

Synthesis, Structure and Luminescence Properties of Four Novel Terbium 2-Fluorobenzoate Complexes

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Four new complexes $[\text{Tb}(\text{2-FBA})_3 \cdot (\text{2-HFBA}) \cdot \text{H}_2\text{O}]_2$ (**1**), $[\text{Tb}(\text{2-FBA})_3 \cdot (4,4'\text{-bpy}) \cdot \text{H}_2\text{O}]_3$ (**2**), $[\text{Tb}(\text{2-FBA})_3 \cdot (2,2'\text{-bpy})]_2$ (**3**), and $[\text{Tb}(\text{2-FBA})_3 \cdot \text{phen} \cdot \text{CH}_3\text{CH}_2\text{OH}]_2 \cdot [\text{Tb}(\text{2-FBA})_3 \cdot \text{phen}]_2$ (**4**) (2-HFBA: 2-fluorobenzoic acid; 4,4'-bpy: 4,4'-bipyridine; 2,2'-bpy: 2,2'-bipyridine; phen: 1,10-phenanthroline) have been synthesized and characterized by X-ray diffraction analysis. Complex **1** is a dimeric molecule with a one-dimensional supramolecular structure formed by hydrogen bonds. Complex **2** is an infinite one-dimensional polymer chain formed by bridging carboxylato groups; its 2D framework structure is formed by hydrogen bonds. The structure of complex **3** contains three independent binuclear molecules in the asymmetric unit. In two of them, two Tb^{3+} ions are held together by four 2-FBA groups, with two of them in a bidentate-bridging mode and the other two in a chelating-bridging mode. In the third, two Tb^{3+} ions are held together by four 2-FBA groups, all of which are in the bidentate-bridging mode. One 2-FBA group and one 2,2'-bpy chelate to one Tb^{3+} ion, resulting in coordination numbers of the central ter-

bium ion of nine and eight, respectively. The structure of complex **4** contains two nonequivalent binuclear molecules in the asymmetric unit – $[\text{Tb}(\text{2-FBA})_3 \cdot \text{phen} \cdot \text{CH}_3\text{CH}_2\text{OH}]_2$ and $[\text{Tb}(\text{2-FBA})_3 \cdot \text{phen}]_2$. In the former, the Tb^{3+} ion is surrounded by eight atoms, five O atoms from five 2-FBA groups, one O atom from one ethanol molecule and two N atoms from phen, and the 2-FBA groups act in monodentate and bridging coordination modes. In the latter, the Tb^{3+} ion is coordinated by nine atoms, seven O atoms from five 2-FBA groups and two N atoms of phen, and the 2-FBA groups link the Tb^{3+} ion in chelating, bridging, and chelating-bridging coordination modes. Complexes **1**, **3**, and **4** emit a bright green light under UV light in the solid state. There are four emission peaks in the luminescence spectra at 488, 543, 584, and 618 nm, corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively, of the Tb^{3+} ion.

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Introduction

Most terbium complexes emit intense green fluorescence and have potential applications in fluorescent probes and in electroluminescent devices.^[1,2] The luminescent intensities of lanthanide complexes depend on their ligands, and some lanthanide carboxylate complexes have good luminescent properties. This kind of lanthanide complex has been studied in recent years due to the variety of structural types and potential applications in catalysis and luminescent probes, etc.^[1–4] We are interested in the structural chemistry of these complexes. Many structural studies on lanthanide carboxylate complexes have been reported. In lanthanide monocarboxylate complexes, the carboxylate groups are coordinated simultaneously to the lanthanide ion in different modes, namely monodentate, chelating, bridging, and

