Inorganica Chimica Acta 387 (2012) 308–313

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

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

Syntheses, crystal structures and physical properties of two unusual 4d–4f heterometallic coordination polymers

Guang-Xiang Liu [a,*], Hong Zhou [a], Xiao-Chun Zha [a], Chun-You Zhang [a], Yan Wang [a], Sadafumi Nishihara [b], Xiao-Ming Ren [c]

[a] School of Biochemical and Environmental Engineering, Nanjing Xiaozhuang University, Nanjing 211171, China
[b] Department of Physical Science, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
[c] Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, China

ARTICLE INFO

Article history:
Received 1 February 2011
Received in revised form 4 February 2012
Accepted 8 February 2012
Available online 1 March 2012

Keywords:
Heterometallic coordination polymer
Pyridine-3,4-dicarboxylic acid
Crystal structure
Luminescence
Magnetism

ABSTRACT

Two novel heterometallic coordination polymers, $[AgSm(pydc)_2]\cdot 2H_2O$ (**1**) and $[AgTb(pydc)_2]_2\cdot H_2O$ (**2**) (H_2pydc = pyridine-3,4-dicarboxylic acid), have been synthesized under hydrothermal conditions, and characterized by elemental analysis, IR, thermogravimetric analysis and single-crystal X-ray diffraction. Complexes **1** and **2** are isomorphous and exhibit 3D open framework heterometallic coordination polymer containing 1D channels occupied by lattice water molecules. To our knowledge, both compounds represent the rare examples of 3D open-framework 4d–4f heterometallic coordination polymers with open framework structure. Moreover, their luminescent and magnetic properties have also been investigated.

1. Introduction

In the last two decades, metal–organic frameworks (MOFs) with well-regulated network structures have provoked significant interest as functional materials displaying potential applications in such fields as magnetism, molecular separation, catalysis, luminescence, and molecule storage [1–12]. Consequently, a variety of MOFs have been reported. However, much work on MOFs has been focusing on the design of lanthanide homometallic system, some interesting efforts have been contributed in the field of the molecular magnetism of lanthanide ions [13–15]. However, the chemistry towards heterometallic MOFs has attracted much less attention. Recently, some lanthanide–transition heterometallic complexes have been successfully obtained from spontaneous assembly of mixed metal ions and ligands containing hybrid donor atoms, such as cyanide [16], carbonyl [17], pyridine-carboxylate ligand [18], amino acids [19,20] and so on. The assembly of three-dimensional (3D) heterometallic complexes, however, is still a formidable task due to the variable and versatile coordination numbers of the lanthanide ions, their low stereochemical preference and also because of competitive reactions between lanthanide and transition metals coordinated to the same organic ligands. As is well-known, the lanthanides have a strong tendency to coordinate to O-donor atoms to form lanthanide-carboxylate coordination polymers [21], and compared to the Ln(III) ions, the transition metal easily bonds to the N-donor atoms [22]. Thus, if a ligand containing both N-donor and O-donor atoms and the transition metal could be introduced to link the lanthanide-carboxylate subunits successfully, the novel heterometallic coordination polymers may be obtained through the recognition of the metal ions and their coordinating atoms [23].

On the other hand, great interest in Ln–Ag heterometallic complexes is recently focused on the nicotinic acid or isonicotinic acid [24–28]. Compared with these two N-heterocyclic acids, pyridine-3,4-dicarboxylic acid (H_2pydc) can show richer coordination modes due to its two carboxylate groups, accordingly, it is an excellent candidate for the construction of metal organic frameworks. Although the synthesis of the monometallic coordination polymers based on H_2pydc ligand has become widespread over the recent years [29–35], investigations on heterometallic coordination polymers containing H_2pydc has not been extensively explored until now [24]. In this paper, we chose pyridine-3,4-dicarboxylic acid as a bifunctional bridging ligand possesses of oxygen and nitrogen donors, which can be chose to as a potential linker between the lanthanide centers and the Ag centers. Herein, we report on the syntheses, crystal structures, luminescence and magnetic properties of two novel 4d–4f heterometallic coordination polymers, $[AgSm(pydc)_2]\cdot 2H_2O$ (**1**) and $[AgTb(pydc)_2]_2\cdot H_2O$ (**2**).

* Corresponding author. Tel./fax: +86 25 86178260.
E-mail address: njuliugx@gmail.com (G.-X. Liu).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2012.02.010

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. The luminescent spectra for the powdered solid samples were measured at room temperature on an Aminco Bowman Series 2 spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The magnetic data were collected in the range of 2–300 K at an applied field of 1000 Oe on a MPMP-XL7 SQUID magnetometer. The diamagnetism was corrected by Pascal constants [36].

