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Synthesis and Crystal Structure of a Three-Dimensional 3*d*–4*f* Heterometallic Coordination Polymer $\{[Sm_2Ni(Pdc)_2(SO_4)_2(H_2O)_6] \cdot H_2O\}_n$[1]

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Abstract—A new 3*d*–4*f* coordination polymer $\{[Sm_2Ni(Pdc)_2(SO_4)_2(H_2O)_6] \cdot H_2O\}_n$ (H_2Pdc = pyridine-3,5-dicarboxylic acid) has been synthesized under hydrothermal conditions and structurally determined by X-ray diffraction method. The X-ray diffraction analysis reveals the compound crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 10.062(4)$, $b = 10.249(4)$, $c = 12.744(5)$ Å, $\alpha = 93.548(4)°$, $\beta = 102.601(4)°$, $\gamma = 94.022(3)°$, $V = 1275.4(8)$ Å^3, $F(000) = 972$, $M_r = 1077.85$, $Z = 2$, $\rho_c = 2.624$ g cm^{-3}, $\mu = 5.55$ mm^{-1}, final $R = 0.0299$, $wR = 0.0805$ for 4716 independent reflections with $R_{int} = 0.0204$. According to the structure determination the complex is a three-dimensional (3D) network structure in which infinite lanthanide-carboxylate chains are linked by $[Ni(SO_4)_2]^{2-}$ metalloligands to form a mixed-metal coordination network.

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INTRODUCTION

The synthesis and characterization of heterometallic organic frameworks, such as lanthanide-transition-metal complexes, have attracted increasing attention because of intriguing structures and potential applications in magnetism, photoluminescence, catalysis, and adsorption [1–3]. However, the development of these heterometallic organic frameworks is still a formidable task due to some complicated factors, such as the choice of organic ligands, the variable coordination number of metal ions, and the competitive reaction between lanthanide and transition metal ions. Because of these factors, the reactions system generates preferably homometallic organic frameworks instead of heterometallic structures. Nevertheless, fortunately, the lanthanides are oxophilic and prefer oxygen to nitrogen atoms, while the transition metal ions have a strong tendency to coordinate N-donors as well as O-donors. Thus, if a ligand containing both N-donor and O-donor atoms and transition metal ion could be introduced to link the lanthanide-carboxylate subunits successfully, the novel 3*d*–4*f* coordination polymers may be obtained though the recognition of the metal ion and their coordinating atoms.

A number of 3*d*–4*f* coordination polymers based on pyridinedicarboxylic acid have been synthesized recently [4–6]. By contrast with these coordination polymers containing only rigid pyridinedicarboxylic ligands, the high-dimensional coordination complexes of 3*d*–4*f* frameworks formed by organic pyridinedicarboxylic acid and inorganic lanthanide sulfate skeletons are still scarce [7–11]. Herein, using pyridine-3,5-dicarboxylic acid (H_2Pdc) as a ligand, a novel 3D coordination polymer $\{[Sm_2Ni(Pdc)_2(SO_4)_2(H_2O)_6] \cdot H_2O\}_n$ (**I**) has been synthesized and structurally determined, representing the first example combining Sm-Ni ions, pyridine-3,5-dicarboxylic acid and inorganic sulfate. The X-ray diffraction analysis indicates the heterometallic coordination polymer is a three-dimensional network structure in which infinite lanthanide-carboxylate chains are linked by $[Ni(SO_4)_2]^{2-}$ metalloligands to form a mixed-metal coordination network.

EXPERIMENTAL

All chemicals and solvents were purchased and used without further purification. Elemental analyses for C, H, and N elements were performed with a Model 240 PerkinElmer elemental analyzer. The infrared spectrum was taken on an Avatar TM 360 E.S.P. IR spectrometer in the 4000–400 cm^{-1} region, using KBr pellets. Thermogravimetry-differential thermal analysis (TG-DTA) of complex **I** was recorded using an SDT 2960 simultaneous thermal analyzer (DTA Instruments, New Castle, DE) in N_2 atmosphere at a heating rate of 10°C min^{-1} from 30 to 800°C.