bridging-chelating modes. Consequently, the complexes are often mononuclear, dinuclear dimers, polymeric chains, or network structures. Generally, lanthanide complexes with only a monoacid form coordination polymers with bridging carboxylato groups, such as $[\text{Nd}(\text{3-CH}_3\text{C}_6\text{H}_4\text{COO})_3]$ and $[\text{Tb}(\text{3-CH}_3\text{C}_6\text{H}_4\text{COO})_3] \cdot [\text{Nd}(\text{2-CH}_3\text{OC}_6\text{H}_4\text{COO})_3 \cdot 4\text{H}_2\text{O}]$,^[6] $[\text{Eu}(\text{4-CH}_3\text{C}_6\text{H}_4\text{COO})_3]$,^[7] and $[\text{Eu}(\text{2,3-DMOBA})_3]_n$ (2,3-DMOBA = 2,3-dimethoxybenzoate).^[8] However, lanthanide complexes with a monoacid and 1,10-phenanthroline (phen) or 2,2'-bipyridine (2,2'-bpy) are commonly dimeric molecules with a bridging linkage of the carboxylato groups, such as in $[\text{Eu}(\text{4-CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{phen})]$,^[9] $[\text{Sm}_2(\text{4-CH}_3\text{C}_6\text{H}_4\text{COO})_6(\text{2,2'-bpy})_2]$,^[10] $[\text{Eu}(m\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{phen})](\text{H}_2\text{O})$,^[11] and $[\text{Eu}_2(\text{3,4-DMBA})_6 \cdot (\text{phen})_2]$ (3,4-DMBA = 3,4-dimethylbenzoate).^[12] In these complexes, the phen or 2,2'-bpy ligand coordinates to the metal in a chelating mode to form a stable five-membered ring. Lanthanide carboxylate complexes containing 2,2'-bpy or phen have interesting structures, with both high stability and intense fluorescence.^[9–12] 4,4'-Bipyridine (4,4'-bpy), however, coordinates to the metal with one or two N atoms, and is weaker than phen or 2,2'-bpy. In this paper terbium and 2-fluorobenzoic acid (2-HFBA) have been used to synthesize a new complex $[\text{Tb}(\text{2-FBA})_3 \cdot (\text{2-HFBA}) \cdot$

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$\text{H}_2\text{O}]_2$ (**1**). When 4,4'-bpy, 2,2'-bpy, or phen was added to the complexes, new mixed-ligand terbium complexes with interesting structures were obtained, namely $\{[\text{Tb}(\text{2-FBA})_3 \cdot (4,4'\text{-bpy}) \cdot \text{H}_2\text{O}]_3\}_n$ (**2**), $[\text{Tb}(\text{2-FBA})_3 \cdot (2,2'\text{-bpy})]_2$ (**3**), and $[\text{Tb}(\text{2-FBA})_3 \cdot \text{phen} \cdot \text{CH}_3\text{CH}_2\text{OH}]_2 \cdot [\text{Tb}(\text{2-FBA})_3 \cdot \text{phen}]_2$ (**4**). Crystal analysis showed that complex **1** is a dimeric molecule, whereas complex **2** is a polymer in which 4,4'-bpy coordinates to Tb^{3+} ion and the 2-FBA groups coordinate to the Tb^{3+} ion in only one bidentate-bridging mode. The structure of complex **3** contains three independent binuclear molecules, and the structure of complex **4** contains two nonequivalent binuclear molecules. These structural features are rare in lanthanide carboxylate complexes. Complexes **1**, **3**, and **4** emit intense green fluorescence.

Results and Discussion

Structural Description of $[\text{Tb}(\text{2-FBA})_3 \cdot (2\text{-HFBA}) \cdot \text{H}_2\text{O}]_2$ (**1**)