2.2. Synthesis of $[AgSm(pydc)_2]\cdot 2H_2O$ (**1**)

A mixture of Sm_2O_3 (0.2 mmol, 69.7 mg), $AgNO_3$ (0.2 mmol, 34.0 mg), pyridine-3,4-dicarboxylic acid (0.2 mmol, 33.4 mg) and water (15 mL) was stirred for 30 min in air. Thereafter, the mixture was sealed in a 23-mL Teflon reactor and was kept under autogenous pressure at 180 °C for 4 days. Yellow octahedron-shaped crystals were filtered off, washed with distilled water, and dried in air (yield: 52% based on Ag). The as-synthesized material is insoluble in water and common organic solvents. *Anal.* Calc. for $C_{14}H_{10}N_2O_{10}AgSm$: C, 26.93; H, 1.61; N, 4.49. Found: C, 26.85; H, 1.69; N, 4.45%. IR (KBr pellet, cm^{-1}): 3432 (m), 1628 (s), 1573 (s), 1477 (m), 1388 (s), 1162 (w), 1091 (w), 892 (w), 844 (m), 714 (m), 672 (w), 541(w).

Table 1
Crystal data and refinement results for complexes **1** and **2**.

Complex	**1**	**2**
Formula	$C_{14}H_{10}N_2O_{10}AgSm$	$C_{28}H_{14}N_4O_{17}Ag_2Tb_2$
Formula weight	624.46	1212.01
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.2745(9)	7.2139(15)
b (Å)	10.4148(13)	10.355(2)
c (Å)	11.5977(14)	11.554(2)
α (°)	99.777(2)	99.443(2)
β (°)	100.950(1)	101.070(3)
γ (°)	95.779(2)	95.396(2)
V (Å^3)	842.08(18)	828.5(3)
Z	2	1
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
D_{calc} (mg m^{-3})	2.463	2.429
F(000)	594	570
θ (°)	2.43–25.50	2.45–26.00
Reflections collected	5873	6751
Independent reflections	3086 [R_{int} = 0.0222]	3197 [R_{int} = 0.0387]
Data/parameters	3086/535	3197/244
Goodness of fit (GOF) on F^2	1.093	1.048
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0303, wR_2 = 0.0764	R_1 = 0.0498, wR_2 = 0.1358
R indices (all data)	R_1 = 0.0351, wR_2 = 0.0786	R_1 = 0.0706, wR_2 = 0.1469
Large difference in peak and hole (e Å^{-3})	0.944 and −1.606	0.980 and −0.966

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

2.3. Synthesis of $[AgTb(pydc)_2]_2\cdot H_2O$ (**2**)

A mixture of Tb_4O_7 (0.1 mmol, 75.0 mg), $AgNO_3$ (0.2 mmol, 34.0 mg), pyridine-3,4-dicarboxylic acid (0.2 mmol, 33.4 mg) and water (15 mL) was stirred for 30 min in air. Thereafter, the mixture was sealed in a 23-mL Teflon reactor and was kept under autogenous pressure at 180 °C for 4 days. Colorless octahedron-shaped crystals were filtered off, washed with distilled water, and dried in air (yield: 43% based on Ag). The as-synthesized material is insoluble in water and common organic solvents. *Anal.* Calc. for $C_{28}H_{14}N_4O_{17}Ag_2Tb_2$: C, 27.75; H, 1.16; N, 4.62. Found: C, 27.86;

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

Ag(1)–N(1)	2.186(5)	Sm(1)–O(2)	2.485(4)
Ag(1)–N(2)#1	2.192(5)	Sm(1)–O(4)#5	2.503(4)
Sm(1)–O(8)#2	2.374(4)	Sm(1)–O(5)	2.509(4)
Sm(1)–O(7)#3	2.415(4)	Sm(1)–O(3)#5	2.565(4)
Sm(1)–O(2)#4	2.415(4)	Sm(1)–O(6)	2.609(4)
Sm(1)–O(3)#4	2.434(4)		
N(1)–Ag(1)–N(2)#1	145.7(2)	O(3)#4–Sm(1)–O(5)	69.91(14)
O(8)#2–Sm(1)–O(7)#3	139.44(13)	O(2)–Sm(1)–O(5)	144.22(13)
O(8)#2–Sm(1)–O(2)#4	74.65(14)	O(4)#5–Sm(1)–O(5)	128.08(14)
O(7)#3–Sm(1)–O(2)#4	74.58(14)	O(8)#2–Sm(1)–O(3)#5	145.22(13)
O(8)#2–Sm(1)–O(3)#4	126.04(14)	O(7)#3–Sm(1)–O(3)#5	73.97(13)
O(7)#3–Sm(1)–O(3)#4	67.88(14)	O(2)#4–Sm(1)–O(3)#5	136.79(13)
O(2)#4–Sm(1)–O(3)#4	73.60(13)	O(3)#4–Sm(1)–O(3)#5	67.49(15)
O(8)#2–Sm(1)–O(2)	75.95(14)	O(2)–Sm(1)–O(3)#5	120.57(12)
O(7)#3–Sm(1)–O(2)	70.88(13)	O(4)#5–Sm(1)–O(3)#5	51.49(13)
O(2)#4–Sm(1)–O(2)	74.64(15)	O(5)–Sm(1)–O(3)#5	92.25(13)
O(3)#4–Sm(1)–O(2)	133.02(13)	O(8)#2–Sm(1)–O(6)	77.08(13)
O(8)#2–Sm(1)–O(4)#5	118.23(15)	O(7)#3–Sm(1)–O(6)	141.99(13)
O(7)#3–Sm(1)–O(4)#5	73.45(14)	O(2)#4–Sm(1)–O(6)	139.69(13)
O(2)#4–Sm(1)–O(4)#5	140.34(13)	O(3)#4–Sm(1)–O(6)	101.66(13)
O(3)#4–Sm(1)–O(4)#5	114.16(13)	O(2)–Sm(1)–O(6)	124.84(13)
O(2)–Sm(1)–O(4)#5	73.15(13)	O(4)#5–Sm(1)–O(6)	78.91(14)
O(8)#2–Sm(1)–O(5)	68.55(14)	O(5)–Sm(1)–O(6)	51.18(14)
O(7)#3–Sm(1)–O(5)	137.72(14)	O(3)#5–Sm(1)–O(6)	68.43(13)
O(2)#4–Sm(1)–O(5)	91.51(13)		

