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A 4d-4f heterometallic coordination polymer: Synthesis, crystal structure and near-infrared luminescent properties

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Abstract: A 4d-4f heterometallic coordination polymer, [AgNd(pydc)$_2$]·2H$_2$O (**1**) (H$_2$pydc=pyridine-3,4-dicarboxylic acid), was synthesized under hydrothermal conditions, and further characterized by elemental analysis, IR, thermogravimetric analysis and single-crystal X-ray diffraction. Complex **1** featured a three-dimensional (3D) framework containing one-dimensional (1D) channels occupied by free water molecules, which was constructed from 1D inorganic heterometallic chains and linear pydc linkers. To our knowledge, complex **1** represented a rare example of 3D open-framework 4d-4f heterometallic coordination polymer. After removal of the water molecules from complex **1**, the remaining material had high thermal stability. Moreover, the near-infrared luminescent properties of **1** were also investigated in the solid state.

Keywords: Heterometallic coordination polymer; pyridine-3,4-dicarboxylic acid; crystal structure; near-infrared luminescence; rare earths

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In recent years, the design and construction of transition-lanthanide metal complexes have been of great interest because of their intriguing network topologies and potential applications, and due to their magnetic properties, their capacity for gas storage, as luminescent materials, and so on[1–6]. A number of lanthanide-transition metal heterometallic complexes have been successfully obtained from spontaneous assembly of mixed metal ions and ligand containing mixed-donor atoms, such as cyanide[7], carbonyl[8], pyridinecarboxylate ligand[9], amino acids[10,11] 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[12], and compared to the Ln(III) ions, the transition metal easily bonds to the N-donor atoms[13]. 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[14]. Pyridine-3,4-dicarboxylic acid as a bifunctional bridging ligand possesses of oxygen and nitrogen donors, which can be chosen to as a potential linker between the lanthanide centers and the transition metal centers.

More recently, many research interests have been focused on designing complexes containing lanthanide ions that show emissions in the near-infrared (IR) region (800–1600 nm), such as Nd(III) and Er(III), which show unprecedented applications in areas such as luminescence bioassays, laser materials, and optical amplifiers[15–18]. On the basis of above-mentioned considerations, we obtained a new 4d-4f coordination polymer, [AgNd(pydc)$_2$]·2H$_2$O (**1**), which was characterized by elemental analysis, IR, thermogravimetric analysis, single crystal diffraction, and by photoluminescence.

1 Experimental

1.1 Materials and physical measurements

All other starting materials were of analytical grade and obtained from commercial sources without further purification. Pyridine-3,4-dicarboxylic acid was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI).

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 NIR luminescence spectra were obtained at room temperature on a BIO-RAD PL9000 photoluminescence system (UK) with an Ar ion laser and the Ge detector worked at liquid nitrogen temperature. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen flow with a heating rate of 10 ºC/min.

1.2 Synthesis

A mixture of Nd(NO$_3$)$_3$·6H$_2$O (0.2 mmol, 87.7 mg),

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$AgNO_3$ (0.2 mmol, 34.0 mg), pyridine-3,4-dicarboxylic acid (0.4 mmol, 66.8 mg) and water (15 ml) was stirred for 30 min in air. Thereafter, the mixture was sealed in a 25 ml Teflon reactor and was kept under autogenous pressure at 180 ºC for 7 d. Pale purple block crystals were filtered off, washed with distilled water, and dried in air (yield: 53% based on Nd). The as-synthesized material was insoluble in water and common organic solvents. Anal. calcd. for $C_{14}H_{10}O_{10}N_2AgNd$: C, 27.19; H, 1.63; N, 4.53%. Found: C, 26.98; H, 1.69; N, 4.51%. IR (KBr, cm^{-1}): 3519 (br), 3059 (m), 1619 (s), 1573 (s), 1547 (s), 1475 (m), 1387 (s), 1161 (w), 1089 (w), 891 (w), 845 (m), 717 (m), 671 (w), 539(w).

1.3 X-ray crystallography

The crystallographic data collections for **1** were carried out on a Bruker Smart Apex II CCD with graphite-monochromated Mo-Kα radiation (λ=0.071073 nm) at 293(2) K using an ω-scan technique. The data were integrated by using the SAINT program[19], which also did the intensities corrected for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program[20]. The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package[21]. The hydrogen atoms of water molecules were located with difference Fourier map and the other hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package[22].

