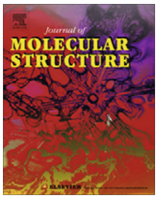
Journal of Molecular Structure 1006 (2011) 83–86

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Hydrothermal *in situ* ligand synthesis and chiral self-assembly with Pr(III)

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ARTICLE INFO

Article history:
Received 29 April 2011
Received in revised form 16 July 2011
Accepted 18 July 2011
Available online 9 August 2011

Keywords:
Hydrolysis
C–O ether bond cleavage
Chiral self-assembly
Magnetic behavior

ABSTRACT

P-4mo-BDCME (5-(pyridine-4-ylmethoxy)-isophthalic acid dimethyl ester) is undergoing hydrolysis, C–O ether bond cleavage and simultaneous self-assembly with Pr(III) to produce a new chiral compound, $[Pr_2(HO–BDC)_3(H_2O)_2]$ (**1** HO–BDC = 5-hydroisophthalic acid), which features a three-dimensional (3D) framework with right-handed helices. Moreover, the magnetic behavior of **1** was investigated in the temperature range of 2–300 K.

1. Introduction

Hydrothermal *in situ* ligand reactions, such as hydroxylation and decarboxylation of aromatic groups, hydrolysis, alkylation, cleavage of C–S or C–C bonds, cycloaddition of organonitriles with ammonia and so on [1], are of current interest. Because they not only can produce novel metal–organic frameworks with fascinating structures and peculiar properties, which cannot be obtained by direct preparation, but also can discover new organic reactions and understand the reaction mechanism. The cleavage of C–O ether bond in organic synthetic chemistry is very important for the transformation of functional groups, so many methods, such as Pd-based catalysts, buffer-acid catalysts and photocatalysts, have been used in the research of the cleavage of C–O ether bonds in the organic reaction [2]. However, hydrothermal *in situ* cleavage of C–O ether bonds of the organic ligand and simultaneous self-assembly with metal ions have rarely been reported before [3]. Therefore, we report here a new compound, $[Pr_2(HO–BDC)_3(H_2O)_2]$ (**1**), which was obtained by the hydrothermal reaction of $Pr(NO_3)_3{\cdot}6H_2O$ and P-4mo-BDCME (5-(pyridine-4-ylmethoxy)-isophthalic acid dimethyl ester) (Scheme 1). Interestingly, this complicate reaction procedure includes *in situ* hydrolysis of ester, ligand C–O ether bond cleavage and simultaneous molecular self-assembly.

2. Experimental

2.1. Materials and methods

All chemicals except P-4mo-BDCME (5-(pyridine-4-ylmethoxy)-isophthalic acid dimethyl ester) were obtained from commercial sources and used without further purification. P-4mo-BDCME was synthesized according to the previously reported procedure [3a]. Element analyses (C and H) were determined with an elemental Vairo EL III analyzer. Infrared spectra using the KBr pellets were measured on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. Thermogravimetric analyses were carried out on a NetzschSTA499C integration thermal analyzer under a nitrogen atmosphere from 30 to 900 °C at a heating rate of 10 °C/min. Powder X-ray diffraction data were collected using PANalytical X'Pert Pro powder diffractometer with Cu Kα radiation and $5° \leqslant 2\theta \leqslant 50°$. The polycrystalline magnetic susceptibility data were collected on a Quantum Design MPMS(SQUID)-XL magnetometer in the temperature range from 2 to 300 K. Single crystal X-ray diffraction was carried out on a Saturn724 diffractometer.

