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Crystal structure of poly[triaqua-(μ_9-biphenyl-3,3′,5,5′-tetracarboxylic-κ^8 *O,O:O,O′: O,O″:O,O‴*) samarium(III)sodium(I)], $C_{16}H_{12}NaSmO_{11}$

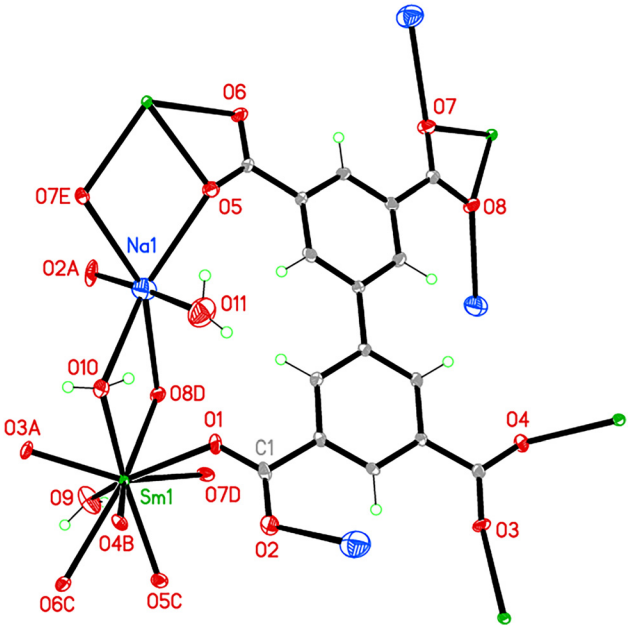

Figure 1: Coordination environment of the Sm(III) and Na(I) ions in title compound. [symmetry codes: A 1 + *x*, 1.5 - *y*, 1/2 + *z*; B -*x*, 1/2 + *y*, 1.5 - *z*; C *x*, 1.5 - *y*, -1/2 + *z*; D 1 - *x*, 1 - *y*, 2 - *z*; E 1 - *x*, 1/2 + *y*, 2.5 - *z*].

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Abstract

$C_{16}H_{12}NaSmO_{11}$, monoclinic, $P2_1/c$ (no. 14), a = 6.9833(14) Å, b = 17.482(3) Å, c = 14.875(4) Å, β = 112.23(3)°, V = 1681.0(7) Å^3, Z = 4, $R_{gt}(F)$ = 0.0343, w$R_{ref}(F^2)$ = 0.0759, T = 293(2) K.

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Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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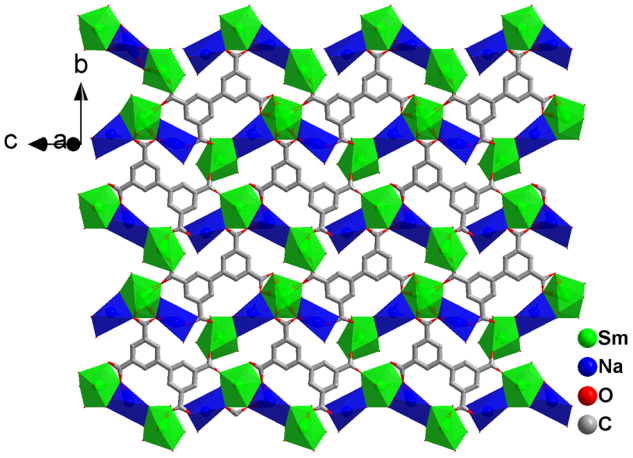

Figure 2: The one-dimensional chain running along the *a*-axis.

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.33 × 0.30 × 0.30 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.59 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	25.5°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7348, 3081, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2944
$N(param)_{refined}$:	262
Programs:	Bruker,[1] SHELX,[2,3] Diamond[4]

1 Source of materials

All chemical reagents were purchased from commercial sources without further purification. The mixture of samarium(III) nitrate hexahydrate (0.088 g, 0.2 mmol) and biphenyl-3,3′,5,5′-tetracarboxylicacid (H_4bpta) (0.033 g, 0.1 mmol) were dissolved in 8 mL CH_3CN/H_2O (1:2 vol ratio). Then the solution was adjusted to approximately pH 7.5 with dilute NaOH solution. The resulting solution was sealed in a 15 ml Teflon-lined autoclave for 72 h at 433 K. Colourless block crystals of the title compound were obtained after cooling to room temperature.

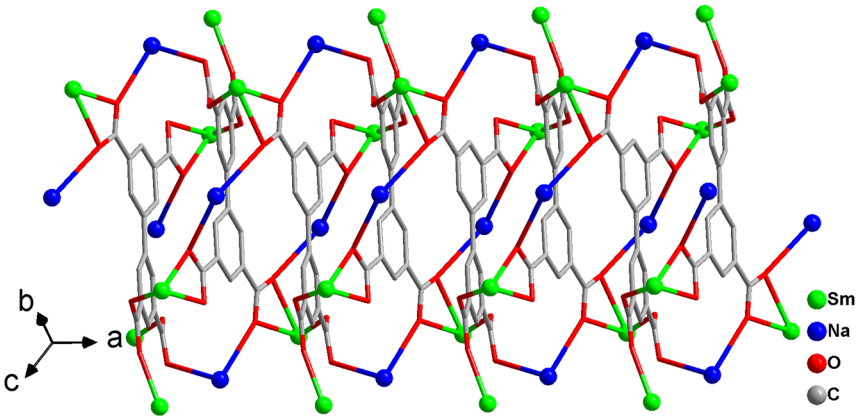

Figure 3: Two-dimensional layered structure of the title compound.

