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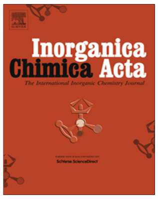

Note

A novel 2D sandwich layered neodymium coordination polymer based on 2,2′-bipyridyl-4,4′-dicarboxylate ligand

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ABSTRACT

A new coordination polymer $\{[Nd(bpdc)_{1.5}(H_2O)]\cdot H_2O\}_n$ **(1)** based on neodymium(III) and 2,2′-bipyridyl-4,4′-dicarboxylic acid (H_2bpdc) has been prepared by hydrothermal method. And it has been characterized by elemental analysis, IR spectrum, thermogravimetric analysis (TGA), single-crystal X-ray diffraction and magnetic properties. The X-ray diffraction study shows that complex **1** has a 2-D (3,4,5)-connected net with $(4\cdot 6^2)_2(4^3\cdot 6^7)_2(4^4\cdot 6^2)$ topology. And the 2-D framework is connected by hydrogen bonds to form an unusual 3-D layered architecture. The TGA indicates that complex **1** has a good thermal stability. And the measured magnetic susceptibility reveals that a weak antiferromagnetic interaction exists in **1**.

1. Introduction

Great attention has been paid to metal–organic framework (MOF) coordination polymers because of their diversiform architectures [1,2] and potential applications in the areas of catalysis, molecular recognition, magnetics and optics [3–8]. The coordination polymers can be specially designed by the careful selection of suitable metal ions and multifunctional organic ligands. These ligands should possess certain features, such as versatile bonding modes, multi-donor or the ability to undergo hydrogen bonds [9–15] which play a dominant role in crystal engineering because of their selectivity and directionality [16,17].

2,2′-Bipyridyl-4,4′-dicarboxylic acid (H_2bpdc) is an excellent N-heterocyclic dicarboxylic ligand, which can provide large possibility for constructing novel structures with N and O donor atoms. Due to the good flexibility of σ-bond, two pyridine rings of H_2bpdc can rotate so that versatile conformations and coordination modes could be formed. In theory, lanthanide and transition-metal ions differ in their coordination numbers and coordination geometries. And it is a good building block for the construction of rare metal polymers through carboxylic groups [18–20]. But up to now, the rare earth metal coordination polymers constructed from H_2bpdc are still rare [21–28] and there are few interesting heterometallic complexes with H_2bpdc [29–31]. Thus, we used H_2bpdc to react with lanthanide(III) salts and hoped that H_2bpdc may coordinate with lanthanide(III) ions in a different manner, which will lead to unusual architectures. Herein, we report the syntheses and crystal structure of a novel neodymium compound named $\{[Nd(bpdc)_{1.5}(H_2O)]\cdot H_2O\}_n$ (**1**). To our knowledge, it is the first reported 2-D (3,4,5)-connected topological structure in rare earth complexes.

2. Experimental details

2.1. Materials and methods

All chemicals and solvents were in analytical grade and used as commercially available. Elemental analyses for C, H and N were carried out on an Elemental Vario EL III elemental analyzer. The infrared spectra were recorded on a Bruker Equinox 55 spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermal analyzer instrument in N_2 at a heating rate of 10 °C min^{-1}. The magnetic susceptibility was measured over 1.8–300 K at the magnetic field of 1000 Oe on a Quantum Design MPMS XL-7 SQUID magnetometer.

2.2. Synthesis of $\{[Nd(bpdc)_{1.5}(H_2O)]\cdot H_2O\}_n$ (**1**)

A mixture of $Nd(NO_3)_3\cdot 6H_2O$ (21.9 mg, 0.05 mmol), H_2bpdc (12.2 mg, 0.05 mmol) and distilled water (8 mL) was sealed in a 25 mL Teflon-lined stainless steel container and kept at 170 °C for 4 days under autogenous pressure and then cooled to room

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Table 1
Crystallographic data of the complex **1**.

