (6)	0.0316 (8)	0.0030 (5)	−0.0005 (5)	−0.0017 (5)
O6W	0.0169 (5)	0.0098 (5)	0.0107 (5)	0.0030 (4)	0.0087 (4)	0.0015 (4)

Geometric parameters (Å, º)

Sm1—O2W	2.3952 (11)	C6—N1	1.3382 (19)
Sm1—O1W	2.4320 (11)	C6—C7	1.497 (2)
Sm1—O8	2.4422 (10)	C8—C9	1.512 (2)
Sm1—O1	2.4434 (11)	C9—N2	1.3360 (18)
Sm1—O5^{i}	2.4707 (11)	C9—C10	1.3896 (19)
Sm1—O7^{i}	2.5092 (11)	C10—C11	1.389 (2)
Sm1—O3	2.5112 (11)	C10—H10	0.9500
Sm1—N2^{i}	2.5693 (12)	C11—C12	1.389 (2)
Sm1—N1	2.5695 (12)	C11—H11	0.9500
O1—C1	1.2673 (17)	C12—C13	1.3914 (19)
O2—C1	1.2516 (18)	C12—H12	0.9500

O3—C7	1.2313 (18)	C13—N2	1.3399 (18)
O4—C7	1.2930 (18)	C13—C14	1.507 (2)
O4—H4	1.01 (3)	O1W—H1WA	0.8499 (10)
O5—C8	1.2683 (17)	O1W—H1WB	0.8500 (10)
O6—C8	1.2505 (17)	O2W—H2WA	0.8500 (10)
O7—C14	1.2681 (17)	O2W—H2WB	0.8500 (10)
O8—C14	1.2495 (17)	O3W—H3WA	0.8499 (10)
C1—C2	1.509 (2)	O3W—H3WB	0.8499 (10)
C2—N1	1.3348 (19)	O4W—H4	1.47 (3)
C2—C3	1.390 (2)	O4W—H4WA	0.8499 (10)
C3—C4	1.391 (2)	O4W—H4WB	0.8499 (11)
C3—H3	0.9500	O5W—H5WA	0.8499 (10)
C4—C5	1.388 (3)	O5W—H5WB	0.8499 (10)
C4—H4A	0.9500	O6W—H6WA	0.8499 (10)
C5—C6	1.388 (2)	O6W—H6WB	0.8499 (10)
C5—H5	0.9500		

O2W—Sm1—O1W	141.52 (4)	C5—C4—C3	119.59 (16)
O2W—Sm1—O8	71.50 (4)	C5—C4—H4A	120.2
O1W—Sm1—O8	70.81 (4)	C3—C4—H4A	120.2
O2W—Sm1—O1	79.99 (4)	C4—C5—C6	117.89 (15)
O1W—Sm1—O1	97.19 (4)	C4—C5—H5	121.1
O8—Sm1—O1	74.54 (4)	C6—C5—H5	121.1
O2W—Sm1—O5^{i}	86.13 (4)	N1—C6—C5	122.90 (15)
O1W—Sm1—O5^{i}	78.35 (4)	N1—C6—C7	112.76 (13)
O8—Sm1—O5^{i}	77.26 (4)	C5—C6—C7	124.34 (14)
O1—Sm1—O5^{i}	151.28 (4)	O3—C7—O4	124.59 (14)
O2W—Sm1—O7^{i}	72.88 (4)	O3—C7—C6	119.70 (13)
O1W—Sm1—O7^{i}	143.96 (4)	O4—C7—C6	115.71 (13)
O8—Sm1—O7^{i}	136.37 (4)	O6—C8—O5	126.15 (13)
O1—Sm1—O7^{i}	75.20 (3)	O6—C8—C9	117.94 (13)
O5^{i}—Sm1—O7^{i}	124.35 (3)	O5—C8—C9	115.89 (12)
O2W—Sm1—O3	140.24 (4)	N2—C9—C10	122.25 (13)
O1W—Sm1—O3	71.63 (4)	N2—C9—C8	114.60 (12)
O8—Sm1—O3	139.39 (4)	C10—C9—C8	123.15 (12)
O1—Sm1—O3	125.34 (4)	C11—C10—C9	118.44 (13)
O5^{i}—Sm1—O3	80.61 (4)	C11—C10—H10	120.8
O7^{i}—Sm1—O3	84.12 (4)	C9—C10—H10	120.8
O2W—Sm1—N2^{i}	75.51 (4)	C10—C11—C12	119.64 (13)
O1W—Sm1—N2^{i}	124.84 (4)	C10—C11—H11	120.2
O8—Sm1—N2^{i}	129.07 (4)	C12—C11—H11	120.2
O1—Sm1—N2^{i}	135.45 (4)	C11—C12—C13	117.95 (13)
O5^{i}—Sm1—N2^{i}	62.69 (4)	C11—C12—H12	121.0
O7^{i}—Sm1—N2^{i}	62.31 (4)	C13—C12—H12	121.0
O3—Sm1—N2^{i}	65.06 (4)	N2—C13—C12	122.55 (13)
O2W—Sm1—N1	133.67 (4)	N2—C13—C14	114.27 (12)
O1W—Sm1—N1	73.83 (4)	C12—C13—C14	123.12 (12)
O8—Sm1—N1	119.53 (4)	O8—C14—O7	126.27 (13)

