

# Lanthanide-Oxalate Coordination Polymers Formed by Reductive Coupling of Carbon Dioxide to Oxalate: $[\text{Ln}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ ( $\text{Ln} = \text{Eu}, \text{Sm}, \text{Ho}, \text{Dy}$ ; $\text{pdc} = \text{Pyridinedicarboxylate}$ )

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Hydrothermal reactions of  $\text{Ln}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu}$  (1),  $\text{Sm}$  (2),  $\text{Ho}$  (3),  $\text{Dy}$  (4)) with 3,5-pyridinedicarboxylic acid (3,5-pdcH<sub>2</sub>) in the presence of 4,4'-bipyridine led to the formation of the 3-D Ln(III)-coordination polymers with a formula unit of  $[\text{Ln}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ . These polymers contain a bridging oxalate ligand ( $\text{C}_2\text{O}_4^{2-}$ ). On the basis of GC-MS study of the mother liquor remaining after the reaction, we proposed that the  $\text{C}_2\text{O}_4^{2-}$  formation proceeds in three steps: (1) Ln(III)-mediated decarboxylation of 3,5-pdcH<sub>2</sub> to give  $\text{CO}_2$ , (2) the reduction of  $\text{CO}_2$  to  $\text{CO}_2^{\cdot -}$  by the Ln(II) species, and (3) the reductive coupling of the two  $\text{CO}_2^{\cdot -}$  radicals to the oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) ion. All polymers were structurally characterized by X-ray diffraction.

**Key Words :** Lanthanide, Oxalate formation, Hydrothermal reaction, X-ray diffraction

## Introduction

Coordination polymers of lanthanide metals are currently under intensive study due to their potential applications as magnetic<sup>1-8</sup> and luminescent materials.<sup>7-13</sup> For the preparation of these polymers, hydrothermal or hydro(solvo)thermal methods are typically employed. Very recently, Zhang reported a wonderful review of the *in situ* ligand synthesis under hydro(solvo)thermal conditions, which includes carbon-carbon bond formation, hydroxylation, tetrazole formation, triazole formation, substitution, alkylation, ether bond formation, hydrolysis, oxidation-hydrolysis, acylation, amination, and decarboxylation.<sup>14</sup>

We have reported several lanthanide coordination polymers from lanthanide nitrates and dicarboxylates (Chart 1: 1,3-bdc = 1,3-benzenedicarboxylate; 2,6-ndc = 2,6-naphthalenedicarboxylate; 2,2'-4,4'-bpdc = 2,2'-bipyridine-4,4'-di-

carboxylate) by hydrothermal reactions:  $[\text{La}_4(1,3\text{-bdc})_6(\text{H}_2\text{O})_5]\cdot \text{H}_2\text{O}$ ,  $[\text{Tb}_4(2,6\text{-ndc})_6(\text{H}_2\text{O})_5]\cdot 5\text{H}_2\text{O}$ , and  $[\text{Tb}_2(2,2'-4,4'\text{-bpdc})_3(\text{H}_2\text{O})_3]\cdot \text{H}_2\text{O}$ .<sup>15,16</sup> Pyridinedicarboxylic acids (pdcH<sub>2</sub>) are often used in preparing coordination polymers of transition metals, and several groups have prepared such polymers from metal nitrates, oxides, acetates, or sulfates and 3,5-, 2,4-, or 2,5-pdc.<sup>5,17-24</sup>

We recently prepared a couple of 3-D terbium-pdc polymers ( $[\text{Tb}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  and  $[\text{Tb}_2(2,4\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ ) by hydrothermal reactions and structurally characterized them by X-ray diffraction.<sup>24</sup> A key structural feature of these polymers is to contain bridging oxalato ligands ( $\text{C}_2\text{O}_4^{2-}$ ). For the formation of the oxalato ligands, we have proposed the reductive coupling of  $\text{CO}_2$  molecules released from the pdc ligands by the C-C bond cleavage. A primary aim of our research is to investigate whether this coupling reactivity to lead to the oxalato formation is general for lanthanide metals. For this aim, we treated several lanthanide nitrates with 3,5-pdcH<sub>2</sub> and found these metals to exhibit such reactivity. Herein, we report the preparation and structures of the lanthanide-oxalate coordination polymers  $[\text{Ln}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu}, \text{Sm}, \text{Ho}, \text{or Dy}$ ). In addition, mechanistic aspects of the oxalate ligand formation are discussed.