Table 1 Crystal data and details of the structure determination for 1

Items	Complex **1**
Empirical formula	$C_{14}H_{10}O_{10}N_2AgNd$
Formula mass	618.35
Temperature/K	293(2)
Crystal system	Triclinic
Space group	*P*-1
a/nm	0.73209(12)
b/nm	1.04579(17)
c/nm	1.1632(2)
α/(º)	100.170(2)
β/(º)	100.846(2)
γ/(º)	96.142(2)
Volume / nm^3	0.8518(2)
Z	2
Calculated density/(mg/m^3)	2.411
Absorption coefficient/mm^{-1}	4.224
Crystal size/mm	0.22×0.18×0.16
F(000)	590
θ range for data collection/(º)	2.42 to 25.50
Reflections collected/unique	5857/3112
Goodness-of-fit on F^2	1.059
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0410, wR_2=0.0955
R indices (all data)	R_1=0.0515, wR_2=0.0996
$\Delta\rho$/(e nm^{-3})	961, –1723

The details of the crystal parameters, data collection and refinement for **1** were summarized in Table 1. Selected bond lengths and bong angles for complex **1** were listed in Table 2. CCDC No. 851454 contained the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Table 2 Selected bond distance (10^{-1} nm) and angles (º) for 1

Bond distances			
Ag1–N1	2.188(6)	Nd1–O6$^{\#2}$	2.456(5)
Ag1–N2$^{\#1}$	2.193(6)	Nd1–O7$^{\#4}$	2.518(5)
Ag1–O3$^{\#6}$	2.642(6)	Nd1–O5	2.521(5)
Nd1–O1	2.409(5)	Nd1–O4$^{\#5}$	2.533(5)
Nd1–O7$^{\#2}$	2.441(5)	Nd1–O6	2.594(4)
Nd1–O2$^{\#3}$	2.442(5)	Nd1–O3$^{\#5}$	2.631(6)
Bond angles			
N1–Ag1–N2$^{\#1}$	145.7(3)	O1–Nd1–O6	146.21(17)
O1–Nd1–O7$^{\#2}$	74.05(17)	O7$^{\#2}$–Nd1–O6	136.21(15)
O1–Nd1–O2$^{\#3}$	138.69(17)	O2$^{\#3}$–Nd1–O6	73.96(16)
O7$^{\#2}$–Nd1–O2$^{\#3}$	74.25(17)	O6$^{\#2}$–Nd1–O6	67.89(18)
O1–Nd1–O6$^{\#2}$	125.16(17)	O7$^{\#4}$–Nd1–O6	120.55(15)
O7$^{\#2}$–Nd1–O6$^{\#2}$	72.58(15)	O5-Nd1–O6	50.89(14)
O2$^{\#3}$–Nd1–O6$^{\#2}$	67.65(16)	O4$^{\#5}$–Nd1–O6	92.37(16)
O1–Nd1–O7$^{\#4}$	76.02(17)	O1–Nd1–O3$^{\#5}$	77.91(17)
O7$^{\#2}$–Nd1–O7$^{\#4}$	74.78(18)	O7$^{\#2}$–Nd1–O3$^{\#5}$	139.26(17)
O2$^{\#3}$–Nd1–O7$^{\#4}$	70.60(16)	O2$^{\#3}$–Nd1–O3$^{\#5}$	142.21(16)
O6$^{\#2}$–Nd1–O7$^{\#4}$	132.27(16)	O6$^{\#2}$–Nd1–O3$^{\#5}$	101.56(16)
O1–Nd1–O5	119.58(17)	O7$^{\#4}$–Nd1–O3$^{\#5}$	125.76(16)
O7$^{\#2}$–Nd1–O5	140.70(18)	O5–Nd1–O3$^{\#5}$	79.30(17)
O$^{\#3}$–Nd1–O5	73.43(18)	O4$^{\#5}$–Nd1–O3$^{\#5}$	50.86(16)
O6$^{\#2}$–Nd1–O5	113.90(15)	O6–Nd1–O3$^{\#5}$	68.57(16)
O7$^{\#4}$–Nd1–O5	73.83(16)	O6$^{\#2}$–Nd1–O4$^{\#5}$	69.83(16)
O1–Nd1–O4$^{\#5}$	68.66(17)	O7$^{\#4}$–Nd1–O4$^{\#5}$	144.41(16)
O7$^{\#2}$–Nd1–O4$^{\#5}$	91.12(17)	O5–Nd1–O4$^{\#5}$	128.02(18)
O2$^{\#3}$–Nd1–O4$^{\#5}$	137.41(16)		

Synn. Codes: #1 *x*, *y*–1, *z*–1; #2 1–*x*, –*y*, 1–*z*; #3 2-*x*, –*y*, 1-*z*; #4 1+*x*, *y*, *z*; #5 *x*-1, *y*, *z*; #6 2–*x*, –*y*, –*z*

2 Results and discussion

2.1 Structural description

The single-crystal X-ray analysis revealed complex **1** crystallized in the triclinic space group *P*$\bar{1}$ and exhibited a novel 3D heterometallic coordination framework. As illustrated in Fig. 1, there are one unique Nd(III) ion, one Ag(I) ion, two crystallographically unique $(pydc)^{2-}$ anions and two lattice water molecules in the asymmetric unit. Each Nd(III) ion is coordinated by nine oxygen atoms from six $(pydc)^{2-}$ ligands in a distorted monocapped square antiprism geometry. The distances of Nd–O bonds range from 0.2409(5) to 0.2631(6) nm, comparable to those in other Nd(III) carboxylate complexes[23,24]. The O–Nd–O bond angles range from 50.86(16)º to 144.41(16)º. As far as Ag(I) ion is concerned, it exhibits a trigonal coordination geometry, being coordinated by each of the two pyridyl nitrogen atoms of the pydc ligands with the Ag–N distances are 0.2188(6) and