O1—Sm1—N1	63.14 (4)	O8—C14—C13	117.83 (12)
O5^{i}—Sm1—N1	138.95 (4)	O7—C14—C13	115.90 (12)
O7^{i}—Sm1—N1	71.36 (4)	C2—N1—C6	118.86 (13)
O3—Sm1—N1	62.37 (4)	C2—N1—Sm1	119.84 (9)
N2^{i}—Sm1—N1	111.35 (4)	C6—N1—Sm1	121.18 (10)
C1—O1—Sm1	125.96 (9)	C9—N2—C13	119.07 (12)
C7—O3—Sm1	123.70 (10)	C9—N2—Sm1^{ii}	118.28 (9)
C7—O4—H4	113.1 (14)	C13—N2—Sm1^{ii}	120.87 (9)
C8—O5—Sm1^{ii}	123.71 (9)	Sm1—O1W—H1WA	130.3 (16)
C14—O7—Sm1^{ii}	125.23 (9)	Sm1—O1W—H1WB	117.5 (15)
C14—O8—Sm1	143.85 (10)	H1WA—O1W—H1WB	112 (2)
O2—C1—O1	125.69 (14)	Sm1—O2W—H2WA	119.0 (15)
O2—C1—C2	117.75 (13)	Sm1—O2W—H2WB	134.2 (14)
O1—C1—C2	116.56 (13)	H2WA—O2W—H2WB	107 (2)
N1—C2—C3	122.34 (14)	H3WA—O3W—H3WB	110 (2)
N1—C2—C1	114.31 (12)	H4—O4W—H4WA	115 (2)
C3—C2—C1	123.35 (14)	H4—O4W—H4WB	132 (2)
C2—C3—C4	118.37 (16)	H4WA—O4W—H4WB	113 (3)
C2—C3—H3	120.8	H5WA—O5W—H5WB	99 (2)
C4—C3—H3	120.8	H6WA—O6W—H6WB	104 (2)

