



Synthesis and Crystal Structures of Sm(III) Complex Assembled from Pyridine-Carboxylate

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(Received: 18 May 2011;

Accepted: 12 November 2011)

AJC-10663

A new pyridinecarboxylato-bridged coordination polymers $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n\{1\}$ (3,4-pbc=3-pyrid-4-ylbenzoic acid) has been synthesized and structurally characterized by elemental analysis, IR and X-ray diffraction. Single crystal X-ray analyses reveal that the carboxylate groups of 3,4-pbc ligands adopt two coordinated mode: *bis*-monodentate ($\mu_2\text{-}\eta^1\text{:}\eta^1$) and bidentate chelating ($\mu_1\text{-}\eta^1\text{:}\eta^1$). Hydrogen bonding interactions are found in compound $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$, which further extend and stabilize the coordination motifs.

Key Words: Coordination polymer, Hydrothermal synthesis, Crystal structure.

INTRODUCTION

In recent years, coordination polymers and supramolecular complexes have attracted much attention, owing to their potential application as functional materials¹⁻³. It is well-known that the structural and functional information of such target materials were constructed by the metal-ligand coordination bonds or intermolecular weak interactions. In this case, the design of new types of ligands such as pyridyl and/or carboxylate groups have been proven to the most important strategy, due to their potential multiple coordination modes⁴⁻⁷. Hydrogen bonds are suitable for the design of polymeric arrangement and crystal engineering because of their important directional interactions and because they can interlink 1-D or 2-D structures into higher-dimensionality systems.

EXPERIMENTAL

All reagents and solvents employed were commercially available and were used as received without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded in the 4000-400 cm^{-1} range with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet.

Preparation of compounds

Synthesis of $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}_n$ (1): The mixture of $\text{SmCl}_3\cdot 6\text{H}_2\text{O}$ (0.037 g, 0.1 mmol) 3-pyrid-4-yl benzoic acid (3,4-pbc) (0.3 mmol, 0.060 g) and H_2O (12 mL) was heated in a 20 mL stainless steel reactor with a Teflon liner at 160 °C for 120 h and then was cooled to room temperature at 2 °C/h.

Yellow block crystals were obtained. Yield: 57 % (based on the initial Sm_2O_3 input). Anal. calcd (%) for $\text{C}_{36}\text{H}_{30}\text{N}_3\text{O}_9\text{Sm}$: C, 62.62; H, 3.50; N, 6.09. Found (%): C, 62.51; H, 3.53; N, 6.07. IR (KBr, ν_{max} , cm^{-1}): 3320 br, 1610 s, 1586 s, 1554 s, 1440 s, 1302 w, 1126 w, 851 m, 623 m.

X-ray crystallography: Suitable single crystals of the Sm(III) complex were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibers, which were

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT
SUMMARY FOR Sm(III) COMPLEX

Empirical formula	$\text{C}_{36}\text{H}_{30}\text{N}_3\text{O}_9\text{Sm}$	Volume (\AA^3)	1626.0 (2)
Formula weight	798.99	Z, Calculated density (mg/m^3)	2, 1.632
Crystal system	Triclinic <i>P</i> -1	<i>F</i> (000)	802
Unit cell dimensions	$a = 9.720(8) \text{\AA}$ $b = 4.020(12) \text{\AA}$ $c = 14.103(11) \text{\AA}$ $\alpha = 90.00$ $\beta = 95.97(3)$ $\gamma = 90.00$	Limiting indices	$-8 \leq h \leq 12$ $-18 \leq k \leq 18$ $-18 \leq l \leq 12$
Goodness-of-fit on F^2	1.062	R indices (all data)	$R_1 = 0.0391$ $wR_2 = 0.0710$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0297$ $wR_2 = 0.0667$	Largest diff. peak and hole ($e/\text{\AA}^3$)	0.869 and -1.093

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}, wR = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}}$$

mounted on a Bruker Smart 1000 CCD diffractometer with a MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K by using an ω scan mode for cell determination and data collection. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL 97 program⁸. Crystal data, intensity collection and structure refinement details are summarized in Table-1. Selected interatomic distances and bond angles are given in Table-2. CCDC: 725802

TABLE-2
SELECTED BOND LENGTHS (\AA) AND BOND ANGLES ($^\circ$)

