

3-Dimensional Terbium Coordination Polymers: $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ and $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (NDC = 2,6-Naphthalenedicarboxylate; BPDC = 2,2'-Bipyridine-4,4'-dicarboxylate)

Dongwon Min and Soon W. Lee*

Department of Chemistry and School of Molecular Science (BK21),
Sungkyunkwan University, Suwon 440-746, Korea
Received April 1, 2002

Three-dimensional terbium coordination polymers with the formulas of $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**2**) (NDC = 2,6-naphthalenedicarboxylate; BPDC = 2,2'-bipyridine-4,4'-dicarboxylate) were prepared by hydrothermal reactions. Both compounds were structurally characterized by X-ray diffraction. Compound **1** has a polymeric structure that contains four distinct Tb metals. Three Tb metals have a square-antiprismatic structure, and the remaining one has a 9-coordinate, triply capped trigonal-prismatic structure. Compound **2** is also a polymer with two distinct Tb metals, both of which have a square-antiprismatic structure. The pyridine nitrogen atoms of the BPDC²⁻ ligand do not coordinate to the metal centers in compound **2**.

Keywords: Terbium, Hydrothermal, 2,2'-Bipyridine-4,4'-dicarboxylic acid, 2,6-Naphthalenedicarboxylic acid, Coordination polymer.

Introduction

There has been tremendous interest in designing and preparing functional solids based on metal-organic coordination networks. Over the past years, many of these networks have exhibited unique properties, including (functional group)- or size-selective sorption, catalysis, gas storage, and molecular recognition.¹⁻¹⁶ The synthesis of coordination polymers containing transition metals has become widespread over the past decade, but there are few reports on lanthanide-metal coordination polymers.

Recently, the synthesis and structural characterization of lanthanum(III)-carboxylate coordination polymers drew attentions.¹⁷⁻¹⁹ We have become interested in preparing coordination polymers with dicarboxylate ligands. For instance, we have obtained a 3-D zinc,²⁰ 3-D cobalt,²¹ 2-D Ni,²² 1-D Cu,²³ 2-D lanthanum,²⁴ and 2-D cobalt²⁵ coordination-polymers by hydrothermal reactions. As a continuation of our research, we set out to prepare terbium coordination polymers with 2,6-naphthalenedicarboxylic acid (NDCH₂) and 2,2'-bipyridine-4,4'-dicarboxylic acid (BPDCH₂). We report herein the preparation and crystal structures of two compounds, $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**2**).

Experimental Section

$\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, sodium acetate ($\text{NaOAc} \cdot 3\text{H}_2\text{O}$), 2,6-naphthalenedicarboxylic acid (NDCH₂), and 2,2'-bipyridine-4,4'-dicarboxylic acid (BPDCH₂) were purchased from Aldrich company. IR spectra were recorded with a Nicolet

205 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) by the Korea Basic Science Institute. TGA analysis was conducted on a TA4000/SDT 2960 instrument.

Preparation of $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (1**).** A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.100 g, 0.229 mmol), NDCH₂ (0.0496 g, 0.229 mmol), and 1 N KOH (0.575 mL, 0.575 mmol) in H₂O (5.0 mL) in the mole ratio of 1.0:1.0:2.5 was heated in a 23-mL-capacity Teflon-lined reaction vessel at 180 °C for four days and then cooled to room temperature by air-cooling. The yellow product was collected by filtration, washed with H₂O (2 × 5 mL), and air-dried to give $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (0.0613 g, 0.0302 mmol, 79% yield). Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_{11}\text{Tb}_4$ ($M_r = 2033.70$): C, 42.5; H, 2.38. Found: C, 42.3; H, 2.31. IR (KBr): 3449, 1602 (C=O), 1547 (C=O), 1490 (C=O), 1417 (C=O), 1356 (C=O), 796, 773, 440 cm⁻¹.

Preparation of $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (2**).** This polymer was prepared similar to polymer **1**. A mixture of $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.100 g, 0.229 mmol), BPDCH₂ (0.0559 g, 0.229 mmol), and NaOAc \cdot 3H₂O (0.0779 g, 0.573 mmol) in H₂O (5.0 mL) in the mole ratio of 1.0:1.0:2.5 was heated for two days to give $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (0.0614 g, 0.0550 mmol, 72% yield). Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{N}_6\text{O}_{16}\text{Tb}_2$ ($M_r = 1116.47$): C, 38.7; H, 2.35; N, 7.52. Found: C, 38.9; H, 2.36; N, 7.54. IR (KBr): 3069, 1601 (C=O), 1581 (C=O), 1546 (C=O), 1466 (C=O), 1421 (C=O), 1403, 1383, 776, 707, 688 cm⁻¹.