Synthesis of I. A mixture of Sm_2O_3 (0.0880 g, 0.25 mmol), $NiSO_4 \cdot 7H_2O$ (0.1310 g, 0.5 mmol), H_2Pdc (0.1672 g, 1 mmol), and deionized water (8.0 mL) was stirred for 30 min in air to form a solution. Then solution was placed in a 23 mL Teflon-lined autoclave and

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kept under autogenous pressure at 443 K for three days and was cooling to room temperature at a rate of 5 K h^{-1}. Green block crystals were collected by filtration in 76% yield (based on Sm) after being washed with water and dried in air.

For $C_{14}H_{20}N_2O_{23}S_2NiSm_2$			
anal. calcd., %:	C, 16.67;	H, 1.98;	N, 2.78.
Found, %:	C, 16.26;	H, 2.13;	N, 2.62.

X-ray structure determination. A green single crystal of complex **I** with approximate dimensions of 0.38 × 0.27 × 0.19 mm was mounted at 293(2) K by using a graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation with an ω scan mode ($2.8° < \theta < 28.3°$). The structure was solved by direct methods with SHELXS-97 program [12] and refined with SHELXL-97 [13] by full-matrix least-squares techniques on F^2. All nonhydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data and experimental details for structural analysis are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bonds are given in Table 3. Supplementary material for complex **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 861482; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In the asymmetric unit of **I**, there are two samarium ions, one nickel ion, two Pdc^{2-} anions, two SO_4^{2-} anions, six coordinated molecules, and one guest water molecule. Each Sm^{3+} ion is eight-coordinated in a distorted square-antiprism coordination geometry by eight oxygen atoms from three oxygen atoms of three Pdc^{2-} anions, three oxygen atoms of two SO_4^{2-} anions, and two oxygen atoms from two coordinated terminal water molecule, respectively. The angles of OSmO bond are in the range of 56.05(11)° to 158.69(12)° and the Sm–O bond distances range from 2.337(3) to 2.542(3) Å (Table 2), which are in agreement with those observed in reported Sm^{3+} complexes [14]. The Ni^{2+} ion exhibits an elongated octahedron geometry, being coordinated by two nitrogen atoms from two Pdc^{2-} anions, two oxygen atoms from two SO_4^{2-} anions, and two oxygen atoms from two terminal water molecules. The Ni–O bond distances range from 2.083(4) to 2.121(4) Å and the two Ni–N bond distances are 2.058(4) and 2.078(4) Å. In this compound, the nitrogen atom from Pdc^{2-} coordinates to Ni^{2+} ion center, the carboxylate groups coordinate to three Sm^{3+} ions in a μ_3-κ^1, κ^1, κ^1 coordination mode (Fig. 1). Owing to the coordination modes of the Pdc^{2-}, two Sm^{3+} ions, and four Pdc^{2-} anions form a basic binuclear unit $Sm_2(Pdc)_4$. The ring A of binuclear units $Sm_2(Pdc)_4$ is

Table 1. Crystallographic parameters and a summary of data collection and refinement for complex **I**

Parameter	Value
Empirical formula	$C_{14}H_{20}N_2O_{23}S_2NiSm_2$
Formula weight	1007.85
Crystal system	Triclinic
Space group	$P\overline{1}$
a, Å	10.062(4)
b, Å	10.249(4)
c, Å	12.744(5)
α, deg	93.548(4)
β, deg	102.601(4)
γ, deg	94.022(3)
V, Å^3	1275.4(8)
Z	2
ρ_c, g cm^{-3}	2.624
Absorption coefficient, mm^{-1}	5.55
F(000)	972
Collected/unique (R_{int})	9552/4716 (0.0204)
Goodness of fit on F^2	1.08
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0299$, $wR_2 = 0.0805$
R_1, wR_2 (all data)	$R_1 = 0.0351$, $wR_2 = 0.0866$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.53/–2.10