Bond	Dist.
Sm(1)-O(1)	2.320(2)
Sm(1)-O(2)#1	2.436(2)
Sm(1)-O(1w)	2.470(2)
Sm(1)-O(4)	2.496(2)
Sm(1)-O(5)	2.326(2)
Sm(1)-O(2w)	2.470(2)
Sm(1)-O(3)	2.549(2)
Sm(1)-O(6)#2	2.419(2)
Angle	($^\circ$)
O(1)-Sm(1)-O(5)	158.51(8)
O(5)-Sm(1)-O(6)#2	107.22(7)
O(5)-Sm(1)-O(2)#1	80.12(7)
O(1)-Sm(1)-O(1w)	89.80(8)
O(1)-Sm(1)-O(6)#2	81.83(7)
O(1)-Sm(1)-O(2)#1	104.74(7)
O(2)#1-Sm(1)-O(6)#2	142.74(8)
O(5)-Sm(1)-O(1w)	74.80(8)
O(6)#2-Sm(1)-O(1w)	73.45(8)
O(1)-Sm(1)-O(2w)	74.81(8)
O(6)#2-Sm(1)-O(2w)	138.61(8)
O(1w)-Sm(1)-O(2w)	72.79(8)

Symmetry code for compounds: (1) #1: 1-x, -y, 1-z; #2: 2-x, -y, 1-z;
(2) #1: -1+x, y, z; #2: 1-x, -1/2+y, 1/2-z

RESULTS AND DISCUSSION

Structure description: The local coordination geometry of polymer $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}$ with the atom-numbering scheme is shown in Fig. 1, which is shown that each Sm(III) center is coordinated to eight atoms: six carboxylate oxygen atoms from four *bis*-monodentate 3,4-pbc⁻ ligands and one chelating 3,4-pbc⁻ ligand and two oxygen atoms from two coordinated water molecular. The Sm(1)-O (carboxylate) distance is from 2.320(2) \AA to 2.549(2) \AA . All Sm^{III} centers are connected by μ_2 -3,4-pbc to form a 1D chain motif, extending along the crystallographic a-direction, the intramolecular adjacent non-bonding Sm...Sm distance is 4.840 \AA . In the net, two neutral chain of the compound **1** are bonded together by strong intermolecular hydrogen bonds to create a double-chain architecture, extending along the crystallographic a-direction. The dihedral angles between pyridine ring and phenyl ring are 55.61° ($\mu_1\text{-}\eta^1$: η^1) and 10.39° ($\mu_2\text{-}\eta^1$: η^1).

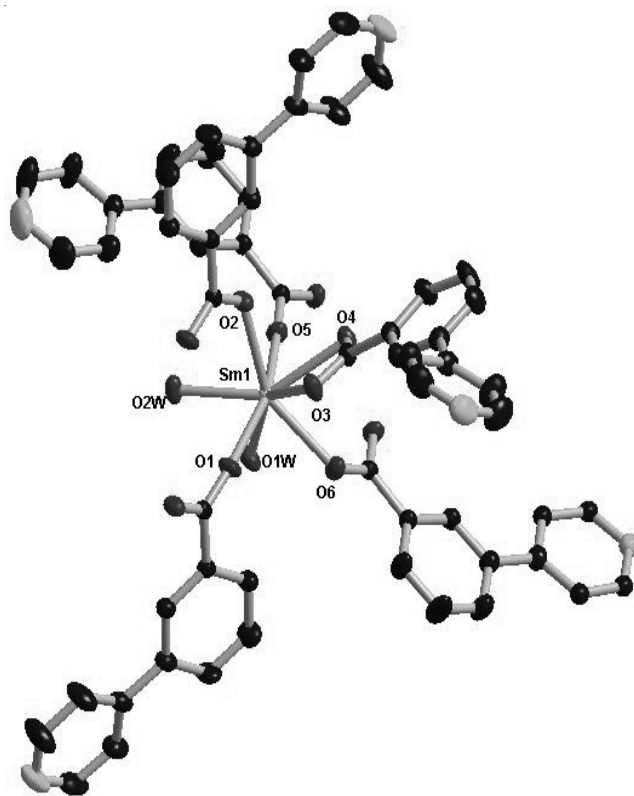


Fig. 1. A portion view of $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}$ showing the coordination environment of Sm(III)