X-ray Structure Determination. All X-ray data were collected with the use of Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-plate monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 25 (for **1**) or 27 (for **2**) reflections in the range of $10.0^\circ < 2\theta$

*Corresponding author. Phone: +82-31-290-7066, Fax: +82-31-290-7075, E-mail: swlee@chem.skku.ac.kr

Table 1. X-ray data collection and structure refinement

	1	2
formula	C ₇₂ H ₄₈ O ₅₁ Tb ₄	C ₃₆ H ₂₆ N ₆ O ₁₆ Tb ₂
fw	2033.70	1116.47
temperature, K	296(2)	295(2) K
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	17.101(1)	11.3590(6)
<i>b</i> , Å	15.245(3)	12.197(1)
<i>c</i> , Å	24.969(4)	14.2601(8)
α , deg	90.000	95.072(7)
β , deg	106.093(9)	103.522(4)
γ , deg	90.000	101.077(6)
<i>V</i> , Å ³	6254(2)	1866.6(2)
<i>Z</i>	4	2
<i>d</i> _{calc} , g cm ⁻³	2.160	1.986
μ , mm ⁻¹	4.570	3.843
<i>T</i> _{min}	0.0963	0.4052
<i>T</i> _{max}	0.5591	0.7979
<i>R</i> ^a (000)	3908	1084
2 θ range (°)	3.550	3.550
scan type	ω	ω
scan speed	variable	variable
No. of reflns measured	10694	6891
No. of reflns unique	10382	6527
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	8893	6235
No. of params refined	965	572
Max. in $\Delta\rho$ (e Å ⁻³)	2.935	0.732
Min. in $\Delta\rho$ (e Å ⁻³)	-1.557	0.923
<i>GOF</i> on <i>F</i> ²	1.035	1.083
<i>R</i>	0.0474	0.0220
<i>wR</i> ₂ ^b	0.1229	0.0578

$$^a wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$$

< 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ -scan data. Structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All calculations were carried out with the use of the SHELXTL programs.²⁶ Details on crystal data and intensity data are given in Table 1. Selected bond distances and bond angles are given in Tables 2 and 3.

A yellow crystal of **1**, shaped as a rod of approximate dimensions 0.52 × 0.20 × 0.18 mm³, was used. The unit-cell parameters and systematic absences, *h*0*l* (*h* + *l* = 2*n* + 1) and 0*k*0 (*k* = 2*n* + 1), unambiguously indicated *P*2₁/*n* as a space group. The water hydrogen atoms could not be located. The remaining hydrogen atoms were generated in ideal positions and refined in a riding model.

A colorless crystal of **2**, shaped as a block of approximate dimensions 0.50 × 0.50 × 0.36 mm³, was used. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: *P*1 and *P* $\bar{1}$. A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *P* $\bar{1}$. The water hydrogen atoms were located in the difference Fourier maps and refined isotropically. The remaining hydrogen atoms were generated in ideal positions.

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-182885 for **1** and CCDC-182884 for **2**). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from