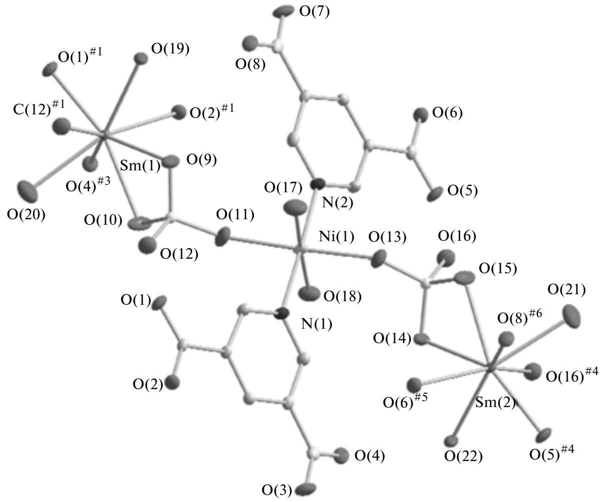

Fig. 1. ORTEP drawing of **I** showing the local coordination environment of Sm^{3+} and Ni^{2+} with thermal ellipsoids at 30% probability. Guest water molecule and all H atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and bond angles (deg) in complex **I***

Bond	d, Å	Bond	d, Å	Bond	d, Å
Sm(1)–O(1)$^{\#1}$	2.339(3)	Sm(1)–O(2)$^{\#2}$	2.393(3)	Sm(1)–O(4)$^{\#3}$	2.420(3)
Sm(1)–O(9)	2.520(3)	Sm(1)–O(12)$^{\#1}$	2.430(4)	Sm(1)–O(19)	2.453(3)
Sm(1)–O(20)	2.486(4)	Sm(2)–O(5)$^{\#4}$	2.337(3)	Sm(2)–O(6)$^{\#6}$	2.398(3)
Sm(2)–O(8)$^{\#5}$	2.393(3)	Sm(2)–O(14)	2.542(3)	Sm(2)–O(16)$^{\#6}$	2.398(4)
Sm(2)–O(21)	2.505(4)	Sm(2)–O(22)	2.450(3)		
Ni(1)–N(1)	2.058(4)	Ni(1)–O(11)	2.121(4)	Ni(1)–O(17)	2.083(4)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)$^{\#1}$Sm(1)O(2)$^{\#2}$	98.41(12)	O(1)$^{\#1}$Sm(1)O(20)	87.65(13)	O(20)Sm(1)O(10)	75.08(14)
O(1)$^{\#1}$Sm(1)O(4)$^{\#3}$	81.72(12)	O(2)$^{\#2}$Sm(1)O(20)	143.38(13)	O(1)$^{\#1}$Sm(1)O(9)	145.20(12)
O(2)$^{\#2}$Sm(1)O(4)$^{\#3}$	72.89(12)	O(4)$^{\#3}$Sm(1)O(20)	72.35(12)	O(2)$^{\#2}$Sm(1)O(9)	82.40(12)
O(1)$^{\#1}$Sm(1)O(12)$^{\#1}$	85.49(12)	O(12)$^{\#1}$Sm(1)O(20)	71.80(13)	O(4)$^{\#3}$Sm(1)O(9)	130.45(12)
O(2)$^{\#2}$Sm(1)O(12)$^{\#1}$	144.40(12)	O(19)Sm(1)O(20)	143.23(12)	O(12)$^{\#1}$Sm(1)O(9)	75.12(12)
O(4)$^{\#3}$Sm(1)O(12)$^{\#1}$	142.28(12)	O(1)$^{\#1}$Sm(1)O(10)	158.69(12)	O(19)Sm(1)O(9)	71.08(11)
O(1)$^{\#1}$Sm(1)O(19)	76.00(12)	O(2)$^{\#2}$Sm(1)O(10)	88.63(13)	O(20)Sm(1)O(9)	112.40(13)
