Xun Feng*, Rui Wang, Xin Yi Wang, Ying Ying Zhang and Xi Xi Jia

Crystal structure of poly[*diaqua-di-μ₂-hydroxido-(μ₄-3,4,5,6-tetrafluoro-1,2-phthalato-κ⁴O:O':O'':O''')-(μ₄-3,4,5,6-tetrafluoro-1,2-phthalato-κ⁵O,O:O':O'':O''')*disamarium(III)] – bipyridine (2/1), C₂₁H₁₁NF₁₆O₁₂Sm₂

<https://doi.org/10.1515/ncrs-2018-0138>

Received May 13, 2018; accepted July 26, 2018; available online October 18, 2018

Abstract

C₂₁H₁₁NF₁₆O₁₂Sm₂, triclinic, *P* $\bar{1}$ (no. 2), *a* = 7.7872(5) Å, *b* = 9.9149(6) Å, *c* = 16.9804(10) Å, α = 79.4970(10)°, β = 76.8620(10)°, γ = 78.1480(10)°, *V* = 1236.80(13) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0411, *wR*_{ref}(*F*₂) = 0.1158, *T* = 293(2) K.

CCDC no.: 1858555

A part of the polymeric title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

An organic compound (3,4,5,6-tetrafluoro-1,2 phthalate acid, abbreviated as Tfpa) (0.047 g, 0.2 mmol) in a solution of water/alcohol (*v/v* = 1.2, 10 mL) was mixed with an aqueous

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.23 × 0.18 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.83 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	25°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	6329, 4361, 0.033
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 3872
<i>N</i> (<i>param</i>) _{refined} :	367
Programs:	Bruker programs [1], SHELX [2]

solution of 0.2 mmol Sm(NO₃)₃ · 6H₂O, 0.042 g and a solution (10 mL) of 4,4'-bipyridine (abbreviated as bipy) (0.2 mmol, 0.032 g). After stirring for 30 min, the pH value was adjusted to 4.5 using nitric acid. The mixture was placed into 25 mL Teflon-lined autoclave and under autogenous pressure this mixture was heated at 155 °C for 72 h, and then the autoclave was cooled over a period of 24 h at a rate 5 °C/h. After filtration, the product was washed with distilled water and then dried. Colorless crystals of title compound were obtained suitable for X-ray diffraction analysis. Yield: 0.0156 g (43%) based on lanthanide element. Elemental analysis (%): calcd. for C₂₁H₁₁NF₁₆O₁₂Sm₂: C 27.36, H 1.20, N 1.52, found: C 27.52, H 1.17, N 1.60. IR (KBr pellet, cm⁻¹): 3339s, 2198s, 1704vs, 1617s, 1546s, 1467s, 12639s, 1132s, 866m, 793s, 660s.

*Corresponding author: Xun Feng, Luoyang Normal University, College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function Oriented Porous Materials, Luoyang, Henan 471934, P.R. China, e-mail: fengqian2004@163.com

Rui Wang, Xin Yi Wang, Ying Ying Zhang and Xi Xi Jia: Luoyang Normal University, College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function Oriented Porous Materials, Luoyang, Henan 471934, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Sm1	0.10291(4)	0.66089(3)	0.42809(2)	0.01455(13)
Sm2	0.58450(4)	0.68458(3)	0.50455(2)	0.01407(13)
FOAA	0.9623(7)	0.6434(6)	0.0192(3)	0.0560(14)*
F1	0.4518(7)	0.4711(7)	0.1642(3)	0.0603(16)
F1AA	0.2178(7)	1.0924(5)	0.7822(3)	0.0424(12)*
F2	0.6675(8)	0.5382(7)	0.0216(4)	0.0639(16)*
F4	1.0449(6)	0.6741(6)	0.1546(3)	0.0477(13)
F5	−0.0309(6)	0.6761(5)	0.7021(3)	0.0391(11)
F6	−0.0720(9)	0.7061(6)	0.8571(3)	0.0575(16)
F7	0.0562(10)	0.9144(7)	0.8989(3)	0.0674(18)
N1	0.3550(11)	0.9429(12)	0.2129(5)	0.060(3)
O1	0.3557(6)	0.5915(5)	0.3233(3)	0.0281(11)
O1W	0.2236(7)	0.8714(5)	0.3722(3)	0.0300(12)
H1WA	0.3143	0.8775	0.4008	0.045*
H1WB	0.2749	0.8701	0.3153	0.045*
O2	0.5393(6)	0.3988(5)	0.3592(3)	0.0211(10)
O2W	0.6545(6)	0.8396(5)	0.5886(3)	0.0254(11)
H2WA	0.7749	0.8089	0.5972	0.038*
H2WB	0.6428	0.9333	0.5606	0.038*
O3	0.6991(7)	0.6237(5)	0.3732(3)	0.0293(12)
O4	0.9823(7)	0.6242(6)	0.3169(3)	0.0382(14)
O5	0.0445(6)	0.8044(5)	0.5441(3)	0.0262(11)
O6	0.3122(6)	0.8569(5)	0.5317(3)	0.0203(10)
O7	−0.1661(6)	0.8305(5)	0.4234(3)	0.0197(10)
O8	0.5717(6)	0.9137(5)	0.3942(3)	0.0249(11)
O9	0.3373(5)	0.5785(4)	0.4962(3)	0.0159(9)
H9	0.2801	0.5795	0.5445	0.024*
O10	0.8701(5)	0.5891(4)	0.5411(3)	0.0160(9)
H10	0.8763	0.6209	0.5827	0.024*
COAA	0.8571(10)	0.6079(8)	0.0896(5)	0.0312(17)*
C1	0.4973(9)	0.5092(7)	0.3142(4)	0.0211(15)
C2	0.6323(9)	0.5422(8)	0.2366(4)	0.0222(15)
C3	0.5968(10)	0.5218(9)	0.1645(5)	0.0316(17)
C4	0.7071(11)	0.5551(9)	0.0915(5)	0.0354(18)*
C5	4696(14)	0.9891(11)	0.0444(7)	0.054(3)*
C6	0.8965(10)	0.6242(8)	0.1610(4)	0.0275(16)
C7	0.7880(8)	0.5921(7)	0.2359(4)	0.0196(14)
C8	0.8280(9)	0.6149(7)	0.3132(4)	0.0226(15)
C9	0.1588(8)	0.8424(6)	0.5712(4)	0.0177(14)
C10	0.1188(8)	0.8701(7)	0.6576(4)	0.0178(13)
C11	0.0309(10)	0.7812(7)	0.7189(5)	0.0249(16)
C12	0.0105(11)	0.7958(8)	0.7987(5)	0.0335(18)
C13	0.0759(12)	0.8999(9)	0.8198(4)	0.0360(19)
C14	0.1591(10)	0.9880(8)	0.7607(4)	0.0272(16)
C15	0.1835(8)	0.9749(7)	0.6795(4)	0.0173(13)
C16	−0.2677(8)	0.9173(6)	0.3836(4)	0.0172(13)
C17	0.3396(16)	0.8533(14)	0.1670(8)	0.069(3)
C18	0.3967(16)	0.8693(13)	0.0824(7)	0.070(3)
C19	0.4805(16)	1.0797(15)	0.0927(8)	0.079(4)
C21	0.4214(16)	1.0572(15)	0.1779(7)	0.074(4)