Table 2. Selected bond distances (Å) and bond angles (°) in **1**

Tb1-O1	2.306(5)	Tb1-O3	2.314(4)	Tb1-O18	2.339(4)
Tb1-O10	2.362(5)	Tb1-O6	2.375(5)	Tb1-O16	2.418(5)
Tb1-O25	2.513(6)	Tb1-O29	2.713(4)	Tb2-O21	2.297(5)
Tb2-O7	2.330(5)	Tb2-O9	2.337(5)	Tb2-O2	2.345(5)
Tb2-O15	2.347(5)	Tb2-O5	2.364(4)	Tb2-O28	2.409(5)
Tb2-O1	2.899(5)	Tb3-O23	2.289(5)	Tb3-O8	2.313(5)
Tb3-O22	2.327(5)	Tb3-O19	2.349(5)	Tb3-O13	2.354(5)
Tb3-O12	2.368(5)	Tb3-O27	2.482(6)	Tb3-O20	2.880(5)
Tb4-O17	2.325(4)	Tb4-O20	2.327(5)	Tb4-O4	2.331(5)
Tb4-O24	2.354(5)	Tb4-O11	2.370(5)	Tb4-O14	2.429(4)
Tb4-O26	2.471(5)	Tb4-O29#1	2.651(4)	Tb(4)-O(23)	2.905(5)
O1-Tb1-O3	146.1(2)	O1-Tb1-O18	86.3(2)	O3-Tb1-O18	90.7(2)
O1-Tb1-O6	76.5(2)	O3-Tb1-O6	135.3(2)	O18-Tb1-O6	76.2(2)
O10-Tb1-O25	139.8(2)	O6-Tb1-O25	138.8(2)	O16-Tb1-O25	73.1(2)
O7-Tb2-O9	151.9(2)	O21-Tb2-O2	125.3(2)	O7-Tb2-O2	75.4(2)
O9-Tb2-O15	76.0(2)	O2-Tb2-O15	78.1(2)	O21-Tb2-O5	146.2(2)
O15-Tb2-O5	131.0(2)	O21-Tb2-O28	76.2(2)	O7-Tb2-O28	75.9(2)
O8-Tb3-O19	123.8(2)	O22-Tb3-O19	75.9(2)	O23-Tb3-O13	77.1(2)
O23-Tb3-O12	81.6(2)	O8-Tb3-O12	151.6(2)	O22-Tb3-O12	86.8(2)
O17-Tb4-O20	145.9(2)	O17-Tb4-O4	90.0(2)	O20-Tb4-O4	87.2(2)
O17-Tb4-O11	137.1(2)	O20-Tb4-O11	75.4(2)	O4-Tb4-O11	78.8(2)

Symmetry transformations used to generate equivalent atoms: #1 = *x* + 1, *y*, *z*

Table 3. Selected bond distances (Å) and bond angles (°) in **2**

Tb1-O12	2.292(2)	Tb1-O2	2.318(2)	Tb1-O6	2.339(2)
Tb1-O15	2.351(3)	Tb1-O11	2.365(2)	Tb1-O8	2.424(2)
Tb1-O14	2.432(2)	Tb1-O7	2.541(2)	Tb2-O4	2.253(2)
Tb2-O1	2.314(2)	Tb2-O10	2.316(2)	Tb2-O3	2.333(2)
Tb2-O7	2.426(2)	Tb2-O13	2.436(2)	Tb2-O5	2.441(2)
Tb2-O6	2.745(2)				
O12-Tb1-O2	82.7(1)	O12-Tb1-O6	85.27(8)	O2-Tb1-O6	73.71(9)
O12-Tb1-O15	98.5(1)	O2-Tb1-O15	143.1(1)	O6-Tb1-O15	69.6(1)
O12-Tb1-O11	83.31(8)	O2-Tb1-O11	69.26(8)	O6-Tb1-O11	142.30(8)
O12-Tb1-O14	77.64(9)	O2-Tb1-O14	140.55(9)	O6-Tb1-O14	136.95(9)
O4-Tb2-O1	86.46(8)	O4-Tb2-O10	96.49(9)	O1-Tb2-O10	147.96(8)
O4-Tb2-O3	98.44(8)	O1-Tb2-O3	140.04(8)	O10-Tb2-O3	71.25(8)
O4-Tb2-O5	74.52(8)	O1-Tb2-O5	75.14(8)	O10-Tb2-O5	74.98(9)