Symmetry codes: #1 $x+2$, $y+1$, $z+1$; #2 $x-1$, y, z; #3 $-x+2$, $-y+2$, $-z$; #4 $-x+1$, $-y+2$, $-z$; #5 $x+1$, y, z.

Table 3
Selected bond lengths (Å) and bond angles (°) for **2**.

N(1)–Ag(1)	2.189(9)	Tb(2)–O(2)#1	2.377(7)
N(2)–Ag(1)	2.213(8)	Tb(2)–O(7)#2	2.431(8)
O(7)–Tb(2)	2.511(8)	Tb(2)–O(6)#4	2.452(7)
O(8)–Tb(2)	2.460(7)	Tb(2)–O(4)#5	2.470(7)
Tb(2)–O(1)#3	2.341(7)	Tb(2)–O(3)#5	2.545(7)
Tb(2)–O(6)#2	2.373(7)		
N(1)–Ag(1)–N(2)	145.6(3)	O(7)#2–Tb(2)–O(4)#5	70.3(2)
O(1)#3–Tb(2)–O(6)#2	75.5(2)	O(6)#4–Tb(2)–O(4)#5	144.0(2)
O(1)#3–Tb(2)–O(2)#1	140.0(2)	O(8)–Tb(2)–O(4)#5	128.2(2)
O(6)#2–Tb(2)–O(2)#1	74.7(2)	O(1)#3–Tb(2)–O(7)	143.9(2)
O(1)#3–Tb(2)–O(7)#2	127.4(2)	O(6)#2–Tb(2)–O(7)	137.5(3)
O(6)#2–Tb(2)–O(7)#2	74.6(3)	O(2)#1–Tb(2)–O(7)	74.4(2)
O(2)#1–Tb(2)–O(7)#2	67.7(2)	O(7)#2–Tb(2)–O(7)	67.0(3)
O(1)#3–Tb(2)–O(6)#4	75.4(2)	O(6)#4–Tb(2)–O(7)	121.1(2)
O(6)#2–Tb(2)–O(6)#4	74.4(3)	O(8)–Tb(2)–O(7)	52.4(2)
O(2)#1–Tb(2)–O(6)#4	71.4(2)	O(4)#5–Tb(2)–O(7)	91.6(2)
O(7)#2–Tb(2)–O(6)#4	133.6(2)	O(1)#3–Tb(2)–O(3)#5	76.6(2)
O(1)#3–Tb(2)–O(8)	116.7(2)	O(6)#2–Tb(2)–O(3)#5	140.7(2)
O(6)#2–Tb(2)–O(8)	139.6(2)	O(2)#1–Tb(2)–O(3)#5	141.4(2)
O(2)#1–Tb(2)–O(8)	73.4(2)	O(7)#2–Tb(2)–O(3)#5	102.0(2)
O(7)#2–Tb(2)–O(8)	114.2(2)	O(6)#4–Tb(2)–O(3)#5	123.7(2)
O(6)#4–Tb(2)–O(8)	72.4(2)	O(8)–Tb(2)–O(3)#5	78.4(2)
O(1)#3–Tb(2)–O(4)#5	68.8(2)	O(4)#5–Tb(2)–O(3)#5	51.7(2)
O(6)#2–Tb(2)–O(4)#5	92.2(2)	O(7)–Tb(2)–O(3)#5	67.6(2)
O(2)#1–Tb(2)–O(4)#5	138.0(2)		

Symmetry codes: #1 $-x$, $-y+2$, $-z$; #2 $-x+1$, $-y+3$, $-z+1$; #3 x, $y+1$, $z+1$; #4 $x-1$, y, z; #5 $x+1$, $y+1$, $z+1$.