## Experimental Section

$\text{Eu}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ ,  $\text{Ho}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ ,  $\text{Dy}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ , 3,5-pdcH<sub>2</sub>, and 4,4'-bipyridine (bpy) were purchased and purified by recrystallization. All polymers were prepared in the same way and obtained as colorless crystals. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute. GC-MS analyses were performed with an Agilent 6890GC/5973N MSD spectrometer at CCRF (Cooperative

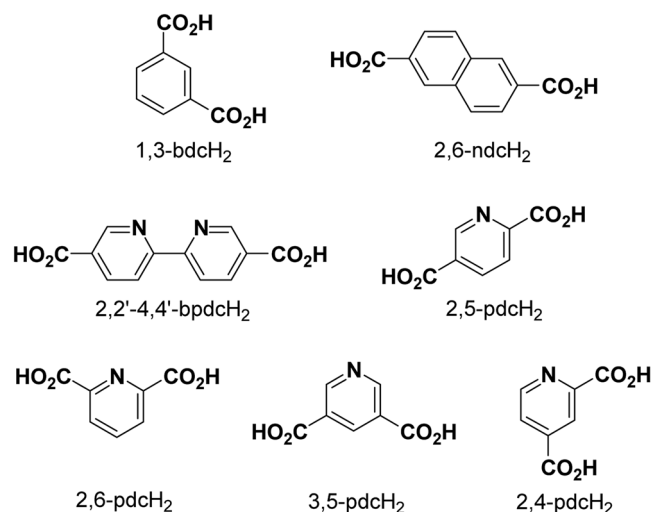


Chart 1

Center for Research Facilities) in the Sungkyunkwan University.

**Preparation of [Eu(3,5-pdc)(CO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (1).** A mixture of Eu(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.100 g, 0.234 mmol), 3,5-pdcH<sub>2</sub> (0.040 g, 0.239 mmol), bpy (0.036 g, 0.230 mmol), and H<sub>2</sub>O (5.0 mL, 0.278 mol) in the mole ratio of 1.000 : 1.044 : 1.004 : 1213 was heated in a 23-mL Teflon-lined vessel at 180 °C for two days and then cooled to room temperature by air-cooling. The colorless crystalline product was collected by filtration, washed with H<sub>2</sub>O (2 × 5 mL) and ethanol (1 × 5 mL), and then air-dried to give polymer **1** (0.034 g, 0.0819 mmol, 35% yield). Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>9</sub>NEu (*M<sub>r</sub>* = 415.12): C, 23.15; H, 2.19; N, 3.37. Found: C, 23.05; H, 1.73; N, 3.02. IR (KBr, cm<sup>-1</sup>): 3487 (m), 3371 (m), 1691 (m, CO), 1638 (s, CO), 1597 (s, CO), 1550 (s, CO), 1451 (m), 1400 (s), 1376 (s).

**Preparation of [Sm(3,5-pdc)(CO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (2).** 44% yield. Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>9</sub>NSm (*M<sub>r</sub>* = 413.51): C, 23.24; H, 2.19; N, 3.39. Found: C, 23.24; H, 2.26; N, 3.76. IR (KBr, cm<sup>-1</sup>): 3537 (m), 3085 (m), 1652 (m, CO), 1603 (s, CO), 1556 (s, CO), 1391 (s, CO), 1294 (m).

**Preparation of [Ho(3,5-pdc)(CO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (3).** 39% yield. Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>9</sub>NHo (*M<sub>r</sub>* = 428.09): C, 22.45; H, 2.12; N, 3.27. Found: C, 22.60; H, 2.14; N, 3.76. IR (KBr, cm<sup>-1</sup>): 3445 (m), 3056 (m), 1652 (s, CO), 1579 (s,

CO), 1451 (s, CO), 1405 (m), 1347 (s), 1304 (m).