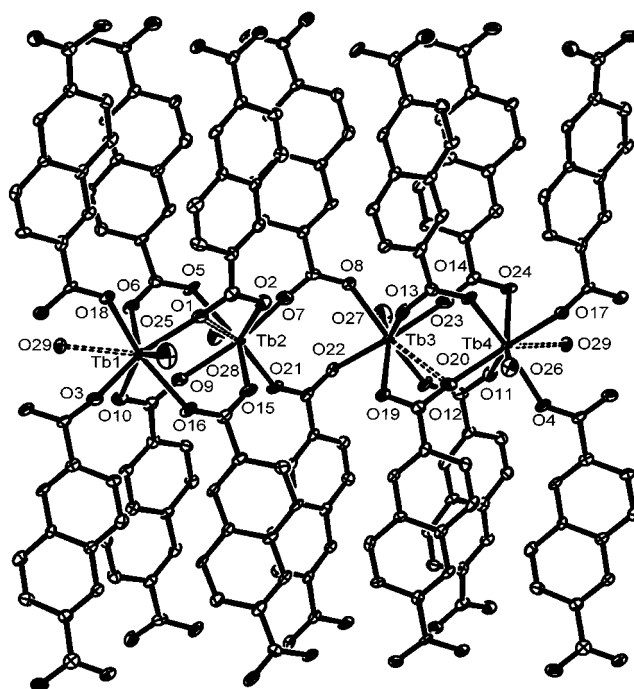
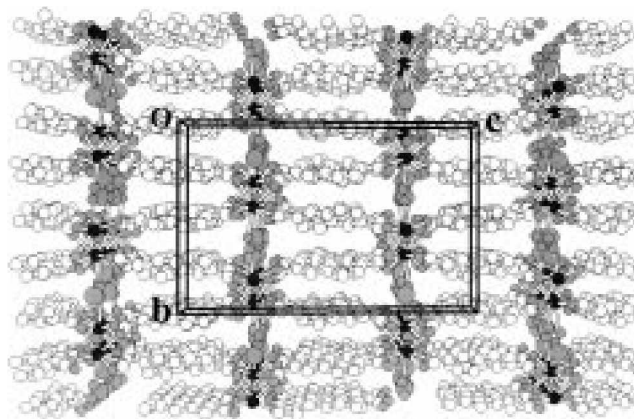
the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Preparation. Compounds have been prepared by hydrothermal reactions. Terbium(III) nitrate reacts with NDCH₂ in the presence of KOH at 180 °C to give [Tb₄(NDC)₆(H₂O)₅]·2H₂O (**1**), a 3-D polymer. Terbium(III) nitrate also reacts with BPDCH₂ in the presence of NaOAc·3H₂O at 180 °C to give [Tb₂(BPDC)₃(H₂O)₃]·H₂O (**2**), another 3-D polymer. We added the base to accelerate the reaction by deprotonating COOH groups. Very recently, Li and co-workers reported the effect of pH on the dimensionality of coordination polymers.²⁷ According to their work, increasing pH leads to the higher connectivity of the ligand and ultimately structures of higher dimensions.

Both crystalline compounds have been characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, and X-ray diffraction. The IR spectrum of **1** exhibits peaks at 1602, 1547, 1490, 1417, and 1356 cm⁻¹ that can be assigned to the asymmetric and symmetric C=O stretches.^{28,29} The IR spectrum of **2** also shows strong peaks characteristic of carboxylate groups at 1601, 1581, 1546, 1466, and 1421 cm⁻¹. Thermogravimetric analysis (TGA) shows that compound **1** loses 5.1% of its mass between 136 and 190 °C, corresponding to the loss of five aqua ligands and two free water molecules (calculated 6.2%). Above 517 °C, the second process occurs with the loss of the ligands. The TGA for **2** shows a weight loss corresponding to four aqua ligands (observed 7.9%, calculated 6.4%) in the temperature range of 198–372 °C. Above 475 °C, the second process occurs with the loss of organic ligands.

Structure. The monomeric unit of polymer **1** is shown in Figure 1. Compound **1** exhibits a three-dimensional structure, which contains four crystallographically independent terbium ions with four distinct coordination geometries. The formal oxidation state of each terbium metal is +3. Three Tb metals (Tb1, Tb2, and Tb3) have an 8-coordinate, square-antiprismatic structure. The remaining Tb metal (Tb4) has a 9-coordinate, triply capped trigonal-prismatic structure.

**Figure 1.** An ORTEP drawing of **1**.**Figure 2.** Ball-stick representation of compound **1** down the *a*-axis. Oxygen atoms are represented as gray circles, terbium atoms as closed circles, and carbon atoms as open circles.

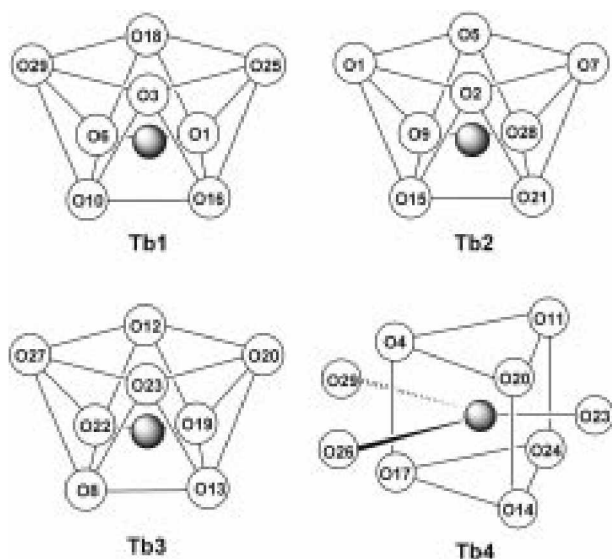


Chart 1. Coordination modes of Tb metals in 1.