2.2. Synthesis

Synthesis of **1**: A mixture of $Pr(NO_3)_3{\cdot}6H_2O$ (0.1310 g, 0.3 mmol), Na_2CO_3 (0.05 g, 0.5 mmol), P-4mo-BDCME (0.0546 g, 0.3 mmol) and H_2O (15 ml) was sealed in a 23 ml Teflon-lined stainless steel autoclave and was heated at 160 °C for 72 h in a programmable oven. Then, the reactor was cooled slowly to room temperature at a rate of 0.5 °C/min. The brown crystals were filtered out and washed with water and ethanol, respectively

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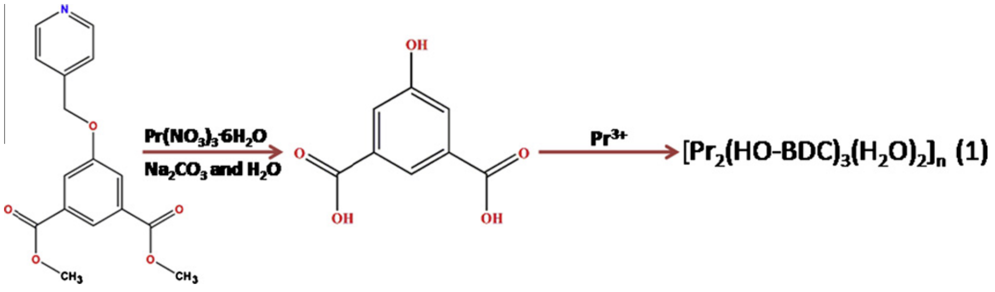
doi:10.1016/j.molstruc.2011.07.033



Scheme 1. *In situ* hydrothermal synthesis of compound 1.

Table 1
Crystallographic data for compound **1**.

Empirical formula	$C_{24}H_{16}O_{17}Pr_2$
F_w	858.16
Crystal system	Orthorhombic
Space group	$I4_1$
a (Å)	17.116(9)
b (Å)	17.116(9)
c (Å)	14.083(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4126(4)
Z	1.377
D_c (g cm^{-3})	2.389
m (mm^{-1})	1644
F(0 0 0)	14,738
Reflns (measured)	3523
Reflns (unique)	0.0455
R_{int}	1.064
GOF on F^2	0.0562
R_1[a] [$I > 2\sigma(I)$]	0.1612
wR_2[b] (all data)	

[a] $R_1 = \sum(F_0 - F_c)/\sum F_0$.
[b] $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

1			
Pr(1)–O(6)	2.419(8)	Pr(1)–O(7)[a]	2.430(10)
Pr(1)–O(2)[a]	2.450(8)	Pr(1)–O(1 W)	2.461(12)
Pr(1)–O(3)[b]	2.495(8)	Pr(1)–O(1)	2.500(8)
Pr(1)–O(4)[c]	2.510(9)	Pr(1)–O(3)[c]	2.874(10)
Pr(1)–O(1)[a]	2.887(10)		
O(6)–Pr(1)–O(7)[a]	131.7(4)	O(6)–Pr(1)–O(2)[a]	75.5(3)
O(7)[a]–Pr(1)–O(2)[a]	122.2(4)	O(6)–Pr(1)–O(1 W)	69.8(5)
O(7)[a]–Pr(1)–O(1 W)	72.2(5)	O(2)[a]–Pr(1)–O(1 W)	76.1(5)
O(6)–Pr(1)–O(3)[b]	156.2(3)	O(7)[a]–Pr(1)–O(3)[b]	70.8(4)
O(2)[a]–Pr(1)–O(3)[b]	99.9(3)	O(1 W)–Pr(1)–O(3)[b]	132.5(5)
O(6)–Pr(1)–O(1)	84.2(3)	O(7)[a]–Pr(1)–O(1)	140.5(4)
O(2)[a]–Pr(1)–O(1)	77.2(4)	O(1 W)–Pr(1)–O(1)	146.5(4)
O(3)[b]–Pr(1)–O(1)	72.0(3)	O(6)–Pr(1)–O(4)[c]	75.9(3)
O(7)[a]–Pr(1)–O(4)[c]	70.0(4)	O(2)[a]–Pr(1)–O(4)[c]	148.3(3)
O(1 W)–Pr(1)–O(4)[c]	81.4(5)	O(3)[b]–Pr(1)–O(4)[c]	111.8(3)
O(1)–Pr(1)–O(4)[c]	113.1(3)	O(6)–Pr(1)–O(3)[c]	74.9(3)
O(7)[a]–Pr(1)–O(3)[c]	103.6(3)	O(2)[a]–Pr(1)–O(3)[c]	134.3(3)
O(1 W)–Pr(1)–O(3)[c]	123.4(5)	O(3)[b]–Pr(1)–O(3)[c]	93.6(2)
O(1)–Pr(1)–O(3)[c]	65.9(3)	O(4)[c]–Pr(1)–O(3)[c]	47.4(3)
O(6)–Pr(1)–O(1)[a]	119.9(3)	O(7)[a]–Pr(1)–O(1)[a]	80.3(3)
O(2)[a]–Pr(1)–O(1)[a]	46.9(3)	O(1 W)–Pr(1)–O(1)[a]	79.8(5)
O(3)[b]–Pr(1)–O(1)[a]	65.7(3)	O(1)–Pr(1)–O(1)[a]	96.3(2)
O(4)[c]–Pr(1)–O(1)[a]	148.5(3)	O(3)[c]–Pr(1)–O(1)[a]	156.8(2)