**Preparation of [Dy(3,5-pdc)(CO<sub>2</sub>)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (4).** 41% yield. Anal. Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>9</sub>NDy (*M<sub>r</sub>* = 425.66): C, 22.57; H, 2.13; N, 3.29. Found: C, 22.52; H, 2.02; N, 3.81. IR (KBr, cm<sup>-1</sup>): 3442 (m), 3056 (m), 1661 (s, CO), 1575 (s, CO), 1455 (s, CO), 1400 (m), 1347 (s), 1300 (m).

**X-ray Structure Determination.** All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with  $\psi$ -scan data. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The C-H hydrogen atoms were generated in idealized positions and refined in a riding model. The O-H hydrogen atoms were located and refined isotropically. All calculations were carried out with the SHELXTL programs.<sup>25</sup> Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 615684 (**1**), 615685 (**2**), 615686 (**3**), and 615687 (**4**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

**Table 1.** X-ray Data Collection and Structure Refinement Details

	Polymer 1	Polymer 2	Polymer 3	Polymer 4
Formula	C <sub>8</sub> H <sub>9</sub> NO <sub>9</sub> Eu	C <sub>8</sub> H <sub>9</sub> NO <sub>9</sub> Sm	C <sub>8</sub> H <sub>9</sub> NO <sub>9</sub> Ho	C <sub>8</sub> H <sub>9</sub> NO <sub>9</sub> Dy
fw	415.12	413.51	428.09	425.66
temp, K	296(2)	293(2)	293(2)	293(2)
crystal dimensions	0.44 × 0.20 × 0.16	0.74 × 0.36 × 0.28	0.70 × 0.26 × 0.24	0.18 × 0.16 × 0.12
crystal shape	block	block	rod	block
crystal syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	7.651(1)	7.667(1)	7.6004(8)	7.622(2)
<i>b</i> , Å	9.860(1)	9.873(1)	9.808(1)	9.833(3)
<i>c</i> , Å	14.852(1)	14.905(1)	14.715(2)	14.762(4)
$\beta$ , deg	98.389(5)	98.365(9)	98.160(9)	98.191(9)
<i>V</i> , Å <sup>3</sup>	1108.3(1)	1116.3(2)	1085.8(2)	1095.1(5)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>cal</sub> , g cm <sup>-3</sup>	2.488	2.461	2.619	2.582
$\mu$ , mm <sup>-1</sup>	5.706	5.307	7.335	6.871
<i>F</i> (000)	796	792	812	808
<i>T</i> <sub>min</sub>	0.6906	0.2434	0.2065	0.2186
<i>T</i> <sub>max</sub>	0.9116	0.5402	0.6714	0.3663
no. of reflns measd	2103	2124	2029	2069
no. of unique reflns	1948	1968	1880	1916
no. of reflns with <i>I</i> > 2σ( <i>I</i> )	1853	1942	1845	1728
no. of params refined	197	196	209	196
max in Δρ (e Å <sup>-3</sup> )	0.620	1.188	0.669	0.743
min in Δρ (e Å <sup>-3</sup> )	-0.450	-2.042	-0.603	-0.781
GOF on <i>F</i> <sup>2</sup>	1.033	1.106	1.127	1.051
<i>R</i> 1 <sup>a</sup>	0.0198	0.0290	0.0200	0.0234
<i>wR</i> 2 <sup>b</sup>	0.0512	0.0780	0.0520	0.0575

<sup>a</sup>*R* = Σ[|*F*<sub>o</sub>| - |*F*<sub>c</sub>|]/Σ|*F*<sub>o</sub>|, <sup>b</sup>*wR*2 = Σ[w(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>