Adjacent Tb centers are bridged by two CO_2^- groups ($\text{Tb2} \cdots \text{Tb3}$ and $\text{Tb1} \cdots \text{Tb4}$) or four CO_2^- groups ($\text{Tb1} \cdots \text{Tb2}$ and $\text{Tb3} \cdots \text{Tb4}$) to result in an infinite 1-D chain in the a -axis direction (Figure 1). These chains are cross-linked by the NDC^{2-} ligands to form a three-dimensional network (Figure 2). The local coordination geometry around Tb1 is an 8-coordinate, square antiprism (Chart 1). Among the eight oxygen atoms bonded to the Tb1 ion, two come from aqua ligands, and six come from six bridging CO_2^- groups. One aqua ligand (O29) links the Tb metals by acting as a μ -O bridging ligand. The square-antiprismatic core comprises two squares (square 1: O3, O18, O25, and O29; square 2: O1, O6, O10, and O16) with their dihedral angle of $4.0(2)^\circ$.

The coordination geometry of Tb2 is also an 8-coordinate, square antiprism. Among the eight oxygen atoms bonded to the Tb2 metal, one comes from one aqua ligand, two from one chelating CO_2^- group, and five from five bridging CO_2^- groups. The square-antiprismatic core comprises two squares (square 1: O1, O2, O5, and O7; square 2: O9, O15, O21, and O28) with their dihedral angle of $12.7(2)^\circ$. The Tb3 metal also has a square-antiprismatic structure with eight oxygen atoms, which consist of one from one aqua ligand, two from one chelating CO_2^- group, and five from five bridging CO_2^- groups. The square-antiprismatic core consists of two squares (square 1: O12, O20, O23, and O27; square 2: O8, O13, O19, and O22) with their dihedral angle of $9.5(2)^\circ$. Interestingly, the coordination geometry of Tb4 is a 9-coordinate, triply capped trigonal-prism. Nine oxygen atoms bonded to the Tb4 ion consist of two from aqua ligands, two from one chelating CO_2^- group, and five from five bridging CO_2^- groups. The trigonal-prismatic core comprises two triangles (triangle 1: O4, O11, and O20; triangle 2: O14, O17, and O24) with their dihedral angle of $4.3(2)^\circ$. Three oxygen atoms (O23, O26, and O29) act as capping agents on the rectangular faces.

The Tb-O bond distances exhibit an extremely wide range of 2.289(5)–2.905(5) Å, and have a much higher range than those reported for $\text{Tb}(\text{isonicotinate})_3(\text{H}_2\text{O})_2$ (2.282(6)–2.450

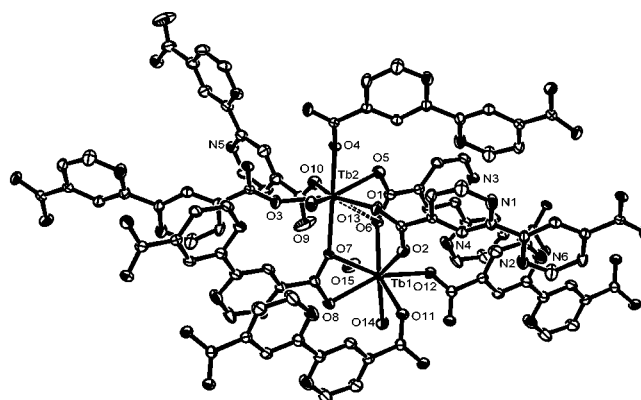


Figure 3. An ORTEP drawing of 2.

(5) Å)³⁰ and $\text{Na}_4\text{K}_2\text{Tb}_2\text{Si}_6\text{O}_{38} \cdot 10\text{H}_2\text{O}$ (2.23(2)–2.38(1) Å).³¹ It is worth noting that three oxygen atoms (O1, O20, and O23) in the CO_2^- groups act as asymmetric μ_2 -O ligands between Tb metals ($\text{Tb1} \cdots \text{Tb2}$, $\text{Tb3} \cdots \text{Tb4}$, and $\text{Tb3} \cdots \text{Tb4}$, respectively). The extremely long Tb-O bonds in the asymmetric Tb-O-Tb bridges are represented by dotted bonds in Figure 1: Tb2-O1 (2.899(5) Å), Tb3-O20 (2.880(5) Å), and Tb4-O23 (2.905(5) Å).