O(2)$^{\#2}$Sm(1)O(19)	72.52(12)	O(4)$^{\#3}$Sm(1)O(10)	81.20(12)	O(10)Sm(1)O(9)	55.48(11)
O(4)$^{\#3}$Sm(1)O(19)	135.12(12)	O(12)$^{\#1}$Sm(1)O(10)	100.46(13)	O(5)$^{\#4}$Sm(2)O(8)$^{\#5}$	83.52(12)
O(12)$^{\#1}$Sm(1)O(19)	74.23(12)	O(19)Sm(1)O(10)	125.28(11)	O(5)$^{\#4}$Sm(2)O(16)$^{\#4}$	86.28(13)
O(8)$^{\#5}$Sm(2)O(16)$^{\#4}$	140.00(12)	O(6)$^{\#6}$Sm(2)O(22)	74.61(12)	O(8)$^{\#5}$Sm(2)O(21)	71.40(12)
O(5)$^{\#4}$Sm(2)O(6)$^{\#6}$	101.57(12)	O(5)$^{\#4}$Sm(2)O(15)	157.32(13)	O(16)$^{\#4}$Sm(2)O(21)	69.22(13)
O(8)$^{\#5}$Sm(2)O(6)$^{\#6}$	73.37(12)	O(8)$^{\#5}$Sm(2)O(15)	82.65(12)	O(6)$^{\#6}$Sm(2)O(21)	143.18(12)
O(16)$^{\#4}$Sm(2)O(6)$^{\#6}$	146.63(13)	O(16)$^{\#4}$Sm(2)O(15)	92.86(13)	O(22)Sm(2)O(21)	141.28(12)
O(5)$^{\#4}$Sm(2)O(22)	76.50(12)	O(6)$^{\#6}$Sm(2)O(15)	91.58(13)	O(15)Sm(2)O(21)	73.71(13)
O(8)$^{\#5}$Sm(2)O(22)	137.64(12)	O(22)Sm(2)O(15)	125.27(11)	O(5)$^{\#4}$Sm(2)O(14)	144.49(12)
O(16)$^{\#4}$Sm(2)O(22)	75.89(12)	O(5)$^{\#4}$Sm(2)O(21)	84.87(13)	O(8)$^{\#5}$Sm(2)O(14)	128.82(12)
O(16)$^{\#4}$Sm(2)O(14)	76.68(12)	O(16)$^{\#6}$Sm(2)O(14)	78.57(12)	O(22)Sm(2)O(14)	69.28(11)
O(15)Sm(2)O(14)	56.05(11)	O(21)Sm(2)O(14)	116.50(12)	N(1)Ni(1)O(11)	91.17(16)
O(18)Ni(1)O(13)	92.59(16)	N(2)Ni(1)O(18)	89.31(16)	N(2)Ni(1)O(11)	87.06(15)
N(1)Ni(1)O(18)	90.89(16)	O(17)Ni(1)O(18)	176.86(15)	O(17)Ni(1)O(11)	93.64(17)
N(2)Ni(1)O(17)	92.26(16)	N(1)Ni(1)O(13)	90.32(15)	O(18)Ni(1)O(11)	89.16(17)
N(1)Ni(1)N(2)	178.22(14)	N(2)Ni(1)O(13)	91.44(15)	O(13)Ni(1)O(11)	177.69(13)
N(1)Ni(1)O(17)	87.63(16)	O(17)Ni(1)O(13)	84.66(16)		