**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg)

<b>Polymer 1</b>					
Eu1–O4	2.322(2)	Eu1–O3	2.321(2)	Eu1–O2	2.378(2)
Eu1–O1	2.352(2)	Eu1–O5	2.449(3)	Eu1–O7	2.477(3)
Eu1–O8	2.474(3)	Eu1–O6	2.487(2)	O5–C8	1.252(4)
O6–C8	1.253(4)	C8–C8#1	1.540(6)		
O5–Eu1–O6	65.61(8)	O7–Eu1–O6	141.30(9)	O8–Eu1–O6	125.96(9)
O6#1–C8–O5	126.1(3)	O6#1–C8–C8#1	116.6(4)	O5–C8–C8#1	117.2(4)
<b>Polymer 2</b>					
Sm1–O4	2.338(3)	Sm1–O3	2.342(3)	Sm1–O2	2.365(3)
Sm1–O1	2.392(3)	Sm1–O5	2.465(3)	Sm1–O8	2.488(3)
Sm1–O7	2.490(4)	Sm1–O6	2.504(3)	O5–C8	1.254(6)
C8–O6#2	1.254(6)	C8–C8#2	1.541(9)		
O5–Sm1–O6	65.43(12)	O7–Sm1–O6	141.12(12)	O8–Sm1–O6	126.02(12)
O5–C8–O6#2	125.6(4)	O6#2–C8–C8#2	116.9(5)	O5–C8–C8#2	117.4(5)
<b>Polymer 3</b>					
Ho1–O4#4	2.278(3)	Ho1–O3#3	2.271(3)	Ho1–O2#5	2.334(3)
Ho1–O1	2.306(3)	Ho1–O5	2.453(3)	Ho1–O7	2.430(3)
Ho1–O8	2.430(3)	Ho1–O6#4	2.409(3)	O5–C8	1.254(5)
C8–O6	1.249(5)	C8–C8#4	1.552(8)		
O5–Ho1–O6#4	66.56(10)	O7–Ho1–O6#4	127.13(11)	O8–Ho1–O6#4	139.58(10)
O6–C8–O5	127.0(4)	O6–C8–C8#4	117.0(4)	O5–C8–C8#4	116.0(4)
<b>Polymer 4</b>					
Dy1–O4	2.350(3)	Dy1–O3	2.326(3)	Dy1–O2	2.289(3)
Dy1–O1	2.288(3)	Dy1–O5	2.421(4)	Dy1–O7	2.441(4)
Dy1–O8	2.454(4)	Dy1–O6	2.464(4)	O5–C8	1.258(6)
C8–O6#6	1.263(6)	C8–C8#6	1.527(10)		
O5–Dy1–O6	66.36(12)	O7–Dy1–O6	141.50(13)	O8–Dy1–O6	125.72(12)
O6#6–C8–O5	125.9(5)	O6#6–C8–C8#6	116.3(5)	O5–C8–C8#6	117.8(6)

Symmetry transformations used to generate equivalent atoms: #1 =  $-x + 1, -y + 1, -z + 1$ ; #2 =  $-x + 1, -y, -z + 2$ ; #3 =  $-x + 1/2, y - 1/2, -z + 1/2$ ; #4 =  $x - 1/2, -y + 3/2, -z + 1/2$ ; #5 =  $-x + 1/2, y + 1/2, -z + 1/2$ ; #6 =  $-x + 1, -y + 2, -z + 2$

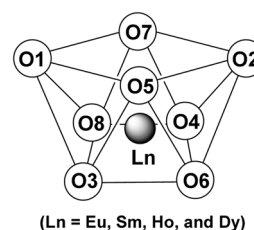
## Results and Discussion

**Preparation.** Heating a mixture of lanthanide nitrate  $\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu}$  (**1**),  $\text{Sm}$  (**2**),  $\text{Ho}$  (**3**), or  $\text{Dy}$  (**4**)), 3,5-pdcH<sub>2</sub>, bpy, and water in a Teflon-lined reaction vessel at 180 °C for two days gave  $[\text{Ln}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  (or  $[\text{Ln}(3,5\text{-pdc})(\text{CO}_2)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ). Although the bpy ligand was added as a linker, the resulting polymers do not contain it. However, we cannot exclude the possibility that bpy acts as a base to deprotonate 3,5-pdcH<sub>2</sub> during the reaction.

All of the polymers have the same formula unit except the central metal and were obtained as colorless crystals, which were characterized by element analysis, IR spectroscopy, and X-ray crystallography. The IR spectra of these polymers display the C=O stretches at 1660–1550  $\text{cm}^{-1}$ .