Symmetry codes:
[a] $-y + 1, x + 1/2, z + 1/4$.
[b] $y - 1/2, -x + 1, z - 1/4$.
[c] $-x + 1/2, -y + 3/2, z - 1/2$.

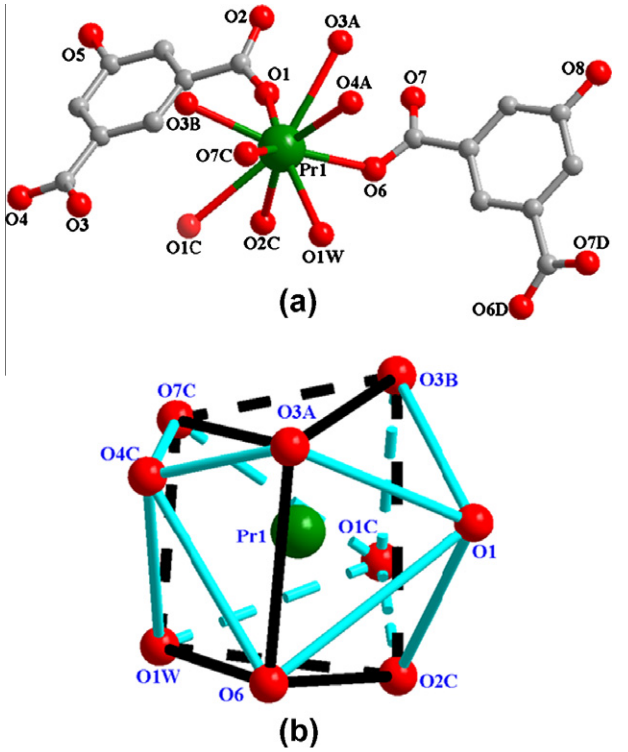


Fig. 1. (a) A view of the coordination environment around the Pr^{3+} ions. Hydrogen atoms associated with carbon atoms and hydroxyl oxygen atoms (O5 and O8) have been omitted for clarity and (b) distorted tricapped trigonal–prismatic coordination polyhedron of the Pr^{3+}. Symmetry codes: (A) $0.5 - x, 1.5 - y, -0.5 + z$; (B) $1 - x, -0.5 + y, -0.25 + z$; (C) $0.5 + x, 1 - y, 0.25 + z$; (D) $-x, 1 - y, z$.

(yield: 65%). Anal.Calc. for **1**, $C_{24}H_{16}O_{17}Pr_2$ (858.16): C, 33.56; H, 1.86; O, 31.70%. Found: C, 33.58; H, 1.83, O, 31.65%. IR (solid KBr pellet, v (cm^{-1})): 2926 (vs), 1615 (vs) 1552 (w), 1437 (s), 1386 (vs), 1351 (s), 1097 (m), 722 (m), 512 (w).

2.3. X-ray crystallography

The X-ray single crystal structure analysis of **1** was performed on Saturn724 diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program [4]. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program [5]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located at their ideal positions. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles are listed in Table 2.