* Symmetry codes: $^{\#1}$ $-x, -y+1, -z$; $^{\#2}$ $x, y+1, z$; $^{\#3}$ $-x+1, -y+1, -z$; $^{\#4}$ $-x+2, -y+1, -z+1$; $^{\#5}$ $-x+1, -y+1, -z+1$; $^{\#6}$ $x, y-1, z$.

eight-membered [$Sm_2O_4C_2$] ring with a Sm–Sm distance of 5.0674(19) Å. The binuclear units are connected to each other by sharing the Pdc^{2-} ligand to give 1D infinite chain-like structure along the x axis containing two kinds of macrocyclic rings: 8-membered ring (ring A) and 16-membered ring [$Sm_2O_4C_{10}$] (ring B). 1D chains are connected by Ni^{2+} ions and further extend, resulting in the assembly of a 2D framework in the yz plane containing 24-membered $Sm_2Ni_2N_4O_4C_{12}$ macrocyclic ring C (Fig. 2b), the 2D framework are further assembled into a 3D organic-inorganic framework by SO_4^{2-} anion with a special

Table 3. Geometric parameters of hydrogen bonds for **I***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	D···A	H···A	
O(17)–H(1*w*)···O(15)$^{\#1}$	0.85	2.737(5)	1.97	149
O(17)–H(2*w*)···O(13)	0.85	2.825(5)	2.19	131
O(18)–H(3*w*)···O(10)$^{\#2}$	0.85	2.779(5)	2.08	139
O(18)–H(4*w*)···O(23)	0.85	2.541(7)	1.70	169
O(19)–H(5*w*)···O(8)	0.85	2.883(5)	2.16	142
O(19)–H(6*w*)···O(3)$^{\#3}$	0.85	2.651(5)	1.81	173
O(20)–H(7*w*)···O(17)$^{\#4}$	0.85	3.289(6)	2.61	138
O(20)–H(8*w*)···O(9)$^{\#4}$	0.85	3.054(5)	2.40	134
O(20)–H(8*w*)···O(21)$^{\#5}$	0.85	3.198(7)	2.54	135
O(21)–H(9*w*)···O(18)$^{\#6}$	0.85	2.996(6)	2.18	160
O(21)–H(10*w*)···O(19)$^{\#1}$	0.85	2.776(5)	2.00	151
O(21)–H(10*w*)···O(9)$^{\#1}$	0.85	3.146(5)	2.56	128
O(22)–H(11*w*)···O(4)	0.85	2.904(5)	2.12	153
O(22)–H(12*w*)···O(7)$^{\#7}$	0.85	2.642(5)	1.80	168
O(23)–H(13*w*)···O(11)	0.85	2.954(7)	2.43	120
O(23)–H(13*w*)···O(10)	0.85	3.449(7)	2.63	162

* Symmetry codes: $^{\#1}$ $-x + 1, -y + 1, -z + 1$; $^{\#2}$ $-x + 1, -y + 1, -z$; $^{\#3}$ $x - 1, y + 1, z$; $^{\#4}$ $-x, -y + 1, -z$; $^{\#5}$ $x - 1, y, z - 1$; $^{\#6}$ $-x + 2, -y + 1, -z + 1$; $^{\#7}$ $x + 1, y - 1, z$.