**Structures.** Because all polymers are isostructural, we will describe only the structure of **1** in detail. The monomer unit of **1** with the atom-numbering scheme is shown in Figure 1. This unit consists of one Eu metal, one 3,5-pdc ligand, one half of the oxalato ligand, and two aqua ligands, together with one free water molecule. The coordination sphere of Eu can be described as a distorted square antiprism, the core of which comprises two squares (square

1: O1, O5, O2, and O7; square 2: O3, O6, O4, and O8) with a dihedral angle of 3.4(1)°. The oxygen atoms forming the square antiprism consist of four oxygen atoms (O1–O4) from the 3,5-pdc ligand, two oxygen atoms (O5 and O6) from the oxalate ligand, and two oxygen atoms (O7 and O8) from the aqua ligands. All these atoms are bonded to the Eu metal in a monodentate manner. The Eu–O bond lengths range from 2.321(2) to 2.487(2) Å (av, 2.408 Å). The 3,5-pdc and oxalate groups act as tetradentate ligands and link neighboring Eu metals to give a compact 3-D network, in which the oxalate ligand links the Eu metals in the [100] direction and two CO<sub>2</sub><sup>−</sup> groups of 3,5-pdc each link Eu metals in the [011]. The 3,5-pdc nitrogen is not bound to the metal. All hydrogen atoms in the aqua ligands and co-crystallized water molecules participate in the O–H···O hydrogen bonds.



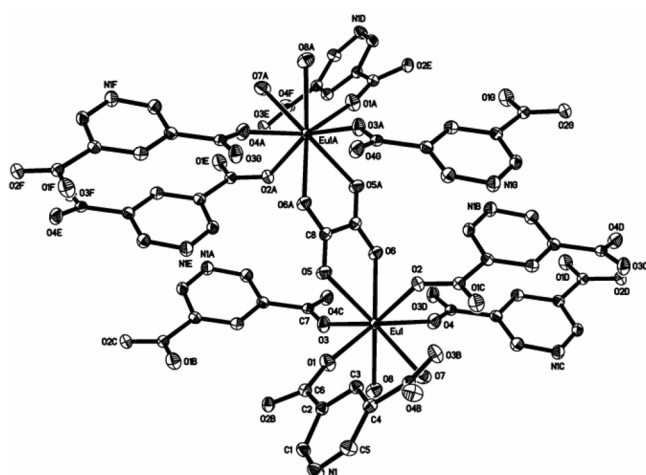


Figure 1. Local coordination environment of Eu in polymer 1.

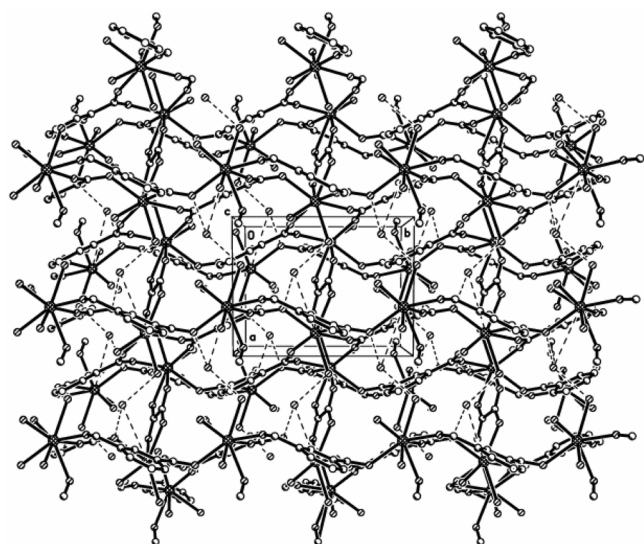


Figure 2. A packing diagram of polymer 1 along the *c*-axis.

The crystal structures of **2–4** are essentially the same as that of **1**. The Ln–O bond lengths are in the range of 2.338(3)–2.504(3) Å (av, 2.423 Å) for **2**, 2.453(3)–2.271(3) Å (2.364 Å) for **3**, or 2.464(4)–2.288(3) Å (2.379 Å) for **4**. The dihedral angle between the squares (square 1: O1, O5, O2, and O7; square 2: O3, O6, O4, and O8) in the square antiprism core is 3.6°(1) for **2**, 6.7°(1) for **3**, or 2.7°(1) for **4**.