Formula formula	$C_{18}H_{13}NdN_3O_8$
M (g mol^{-1})	543.54
T (K)	296
Crystal system	orthorhombic
Space group	*Pnma*
a (Å)	14.094(1)
b (Å)	21.883(2)
c (Å)	12.052(1)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3717.0(5)
Z	8
D_{calc} (mg m^{-3})	1.935
μ (mm^{-1})	2.848
F(000)	2112
Reflections. collected	17614
Independent reflections	3407 (R_{int} = 0.0297)
θ Range (°)	1.86–25.10
Goodness-of-fit (GOF) on F^2	1.093
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0476, wR_2 = 0.1374
R indices (all data)	R_1 = 0.0501, wR_2 = 0.1392

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

Bond lengths (Å)			
Nd(1)–O(1)#1	2.355(6)	Nd(1)–O(6)#3	2.58(3)
Nd(1)–O(7)	2.39(3)	Nd(1)–N(1)	2.626(6)
Nd(1)–O(3)#2	2.429(6)	Nd(1)–N(2)	2.688(7)
Nd(1)–O(8)	2.461(7)	Nd(1)–O(4)#2	2.754(6)
Nd(1)–O(5)#3	2.514(13)		
Angles (°)			
O(1)#1–Nd(1)–O(7)	146.1(7)	O(8)–Nd(1)–N(1)	81.3(2)
O(1)#1–Nd(1)–O(3)#2	135.0(2)	O(5)#3–Nd(1)–N(1)	68.2(4)
O(7)–Nd(1)–O(3)#2	64.2(9)	O(6)#3–Nd(1)–N(1)	127.7(5)
O(1)#1–Nd(1)–O(8)	80.4(2)	O(1)#1–Nd(1)–N(2)	132.1(2)
O(7) –Nd(1)–O(8)	133.5(7)	O(7)–Nd(1)–N(2)	73.8(8)
O(3)#2–Nd(1)–O(8)	80.1(3)	O(3)#2–Nd(1)–N(2)	75.6(2)
O(1)#1–Nd(1)–O(5)#3	82.5(4)	O(8)–Nd(1)–N(2)	68.9(2)
O(7)–Nd(1)–O(5)#3	68.2(8)	O(5)#3–Nd(1)–N(2)	104.0(4)
O(3)#2–Nd(1)–O(5)#3	130.5(4)	O(6)#3–Nd(1)–N(2)	146.2(8)
O(8)–Nd(1)–O(5)#3	147.3(3)	N(1)–Nd(1)–N(2)	60.5(2)
O(1)#1–Nd(1)–O(6)#3	79.0(7)	O(1)#1–Nd(1)–O(4)#2	85.18(19)
O(7)–Nd(1)–O(6)#3	72.5(11)	O(7)–Nd(1)–O(4)#2	104.3(10)
O(3)#2–Nd(1)–O(6)#3	90.6(5)	O(3)#2–Nd(1)–O(4)#2	49.9(2)
O(8)–Nd(1)–O(6)#3	139.7(7)	O(8)–Nd(1)–O(4)#2	69.0(2)
O(5)#3–Nd(1)–O(6)#3	62.0(6)	O(5)#3–Nd(1)–O(4)#2	136.8(4)
O(1)#1–Nd(1)–N(1)	79.7(2)	O(6)#3–Nd(1)–O(4)#2	75.1(6)
O(7)–Nd(1)–N(1)	103.6(10)	N(1)–Nd(1)–O(4)#2	148.6(2)
O(3)#2–Nd(1)–N(1)	135.9(2)	N(2)–Nd(1)–O(4)#2	114.74(19)

Symmetry transformations used to generate equivalent atoms: #1 $x - 1/2$, y, $-z + 5/2$; #2 $x - 1/2$, y, $-z + 3/2$; #3 x, y, $z + 1$.

