3-Dimensional 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)

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Three-dimensional terbiium 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, tripolyhedral-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 BPDC\(^{2-}\) ligand do not coordinate to the metal centers in compound 2.

Keywords: Terbiium, 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. 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 attention. We have become interested in preparing coordination polymers with dicarboxylate ligands. For instance, we have obtained a 3-D zinc, 3-D cobalt, 2-D Ni, 1-D Cu, 2-D lanthanum, and 2-D cobalt \(^2\) coordination polymers by hydrothermal reactions. As a continuation of our research, we set out to prepare terbiium coordination polymers with 2,6-naphthalenedicarboxylic acid (NDC\(_2\)) and 2,2'-bipyridine-4,4'-dicarboxylic acid (BPDC\(_2\)). We report herein the preparation and structural characterization 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

\(\text{TB}(\text{N}_3\text{O})_5\cdot 5\text{H}_2\text{O}\), sodium acetate (NaOAc-3\text{H}_2\text{O}), 2,6-naphthalendicarboxylic acid (NDC\(_2\)), and 2,2'-bipyridine-4,4'-dicarboxylic acid (BPDC\(_2\)) 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 \(\text{TB}(\text{N}_3\text{O})_5\cdot 5\text{H}_2\text{O}\) (0.100 g, 0.229 mmol), NDC\(_2\) (0.0496 g, 0.229 mmol), and 1 N KOH (0.575 mL, 0.575 mmol) in \(\text{H}_2\text{O}\) (5 mL) in the molar ratio of 1:1:0:2.5 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 \(\text{H}_2\text{O}\) (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. Calculated for \(\text{C}_{238}\text{H}_{37}\text{O}_{17}\text{TB}_4\): M = 2035.70; C: 42.52; H: 2.38. Found: C: 42.3; H: 2.31. IR (KBr): 3419, 1602 (C=O), 1547 (C=O), 1490 (C=O), 1417 (C=O), 1356 (C=O), 766, 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 \(\text{TB}(\text{N}_3\text{O})_5\cdot 5\text{H}_2\text{O}\) (0.100 g, 0.229 mmol), BPDC\(_2\) (0.0559 g, 0.229 mmol), and NaOAc-3\text{H}_2\text{O} (0.0779 g, 0.573 mmol) in \(\text{H}_2\text{O}\) (5 mL) in the molar 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, 0.0560 mmol, 72% yield). Anal. Calculated for \(\text{C}_{53}\text{H}_{27}\text{O}_{31}\text{TB}_2\): M = 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° < 2θ < 25.0°.
3-Dimensional Terbium Coordination Polymers


Table 1. X-ray data collection and structure refinement

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\(wR2 = \sqrt{\frac{\sum\left(F^2 - F_c^2\right)^2}{\left|\sum\left(F^2\right)\right|}}\)

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

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Symmetry transformations used to generate equivalent atoms: \(\tilde{e} \ ={ } x\ 1/2,\ 1/2,\ z\)

< 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 \(\psi\)-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 SHELXL97 programs. 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 mm\(^2\), was used. The unit-cell parameters and systematic absences, \(h0l\) \((h+l = 2n+1)\) and \(00l\) \((k = 2n + 1)\), unambiguously indicated \(P2_1/n\) 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 × 0.36 × 0.36 mm\(^2\), was used. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: \(P1\) and \(P1\). A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in \(P1\). 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-1828884 for 1 and CCDC-1828884 for 2). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from...
Table 3. Selected bond distances (Å) and bond angles (°) in 2

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<th>Bond/Distance</th>
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Preparation. Compounds have been prepared by hydrothermal reactions. Terbium(III) nitrate reacts with NDCH₂ in the presence of KOH at 180 °C to give \( [\text{Tb}·(\text{NDCH}_2)_2\text{H}_2\text{O}]·2\text{H}_2\text{O} \) (1), a 3-D polymer. Terbium(III) nitrate also reacts with BPDCH₂ in the presence of NaOAc 3H₂O at 180 °C to give \( [\text{Tb}·(\text{BPDCH}_2)_2\text{H}_2\text{O}]·\text{H}_2\text{O} \) (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. 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. 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.
Adjacent Tb centers are bridged by two CO$_2^-$ groups (TB$_2$=TB$_3$ and TB$_1$=TB$_4$) or four CO$_3^-$ groups (TB$_1$=TB$_2$ and TB$_3$=TB$_4$) 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-antiprismonic 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-antiprismonic 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-antiprismonic 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-antiprismonic 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-prismonic 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)-2.965(5) Å, and have a much higher range than those reported for Tb(isonicotinate)$_2$(H$_2$O)$_2$: 2.282(6)-2.150 (5) Å$^{31}$ and Na$_4$K$_4$Tb$_3$Si$_6$O$_{38}$·10H$_2$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-O ligands between Tb metals (Tb1···TB2, Tb3···TB4, and TB3···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 Tb1-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···Tb distances [Tb1···TB2: 4.066(0), TB2···TB3: 5.192(1); Tb3···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 $a$ 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

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**Figure 3** An ORTEP drawing of 2.

**Figure 4** Ball-and-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.
oxygen atom (O6) in the CO$_3^-$ 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$_3^-$ group, and four from four bridging CO$_3^-$ 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)$^\circ$. The Tb2 ion is coordinated by eight oxygen atoms, which consist of one from one aqua ligand, two from one chelating CO$_3^-$ group, and five from five bridging CO$_3^-$ 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)$^\circ$.

Figure 4 shows an extremely complicated 3-D polymeric structure of 2. Among the CO$_3^-$ 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$_3^-$ 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-O bridging ligands, three aqua ligands (O13, O14, and O15) and nine CO$_3^-$ 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, [Tb$_2$(NDC)$_2$(H$_2$O)$_2$]H$_2$O (1) and [Tb$_2$(BPDC)$_2$(H$_2$O)$_4$]H$_2$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.