#### Mechanistic Aspects of the Oxalate Ligand Formation.

To obtain a clue to the mechanism for the formation of the oxalato ligand, we analyzed the components of the mother liquor remaining after the reaction by GC-MS. The GC-MS spectrum of the mother liquor taken from the preparation of polymer **2** displays several molecular ion peaks at *m/e* = 111, 156, 168, and 194. Although we cannot identify the peak at *m/e* = 194, the *m/e* = 156 peak can be assigned to the starting bpy ligand. Another peak at *m/e* = 168 peak corresponds to the protonated 3,5-pdcH<sub>2</sub> acid (3,5-pdcH<sub>3</sub><sup>+</sup>). We particularly noticed the peak at *m/e* = 111, which may correspond to 3,5-dihydroxypyridine (Chart 2).

One-electron oxidation of a carboxylate ion is known to

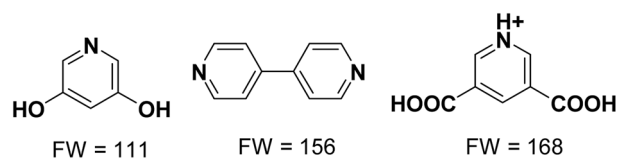
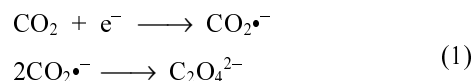


Chart 2

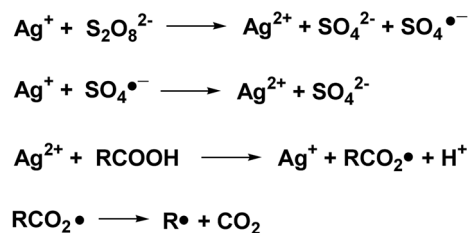
generate a radical, which may undergo decarboxylation. Strong one-electron oxidants such as Mn(III), Ag(II), Ce(IV), and Pb(IV) metal ions exhibit a high reactivity toward such oxidation, and these ions are also capable of oxidizing radical intermediates.<sup>26–29</sup> For example, the oxidative decarboxylation of an acid by Ag(I) in the presence of peroxydisulfate gives an alkyl radical and CO<sub>2</sub>, as shown in Scheme 1.<sup>27</sup>

CO<sub>2</sub> is known to be reduced through a series of electron- and proton-transfer steps to give various products. The CO<sub>2</sub>-to-C<sub>2</sub>O<sub>4</sub><sup>2–</sup> reduction is usually described by eq. (1); that is, it consists of the anionic CO<sub>2</sub><sup>•–</sup> radical formation and the subsequent radical coupling. Whereas electrochemical reductions of CO<sub>2</sub> to oxalate are relatively common, the corresponding chemical reductions that give structurally well-characterized metal-oxalate compounds are rare.<sup>24, 30–34</sup>

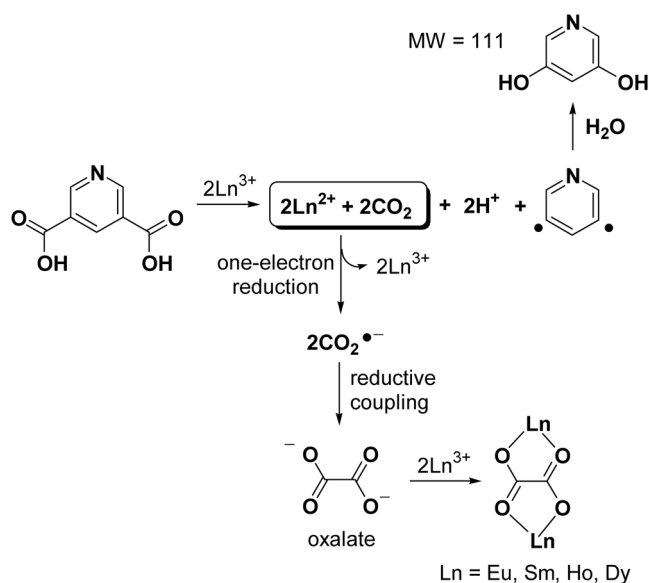


One possible mechanism for the formation of the oxalato ligand in our case is proposed in Scheme 2. The ligand formation might proceed in three steps. The first step is the Ln(III)-mediated decarboxylation (or the C–C bond cleavage) of 3,5-pdcH<sub>2</sub> to give the 3,5-pyridine diradical, CO<sub>2</sub>, and Ln(II) species. The second step is the reduction of CO<sub>2</sub> to the anionic radical CO<sub>2</sub><sup>•–</sup> by the Ln(II) species. In the final step, the two CO<sub>2</sub><sup>•–</sup> radicals reductively couple to the oxalate (C<sub>2</sub>O<sub>4</sub><sup>2–</sup>) ion, which eventually coordinates to two Ln(III) metals.