2 Experimental details

The structure was solved with the ShelXT[2] structure solution program and refined with the ShelXL.[3] The hydrogen atoms on C atoms were positioned geometrically and refined using the riding model, with C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), and hydrogen atoms of water were located from a difference Fourier map with O–H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O).

3 Comment

Metal-organic frameworks (MOFs) have attracted increasing attention due to their diverse structures with strong designability, high porosity and large specific surface area, and excellent optical properties, showing broad application prospects in gas storage,[5] separation,[6] catalysis,[7] sensing,[8] and optoelectronic materials.[9] Among them, lanthanide based MOFs (Ln–MOFs) have become an important platform for the design of multifunctional materials, thanks to the unique 4*f* electronic configuration (such as excellent luminescent properties, high coordination numbers, and magnetism).[10] However, the coordination behavior of rare earth ions is easily restricted by the ligand configuration. How to achieve stable high-dimensional Ln–MOF structures through ligand design and further regulate their physicochemical properties remains one of the key challenges in this field.[11]

Rigid carboxylate ligands, which combine the structural directivity of rigid ligands and the conformational adaptability of ligands,[12] provide an ideal choice for constructing novel Ln–MOFs. For example, rigid dicarboxylate or polycarboxylate ligands[13–15] feature several hard *O*,*O*-chelating sites, can bind several metal ions. In addition, the carboxylate groups can adopt monodentate and chelating or bridging modes, thus forming unique topological networks or functionalized channel structures with rare earth ions. Moreover, the variable conformations of such ligands may induce dynamic responses of the framework to external *stimuli* (such as temperature, pressure, or guest molecules).[16]

In this paper, a rigid planar biphenyl-3,3′,5,5-tetracarboxylicacid (H_4bpta) ligand was strategically employed to react with samarium nitrate under alkaline conditions, yielding a heteronuclear Na(I)–Sm(III)-based MOF featuring a three-dimensional network architecture. Single crystal X-ray diffraction analysis reveals that the title complex crystallizes in the space group $P2_1/c$. The asymmetric unit comprises one crystallographically unique Sm(III) ion, one Na(I) ion, one fully deprotonated bpta^{4-} ligand, and three coordinating water molecules. As shown in Figure 1, the Sm(III) center presents a nine-coordinate tricapped triangular prismatic geometry, coordinating with seven carboxylate oxygen atoms from five bpta^{4-} ligands and two water molecules (O1, O3A, O4B, O5C, O6C, O7D, O8D, O9, and O10; symmetry codes: A 1 + *x*, 1.5 − *y*, 1/2 + *z*; B −*x*, 1/2 + *y*, 1.5 − *z*; C *x*, 1.5 − *y*, −1/2 + *z*; D 1 − *x*, 1 − *y*, 2 − *z*). The Sm–O bond lengths range from 2.308(3) to 2.672(4) Å, consistent with previously reported samarium complexes.[17–20] Notably, the Na(I) ion exhibits a distorted octahedral coordination environment, where the equatorial plane is formed by three carboxylate oxygen atoms (O5, O7E, and O8D; symmetry codes: *E* 1 − *x*, 1/2 + *y*, 2.5 − *z*) from bpta^{4-} ligands and a bridging water molecule (O10), and two axial positions are occupied by an oxygen atom (O2A) from bpta^{4-} and a terminal water molecule (O11). The Na–O bond lengths are 2.720(4) to 2.877(5) Å, while the O–Sm–O angles range from 50.83(11)° to 152.37(14)°.

In the crystal structure, the bpta^{4-} ligand exhibits a μ_9-κ^{11}-coordination mode, simultaneously linking five Sm(III) and four Na(I) ions. The 3,3′-carboxylate groups adopt *syn*-anti and μ–O bridging configurations to connect the heteronuclear metal centers, forming a one-dimensional zigzag $[SmNa(COO)_2]_n$ chain with Na···Sm separations of 4.283–4.348 Å. Along the *a* axis direction, sequential Sm(III) and Na(I) ions are further connected through the

carboxylate groups of the coupled $bpta^{4-}$ ligands, constructing a one-dimensional chain structure with a 22-membered ring (Figure 2).

On the *bc*-plane, Sm(III)- and Na(I)-centered polyhedra are connected *via* shared edges to form an asymmetric tetraatomic metal cluster unit. These clusters are further linked by carboxylate groups into infinite one-dimensional chains extending along the *c*-axis. Adjacent chains are bridged by $bpta^{4-}$ ligands, constructing two-dimensional layer (Figure 3). Such two-dimensional layered structures stack to form a three-dimensional network structure.

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