The hydrogen bonding system in $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}$ consists of the uncoordinated nitrogen atom N1 and N2 on the carboxylate group, with the hydrogen atoms H1WA (symmetry code: 1-x, -1-y, 1-z) and H2WA (symmetry code: 1-x, -y, 1-z) from the coordinated water molecules of the neighboring chain. The distances of H1WA...N1 and H2WA...N2 are 1.948(11) \AA and 1.929(11) \AA , respectively. The corresponding O1W...N1 and O2W...N2 distances are 2.786(4) \AA and 2.763(4) \AA , the angles of O1W-H1WA...N1 and O2W-H2WA...N2 are $174(3)^\circ$ and $167(3)^\circ$. There also exist intramolecular hydrogen bonds between the coordinating water molecules (O1W and O2W) and the COO⁻ group (O3 and O4), with an H1WB...O4 distance of 1.945(10) \AA (symmetry code: 2-x, -y, 1-z) and an H2WB...O3 distance of 1.964(12) \AA (symmetry code: 1-x, -y, 1-z). There is no doubt that these strong hydrogen bonding interactions contribute significantly to the alignment of the molecules of the present compound in the crystalline state.

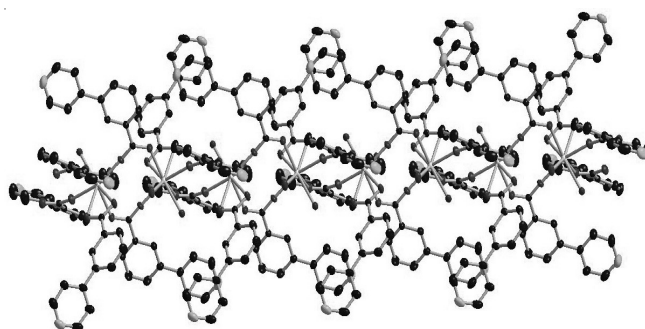


Fig. 2. 1D chain structure of $\{[\text{Sm}(3,4\text{-pbc})_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}\}$

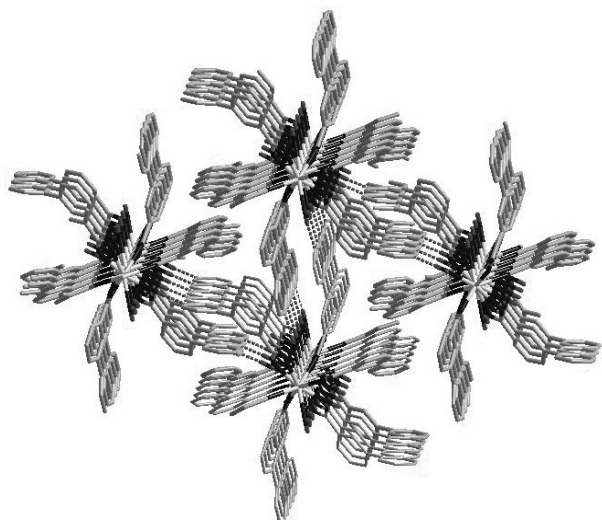


Fig. 3. View of hydrogen bonding interactions between the chains are indicated as dashed line for compound **1**

REFERENCES

1. B.O. Patrick, C.L. Stevens, A. Storr and R.C. Thompson, *Polyhedron*, **24**, 2242 (2005).
2. Y.H. Wen, J.K. Cheng, Y.L. Feng, J. Zhang, Z.L. Li and Y.G. Yao, *Inorg. Chim. Acta*, **358**, 3347 (2005).
3. X.L. Wang, C. Qin, E.B. Wang and L. Xu, *J. Mol. Struct.*, **749**, 45 (2005).
4. F. Guo, *J. Coord. Chem.*, **62**, 3606 (2009).
5. T.B. Lu and R.L. Luck, *Inorg. Chim. Acta*, **351**, 345 (2003).
6. F. Guo, *J. Coord. Chem.*, **62**, 3621 (2009).
7. R.Q. Zhong, R.Q. Zou, M. Du, L. Jiang, T. Yamada, G. Maruta, S. Takeda and Q. Xu, *Cryst. Eng. Comm.*, **10**, 605 (2008).
8. G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, (1997).