A couple of examples of decarboxylation of aromatic carboxylic acids under hydrothermal conditions have been observed. For example, Lu and co-workers found the decarboxylation of benzenetricarboxylic acid (btcH<sub>3</sub>) in the reaction of Cu(OAc)<sub>2</sub>, btcH<sub>3</sub>, 2,2-bipyridine·HCl, and NH<sub>3</sub>·H<sub>2</sub>O (eq 2).<sup>35</sup> Zhang also observed such reactivity for 2-pyrazinecarboxylic acid in the reaction of CuBr<sub>2</sub> and that acid (eq 3).<sup>14</sup> We do believe that the peak at *m/e* = 111 in the GC-MS spectra of the mother liquor of polymer **2** corresponds to 3,5-dihydroxypyridine, which was formed by the reaction of the 3,5-pyridine diradical with the solvent

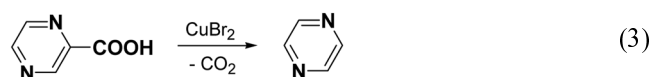
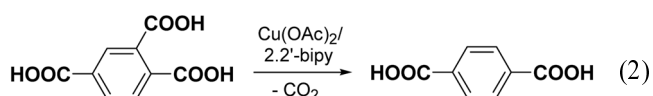


Scheme 1



Scheme 2

(water) under hydrothermal conditions. As mentioned in the Introduction section, we previously prepared a couple of Tb-pdc polymers,  $[\text{Tb}_2(3,5\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  and  $[\text{Tb}_2(2,4\text{-pdc})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$ , from  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and the corresponding pdcH<sub>2</sub>.<sup>24</sup> These polymers contain the oxalato ligand ( $\text{C}_2\text{O}_4$ ), which has never been added to the reaction mixture. By contrast, the corresponding reactions with dicarboxylates (bdc, 2,6-ndcH<sub>2</sub>, or 2,2'-4,4'-bpdcH<sub>2</sub>) produced the oxalate-free products,  $[\text{La}_4(\text{bdc})_6(\text{H}_2\text{O})_5](\text{H}_2\text{O})$ ,  $[\text{Tb}_4(\text{ndc})_6(\text{H}_2\text{O})_5] \cdot 5\text{H}_2\text{O}$  and  $[\text{Tb}_2(\text{bpdc})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  (Chart 1).<sup>15,16</sup> From the previous results mentioned above and the results in this study, such a conclusion could be drawn: whereas pyridine dicarboxylic acids (pdcH<sub>2</sub>) may undergo decarboxylation to give the oxalato ligand, simple dicarboxylic acids (bdc, 2,6-ndcH<sub>2</sub>, and 2,2'-4,4'-bpdcH<sub>2</sub>) do not.



In summary, we prepared four 3-D lanthanide coordination polymers, Ln-oxalate-(3,5-pdc) (Ln = Eu, Sm, Ho, or Dy), by hydrothermal reactions. X-ray structure analyses revealed that all polymers contained the oxalato ( $\text{C}_2\text{O}_4^{2-}$ ) ligand in common. On the basis of GC-MS study, we proposed that the  $\text{C}_2\text{O}_4^{2-}$  formation proceeds in three steps: (1) Ln(III)-mediated decarboxylation of 3,5-pdcH<sub>2</sub> to give  $\text{CO}_2$ , (2) the reduction of  $\text{CO}_2$  to  $\text{CO}_2^{\bullet-}$  by the Ln(II) species, and (3) the reductive coupling of the two  $\text{CO}_2^{\bullet-}$  radicals to the oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) ion.

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