The bonding parameters mentioned above suggest the flexibility in the coordination of terbium ions, which might have facilitated the formation of infinite frameworks of polymer 1 with unusual coordination numbers and geometries. The very long Tb \cdots Tb distances { $\text{Tb1} \cdots \text{Tb2}$: 4.066(0); $\text{Tb2} \cdots \text{Tb3}$: 5.192(1); $\text{Tb3} \cdots \text{Tb4}$: 4.054(0) Å} indicate no direct Tb-Tb interactions. The crystal structure of polymer 1 shows an extended one-dimensional channel of about 4.78×4.19 Å along the c axis. Water guest molecules are packed into the channels in the crystal structure.

The monomeric unit of 2 is illustrated in Figure 3. Compound 2 contains two crystallographically independent terbium ions with two distinct coordination geometries. The formal oxidation state of each terbium metal is +3. One

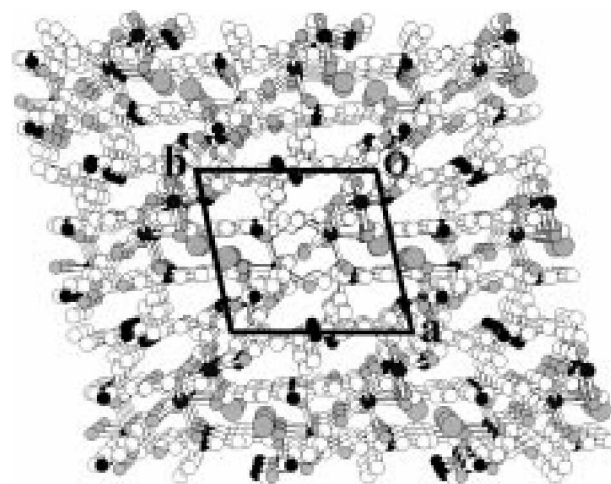


Figure 4. Ball-stick representation of compound 2 down the c -axis. Nitrogen atoms are represented as closed circles, terbium atoms as crossed gray circles, oxygen atoms as gray circles, and carbon atoms as open circles.

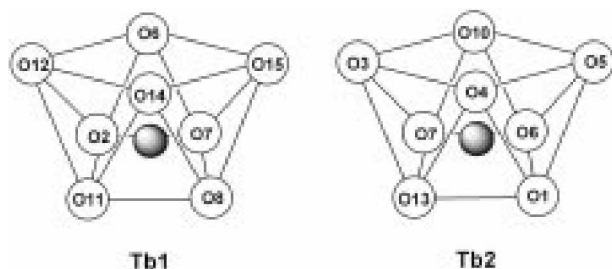


Chart 2. Coordination modes of Tb metals in **2**.

oxygen atom (O6) in the CO_2^- group links the Tb metals, acting as an asymmetric bridging ligand to give two very different Tb-O bond distances (Tb1-O6: 2.339(2) Å; Tb2-O6: 2.745(2) Å). Interestingly, the BPDC $^{2-}$ ligand acts as a tetradentate ligand without involving the pyridine nitrogen atoms in bonding to the terbium metal. The very long Tb1...Tb2 distance of 4.055(0) Å indicates no direct Tb-Tb interactions.

Both Tb metals have a square-antiprismatic structure. The local coordination geometry around Tb1 can be described as 8-coordinate, square-antiprismatic (Chart 2). Eight oxygen atoms bonded to the Tb1 ion are composed of two from aqua ligands, two from one chelating CO_2^- group, and four from four bridging CO_2^- groups. The square-antiprismatic core comprises two squares (square 1: O2, O7, O8, and O11; square 2: O6, O12, O14, and O15) with their dihedral angle of 2.5(0.1)°. The Tb2 ion is coordinated by eight oxygen atoms, which consist of one from one aqua ligand, two from one chelating CO_2^- group, and five from five bridging CO_2^- groups. The square-antiprismatic core comprises two squares (square 1: O1, O6, O7, and O13; square 2: O3, O4, O5, and O10) with their dihedral angle of 8.8(2)°.