The structure of complex **1** is shown in Figure 1 (part a), which shows that the Tb^{3+} ion is coordinated by seven oxygen atoms from 2-FBA groups, one oxygen atom from one 2-HFBA ligand, and one oxygen atom from water, giving a coordination number of nine. The two Tb^{3+} ions are linked together by four bridging carboxylato groups to form a centrosymmetric dimeric unit, which is rare for lanthanide carboxylate complexes. The majority of known lanthanide complexes containing a monoacid display a one-dimensional polymer chain, such as in $[\text{Tb}(\text{3-CH}_3\text{C}_6\text{H}_4\text{COO})_3]_n$,^[5] $[\text{Nd}(\text{2-CH}_3\text{OC}_6\text{H}_4\text{COO})_3 \cdot 4\text{H}_2\text{O}]_n$,^[6] and $[\text{Eu}(\text{2,3-DMOBA})_3]_n$.^[8] The distance between two Tb^{3+} ions is 3.951(3) Å (Table 1). All the 2-FBA groups are coordinated to the Tb^{3+} ion and can be classified into three different coordination modes: the carboxylato groups O5–C15–O6 are in a chelating mode, in which two O atoms coordinate to the same Tb^{3+} ion, the carboxylato groups O1–C1–O2 are in a bridging mode, in which two O atoms coordinate to two different Tb^{3+} ions to form a bidentate bridge, and the carboxylato groups O3–C8–O4 are in a chelating-bridging mode, in which two O atoms chelate one Tb^{3+} ion and one of them also simultaneously links to another Tb^{3+} ion, forming a tridentate bridge. The 2-HFBA ligand binds in a monodentate mode through a single oxygen atom to the Tb^{3+} ion. It is not common to observe a monodentate carboxylic acid ligand coordinated to a lanthanide center. The Tb–O bonds have an average length of 2.436 Å and the O–Tb–O bond angles lie in the range 50.2(2)–148.7(3)°. There is a bonding water molecule (O9) at a distance of 2.410(7) Å to the Tb^{3+} ion, which takes part in hydrogen bonds with the coordinated oxygen of carboxylato groups and the fluorine atoms in the benzene ring $[\text{O9} \cdots \text{H9A} \cdots \text{O5} \text{ } (-x+1, -y, -z+2) \text{ with } d(\text{O9} \cdots \text{O5}) = 2.754 \text{ Å and } \angle \text{O9-H9A-O5} = 166.16^\circ; \text{O9-H9B} \cdots \text{F2} \text{ } (-x+1, -y, -z+2) \text{ with } d(\text{O9} \cdots \text{F2}) = 3.047 \text{ Å and } \angle \text{O9-H9B-F2} = 153.38^\circ]$ to form a one-