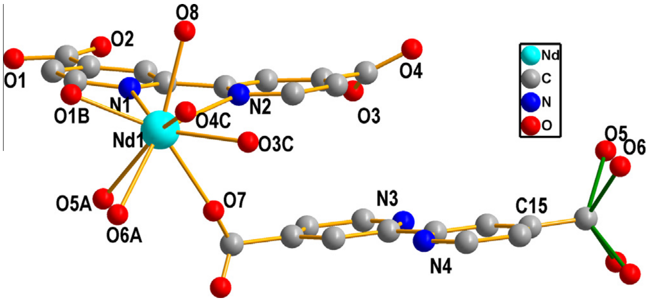
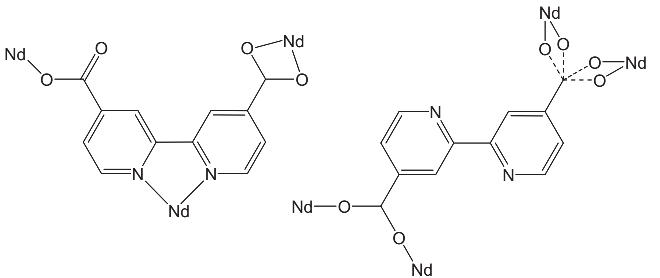


Fig. 1. The coordination environment of Nd^{3+} ion in **1**. Symmetry code: (A) x, y, $1 + z$; (B) $-1/2 + x$, y, $5/2 - z$; (C) $-1/2 + x$, y, $3/2 - z$ (free water molecule and hydrogen atoms are omitted for clarity).



(1) bpdc^A (2) bpdc^B

Scheme 1. Coordination mode of bpdc^{2-} ligands in compound **1.**

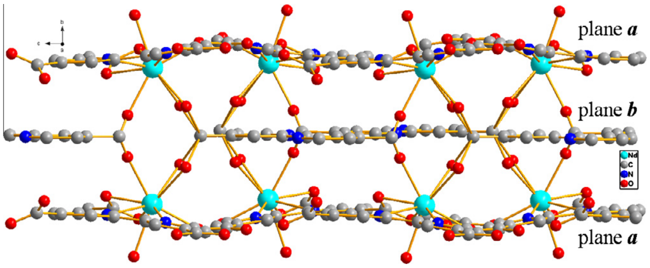


Fig. 2. 2-D sandwich structure viewed along *a*-axis.

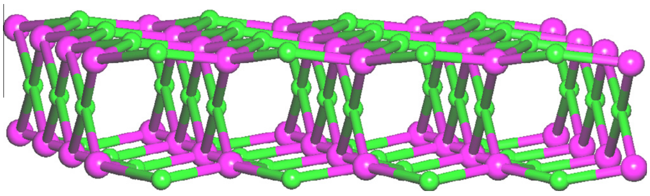


Fig. 3. Schematic representations of the 2-D (3,4,5)-connected topological network.

Table 3
Hydrogen bonding interactions in **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(8)–H(8B)···O(2)#1	0.78	2.00	2.772(9)	170.9
O(8)–H(8A)···O(4)#2	0.85	1.91	2.760(9)	177.6

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $-y$, $-z + 2$; #2 $-x + 1/2$, $-y$, $z + 1/2$.

temperature at a rate of 5 °C h^{-1}. Bright yellow transparent block crystals were collected, washed by distilled water and then dried in air. Yield: 35%. Elemental *Anal.* Calc. for $C_{18}H_{13}NdN_3O_8$ (543.54): C, 39.77; H, 2.41; N, 7.73. Found: C, 39.71; H, 2.81; N, 7.51%. IR data (KBr, cm^{-1}): 3390(b), 1586(m), 1542(s), 1403 (s), 1368 (s), 1294 (w), 1228(w), 865(w), 748(m), 690(m).

2.3. X-ray single crystal determinations

The crystallographic data sets were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were performed by using SADABS program. The structure was solved by direct