Figure 4 shows an extremely complicated 3-D polymeric structure of **2**. Among the CO_2^- oxygen atoms, only one oxygen atom (O9) does not bond to Tb and participates in the intramolecular O15-H...O9 hydrogen bond as a hydrogen-acceptor. The remaining CO_2^- oxygen atoms bond to Tb metals and link them to produce a polymeric structure. Whereas two oxygen atoms (O6 and O7) directly link the Tb metals by acting as μ_2 -O bridging ligands, three aqua ligands (O13, O14, and O15) and nine CO_2^- oxygen atoms (O1-O5, O8, and O10-O12) bond to only one Tb metal. The crystal structure of polymer **2** shows an extended one-dimensional channel of about 3.99×7.25 Å along the *c* axis. Water guest molecules are packed into the channels in the crystal structure.

In summary, two three-dimensional coordination polymers, $[\text{Tb}_4(\text{NDC})_6(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Tb}_2(\text{BPDC})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**2**), have been synthesized by the hydrothermal reaction in relatively high yields. The structure of polymer **1** is unique in that it contains four distinct 8- or 9-coordinate Tb ions with a different coordination environment for each Tb: three square-antiprisms and one triply capped trigonal-prism. Polymer **1** has a small channel of about 4.78×4.19 Å. Polymer **2** contains two distinct 8-coordinate, square-antiprismatic Tb ions, and has a relatively small channel of about 3.99×7.25 Å.

Acknowledgment. This work was supported by the Brain Korea 21 Project.

References

- Swieger, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.
- Macdonald, J. C.; Dorrestein, P. C.; Pilley, M. M.; Foote, M. M.; Lundberg, J. L.; Henning, R. W.; Schultz, A. J.; Manson, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 11692.
- Li, H.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
- Huang, X. Y. *J. Coord. Chem.* **1999**, *47*, 269.
- Braga, D.; Grepioni, F. *Coord. Chem. Rev.* **1999**, *183*, 19.
- Reineke, T. M.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2590.
- Evans, O. R.; Xiong, R.-G.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 536.
- Evans, O. R.; Wang, Z.; Xiong, R.-G.; Foxman, B. M.; Lin, W. *Inorg. Chem.* **1999**, *38*, 2969.
- Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117.
- Hagman, P. J.; Hagman, D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2638.
- Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.
- Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.
- Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272.
- Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.
- Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1995**, *374*, 727.
- Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792.
- Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651.
- Baggio, R.; Garland, M. T.; Perec, M.; Vega, D. *Inorg. Chem.* **1996**, *35*, 2396.
- Wang, S.; Pang, Z.; Smith, K. D. L.; Wagner, M. J. *J. Chem. Soc., Dalton Trans.* **1994**, 955.
- Min, D.; Yoon, S. S.; Lee, C. Y.; Suh, M.; Hwang, Y.-J.; Han, W. S.; Lee, S. W. *Bull. Korean Chem. Soc.* **2001**, *22*, 531.
- Min, D.; Yoon, S. S.; Lee, J. H.; Suh, M.; Lee, S. W. *Inorg. Chem. Commun.* **2001**, *4*, 297.
- Min, D.; Yoon, S. S.; Lee, C. Y.; Han, W. S.; Lee, S. W. *Bull. Korean Chem. Soc.* **2001**, *22*, 1041.
- Min, D.; Yoon, S. S.; Jung, D. Y.; Lee, C. Y.; Kim, Y.; Han, W. S.; Lee, S. W. *Inorg. Chim. Acta* **2001**, *324*, 293.
- Kim, H. J.; Min, D.; Hoe, H. S.; Lee, S. W. *J. Korean Chem. Soc.* **2001**, *45*, 507.
- Min, D.; Yoon, S. S.; Lee, S. W. *Inorg. Chem. Commun.* **2002**, *5*, 143.
- Bruker, *SHELXL*, Structure Determination Software Programs; Bruker Analytical X-ray Instruments Inc.: Madison, Wisconsin, USA, 1997.
- Pan, L.; Frydek, T.; Sander, M. B.; Huang, X.; Li, J. *Inorg. Chem.* **2001**, *40*, 1271.
- Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983.
- Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972.
- Ma, L.; Evans, O. R.; Foxman, B. M.; Lin, W. *Inorg. Chem.* **1999**, *38*, 5837.
- Ananias, D.; Ferreira, A.; Rocha, J.; Ferreira, P.; Rainho, J. P.; Morais, C.; Carlos, L. D. *J. Am. Chem. Soc.* **2001**, *123*, 5735.