Sm1—O1—C1—O2	178.70 (11)	C10—C11—C12—C13	2.4 (2)
Sm1—O1—C1—C2	−1.16 (18)	C11—C12—C13—N2	−2.8 (2)
O2—C1—C2—N1	177.56 (14)	C11—C12—C13—C14	174.28 (13)
O1—C1—C2—N1	−2.6 (2)	Sm1—O8—C14—O7	−0.5 (3)
O2—C1—C2—C3	−2.8 (2)	Sm1—O8—C14—C13	−179.20 (10)
O1—C1—C2—C3	177.02 (16)	Sm1^{ii}—O7—C14—O8	172.44 (11)
N1—C2—C3—C4	0.7 (3)	Sm1^{ii}—O7—C14—C13	−8.81 (17)
C1—C2—C3—C4	−178.89 (18)	N2—C13—C14—O8	−167.61 (13)
C2—C3—C4—C5	−1.8 (3)	C12—C13—C14—O8	15.1 (2)
C3—C4—C5—C6	0.9 (3)	N2—C13—C14—O7	13.53 (18)
C4—C5—C6—N1	1.3 (3)	C12—C13—C14—O7	−163.75 (13)
C4—C5—C6—C7	−178.78 (18)	C3—C2—N1—C6	1.4 (2)
Sm1—O3—C7—O4	178.63 (11)	C1—C2—N1—C6	−179.02 (13)
Sm1—O3—C7—C6	−0.58 (19)	C3—C2—N1—Sm1	−174.76 (13)
N1—C6—C7—O3	4.5 (2)	C1—C2—N1—Sm1	4.83 (17)
C5—C6—C7—O3	−175.46 (16)	C5—C6—N1—C2	−2.4 (2)
N1—C6—C7—O4	−174.77 (13)	C7—C6—N1—C2	177.65 (13)
C5—C6—C7—O4	5.3 (2)	C5—C6—N1—Sm1	173.72 (13)
Sm1^{ii}—O5—C8—O6	163.39 (12)	C7—C6—N1—Sm1	−6.26 (17)
Sm1^{ii}—O5—C8—C9	−17.75 (17)	C10—C9—N2—C13	2.4 (2)
O6—C8—C9—N2	178.29 (13)	C8—C9—N2—C13	−178.01 (12)
O5—C8—C9—N2	−0.67 (19)	C10—C9—N2—Sm1^{ii}	−162.53 (11)
O6—C8—C9—C10	−2.1 (2)	C8—C9—N2—Sm1^{ii}	17.07 (15)
O5—C8—C9—C10	178.93 (13)	C12—C13—N2—C9	0.4 (2)
N2—C9—C10—C11	−2.6 (2)	C14—C13—N2—C9	−176.91 (12)

C8—C9—C10—C11	177.79 (13)	C12—C13—N2—Sm1^{ii}	164.91 (10)
C9—C10—C11—C12	0.1 (2)	C14—C13—N2—Sm1^{ii}	−12.39 (16)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O2^{iii}	0.85 (1)	1.88 (1)	2.7218 (16)	169 (2)
O1*W*—H1*WB*···O7	0.85 (1)	1.91 (1)	2.7103 (15)	157 (2)
O2*W*—H2*WA*···O3*W*	0.85 (1)	1.87 (1)	2.7115 (16)	170 (2)
O2*W*—H2*WB*···O6*W*^{iv}	0.85 (1)	1.90 (1)	2.7193 (16)	163 (2)
O3*W*—H3*WA*···O5^{v}	0.85 (1)	2.04 (1)	2.8679 (15)	164 (2)
O3*W*—H3*WB*···O6^{vi}	0.85 (1)	2.01 (1)	2.8568 (16)	173 (2)
O4*W*—H4*WA*···O2^{vii}	0.85 (1)	1.79 (1)	2.6360 (18)	174 (3)
O4*W*—H4*WB*···O5*W*	0.85 (1)	2.05 (2)	2.773 (2)	143 (3)
O5*W*—H5*WA*···O1^{vii}	0.85 (1)	2.10 (1)	2.9340 (17)	167 (2)
O5*W*—H5*WB*···O6*W*^{viii}	0.85 (1)	2.14 (1)	2.9579 (19)	162 (2)
O6*W*—H6*WA*···O3*W*^{ix}	0.85 (1)	2.10 (1)	2.8696 (16)	151 (2)
O6*W*—H6*WB*···O6	0.85 (1)	1.83 (1)	2.6828 (16)	177 (2)
O4—H4···O4*W*	1.01 (3)	1.47 (3)	2.4703 (19)	174 (2)

Symmetry codes: (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) −*x*+2, −*y*, −*z*+1; (v) *x*, *y*, *z*+1; (vi) −*x*+2, *y*+1/2, −*z*+3/2; (vii) *x*, *y*+1, *z*; (viii) *x*, *y*+1, *z*+1; (ix) *x*, *y*, *z*−1.