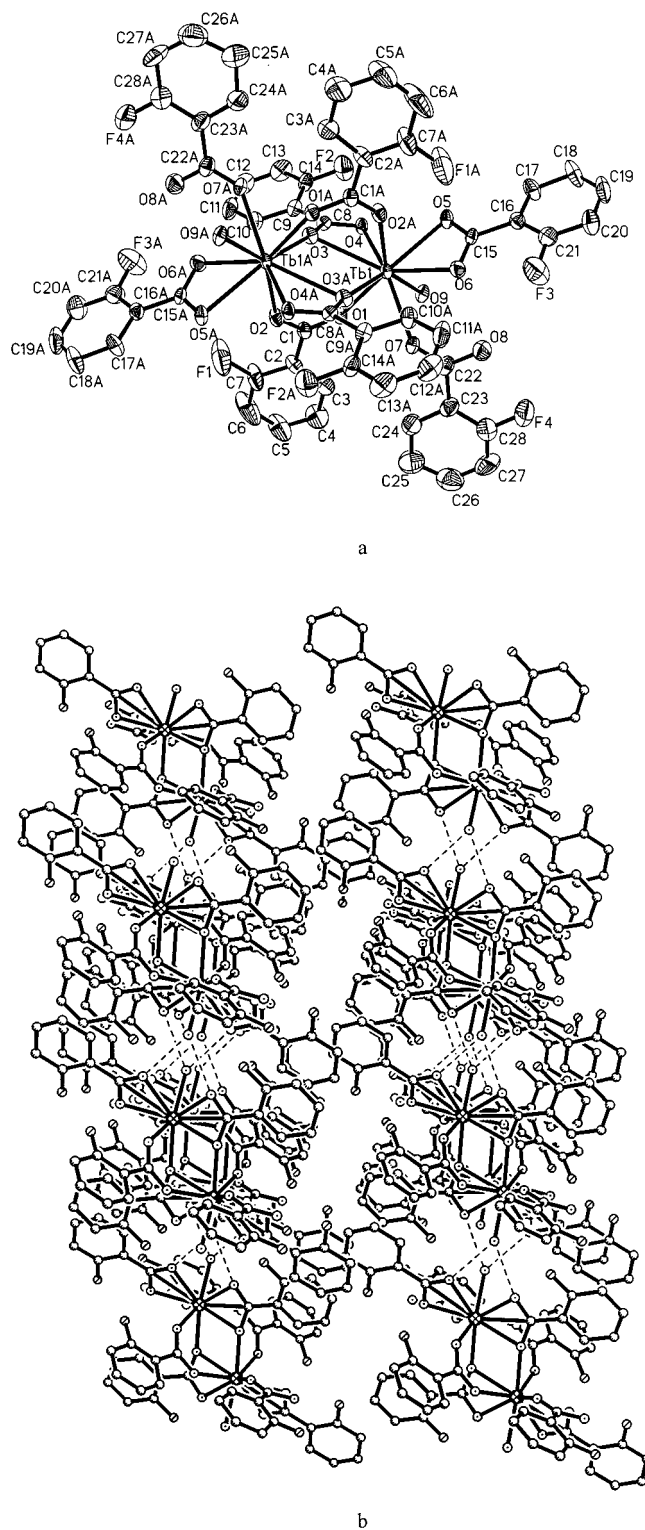


Figure 1. Molecular structure of complex **1** (a) and the packing diagram viewed along the *b*-axis (b). All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

dimensional supramolecular chain (Figure 1, part b). This case is different from the three complexes with a one-dimensional polymeric structure mentioned above.

Table 1. Bond lengths [Å] and angles [°] for complex 1.

Tb(1)–O(3)#1 ^[a]	2.316(8)	Tb(1)–O(1)	2.329(8)
Tb(1)–O(2)#1	2.333(8)	Tb(1)–O(6)	2.409(8)
Tb(1)–O(9)	2.410(7)	Tb(1)–O(4)	2.426(8)
Tb(1)–O(7)	2.462(9)	Tb(1)–O(5)	2.546(8)
Tb(1)–O(3)	2.668(8)		
O(3)#1–Tb(1)–O(1)	78.1(3)	O(3)#1–Tb(1)–O(2)#1	73.6(3)
O(1)–Tb(1)–O(2)#1	135.3(3)	O(3)#1–Tb(1)–O(6)	100.3(3)
O(1)–Tb(1)–O(6)	142.0(3)	O(2)#1–Tb(1)–O(6)	77.6(3)
O(3)#1–Tb(1)–O(9)	141.5(3)	O(1)–Tb(1)–O(9)	74.6(3)
O(2)#1–Tb(1)–O(9)	143.9(3)	O(6)–Tb(1)–O(9)	85.6(3)
O(3)#1–Tb(1)–O(4)	125.5(3)	O(1)–Tb(1)–O(4)	79.5(3)
O(2)#1–Tb(1)–O(4)	89.5(3)	O(6)–Tb(1)–O(4)	126.6(3)
O(9)–Tb(1)–O(4)	75.3(3)	O(3)#1–Tb(1)–O(7)	73.9(3)
O(1)–Tb(1)–O(7)	73.7(3)	O(2)#1–Tb(1)–O(7)	128.0(3)
O(6)–Tb(1)–O(7)	69.6(3)	O(9)–Tb(1)–O(7)	72.7(3)
O(4)–Tb(1)–O(7)	142.5(3)	O(3)#1–Tb(1)–O(5)	139.9(3)
O(1)–Tb(1)–O(5)	141.9(3)	O(2)#1–Tb(1)–O(5)	72.4(3)
O(6)–Tb(1)–O(5)	52.0(3)	O(9)–Tb(1)–O(5)	72.1(3)
O(4)–Tb(1)–O(5)	74.7(3)	O(7)–Tb(1)–O(5)	112.4(3)
O(3)#1–Tb(1)–O(3)	75.3(3)	O(1)–Tb(1)–O(3)	68.4(3)
O(2)#1–Tb(1)–O(3)	71.4(3)	O(6)–Tb(1)–O(3)	148.7(3)
O(9)–Tb(1)–O(3)	117.5(3)	O(4)–Tb(1)–O(3)	50.2(2)
O(7)–Tb(1)–O(3)	134.9(3)	O(5)–Tb(1)–O(3)	112.3(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y, -z + 2$.