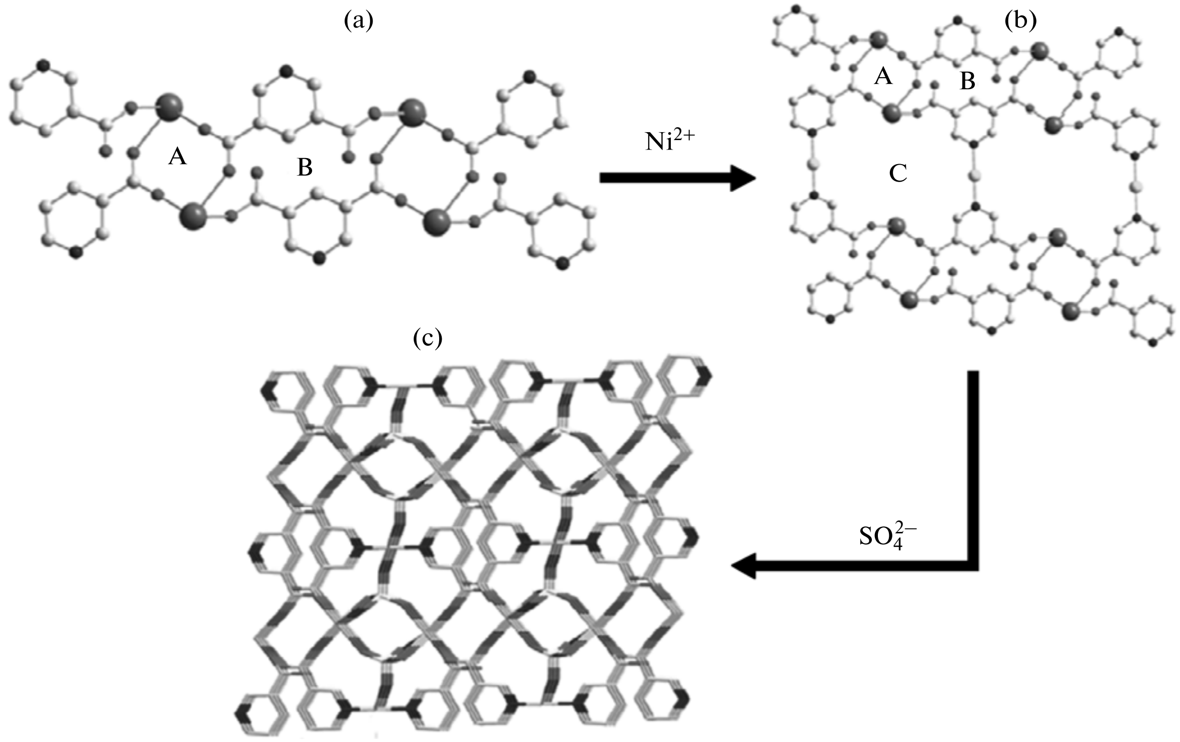

Fig. 2. View of the innite 1D chain built by the [$Sm_2(Pdc)_4$] subunit via share the Pdc^{2-} ligand (a); the 2D layer structure based on [$Sm_2(Pdc)_4$] chain and nickel (b); the 3D network structure of **I**. All H atoms and water molecules are omitted for clarity (c).

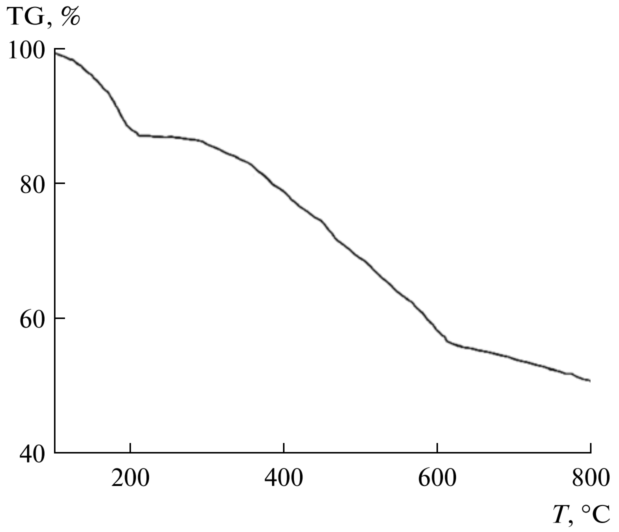

Fig. 3. TG curve for **I**.

μ_3-κ^2, κ^1, κ^1 tetradentate coordination mode to connect one Sm^{3+} and one Ni^{2+} ion of the ring C, another adjacent Sm^{3+} from another ring C along *x* axis. That is, SO_4^{2-} anion serves as an auxiliary supporting bridge to connect the neighboring ring C. This kind of coordination mode results in the formation of a complicated 3D network structure (Fig. 2c). In other words, the 3D 3*d*–4*f* heterometal coordination framework is constructed from the 1D infinite lanthanide-carboxylate chains linked by $[Ni(SO_4)_2]^{2-}$ metalloligands. In addition, many kinds of different interesting hydrogen bonds are observed in the crystal structures of **I**, and some of them are listed in Table 3. These hydrogen bonds further stabilize the solid state structure of compound **I**.

In the FT-IR spectrum of complex **I**, the broad medium absorption bands centered at 3418 cm^{-1} correspond to the O–H stretching frequency of water. The features at 1597 cm^{-1} are attributed to the asymmetric stretching vibrations of the carboxylate group, and the strong vibration appearing around 1413 and 1385 cm^{-1} correspond to symmetric stretching vibrations of the carboxylate group. The absence of bands at the region of 1690–1730 cm^{-1} suggests that all carboxylic groups are deprotonated. All these results are in agreement with the structure.

The thermal stability of **I** was examined by the thermogravimetric analyses (TGA) in N_2 atmosphere with a heating rate of 10°C min^{-1} from 30 to 800°C. As shown in Fig. 3, it indicates that **I** experiences three steps of weight loss. It can be seen from the TG curve of **I** that the first weight loss of 12.8% from 80 to 200°C corresponding to the removal of the noncoordination and coordination water molecules (calc. 12.50%). The second weight loss of 33.76% from 250 and 610°C is due to the release of organic Pdc^{2-} ligands (calc. 32.74%). The third weight loss above 610°C corresponds to the decomposition of sulfates with high thermal stability.

In summary, we synthesized a new 3*d*–4*f* heterometallic polymer by a hydrothermal approach. X-ray single-crystal data indicates the compound is a three-dimensional network structure in which infinite lanthanide-carboxylate chains are linked by $[Ni(SO_4)_2]^{2-}$ metalloligands to form a mixed-metal coordination network. Furthermore, the thermal propertry of the compound was discussed.

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