Experimental details

The coordinates of the H-atoms at the water molecules were refined with the O-H distance restrained to 0.85 Å. The *U*_{iso}

values of the hydrogen atoms of methyl groups were set to 1.5*U*_{eq}(C) and the *U*_{iso} values of all other hydrogen atoms were set to 1.2*U*_{eq}(C, N).

Discussion

It is well known that aromatic multi-carboxylic acid, and the corresponding deprotonated anions such as isophthalic acid are very important building blocks of many important compounds widely used in many fields [3, 4]. Lanthanide 3+ ions are usually selected as luminescent centers owing to their high luminescent quantum yield, long lifetime and large Stokes shifts [5]. In order to further study the coordination behavior and role of samarium(III) cation in the selfassembly processes in the presence of fluorine substituted dicarboxylate and nitrogen-heterocyclic compound, the title complex has been synthesized and systematically characterized.

The structure contains two discrete parts: a 4,4'-bipyridine molecule and a Sm(III) coordination polymer. The asymmetric unit of the coordination unit polymer consists of two kinds of Sm(III) ion, two Tfpa ligands, two hydroxido ligands and two coordination water molecules, as illustrated in the figure. In this unit, the first Sm(III) ion is eight folded coordinated with an O₈ donor set, among which five oxygen atoms are derivated from Tfpa ligand, one oxygen atom is from water molecule, another oxygen atom is derivated from hydroxyl group, completing the dodecahedron geometry around the central ion. As for the second Sm(III) cation, it is coordinated with an O₉ donor set, the polyhedron around this Sm(III) ion is best described as a distorted monocapped anti-prism, as shown in the figure. The oxygen atoms are derivated from Tfpa ligand, water molecule, and hydroxyl group, respectively. The bipy does not coordinate with the Sm(III) ion. This is obvious different from the transition metal compound [6]. The first kind of Tfpa ligand using two carboxylate bridging two adjacent Sm(III) cations, and the second kind of Tfpa ligand one carboxylate connects two adjacent Sm(III) cations in both chelate and mono coordination fashions. Both oxygen atoms from hydroxyl group adopt μ₃-fashion connecting three neighboring Sm(III) ions. This coordination mode is also found in other lanthanide compound [7]. The Sm(III)–O bond distances are in range from 2.310(3) to 2.668(4) Å, with average of 2.48 Å. Bond angles of O–Sm(III)–O are in range of 41.34(8) to 159.19(8)°. All the bond lengths and bond angles are in accordance to the reported relevant literatures [8]. As for another carboxylate, it employs mono coordination mode linking two adjacent Sm(III) ions in the same time. Two carboxylate from the Tfpa ligand doubly bridges two adjacent Sm(III) cations, resulting in the dinuclear units with Sm···Sm separation of just 3.922 Å. The dinuclear units are further connected into one dimensional double chain through the carboxylate from the Tfpa ligand [9, 10]. This coordination

architecture is different from similar lanthanide compound based on fluorine substituted ligand [11].

Acknowledgements: This work was supported by the Foundation for Science & Technology Innovation Talents in Henan province (Nos. 14HASTIT014 and 164100510012), Natural Science Foundation of China (Nos. 21671114 and U1604143), and the Tackle Key Problem of Science and Technology Project of Henan Province, China (no. 182102310897).

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