Structural Description of $\{[\text{Tb}(\text{2-FBA})_3 \cdot (4,4'\text{-bpy}) \cdot \text{H}_2\text{O}]_3\}_n$ (2)

The structure of complex 2 is shown in Figure 2 (part a), which shows that each terbium ion is connected by six oxygen atoms from six 2-FBA groups, one oxygen atom from water, and one nitrogen atom from a 4,4'-bpy molecule. The 2-FBA groups coordinate the terbium ion in only a bidentate-bridging mode. Complexes in which carboxylato groups coordinate a metal in only one coordination mode, such as $[\text{Nd}(\text{3-CH}_3\text{C}_6\text{H}_4\text{CO}_2)_3]^{[5]}$ and $[\text{Eu}(\text{4-CH}_3\text{C}_6\text{H}_4\text{COO})_3]^{[7]}$ in which the carboxylato groups adopt only one bridging-chelating mode, are not common. Two adjacent Tb^{3+} ions are connected by four bridging O1–C1–O2 and O3–C8–O4 groups to form a dimeric unit. These dimeric units are linked by two simple bridging carboxylato groups (O5–C15–O6) to form a one-dimensional polymer chain along the [1,0,0] direction. The distances between two adjacent Tb^{3+} ions in the polymer chain are 4.269 Å (Tb1...Tb1A) within the dimeric unit and 5.637 Å between the dimeric units (Table 2). The Tb1A...Tb1...Tb1B angle is 159.1°, and the Tb–O_{carboxyl} distances range from 2.470(4) Å to 2.513(4) Å, with a mean value of 2.492 Å. The O–Tb–O bond angles are in the range 71.70(14)–143.71(14)°, and the Tb–O_{water} bond length is 2.566(4) Å. The 4,4'-bpy ligand coordinates to Tb^{3+} ion through one N atom. There is a bonding nitrogen atom (N1) of 4,4'-bpy at a distance of 2.851(5) Å to the Tb^{3+} ions. The two pyridyl rings are not coplanar, and have a dihedral angle of 146.0°. The uncoordinated N atom of 4,4'-bpy forms a hydrogen bond with coordinated water [O7–H7A...N2B, with $d(\text{O7} \cdots \text{N2B}) = 2.857$ Å and $\angle \text{O7-H7A-N2B} = 170.0^\circ$]. Adjacent 1D chains are interlinked by these hydrogen bonds to form a two-dimensional supramolecular network structure along the [1,0,1] direction (Figure 2, part b). Complex 2 is

different from the complex $[\text{Tb}_2(\text{O}_2\text{CPh})_6(4,4'\text{-bpy})]_n^{[1]}$ in which 4,4'-bpy bridges two different metals with two N atoms. Complex 2 is also different from the complexes $\{[\text{Eu}(m\text{-MOBA})_3 \cdot 2\text{H}_2\text{O}]/2(4,4'\text{-bpy})\}_\infty$ ($m\text{-MOBA} = m\text{-methoxybenzoate}$)^[13] and $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3 \cdot (4,4'\text{-Hbpy})\}_\infty$ ($\alpha\text{-FURA} = \alpha\text{-furoate}$)^[14] in which the 4,4'-bpy molecule does not coordinate to the metal. Lanthanide carboxylate complexes containing coordinated 4,4'-bpy are less common due to the weak coordination of 4,4'-bpy in this kind of complex.

Table 2. Bond lengths [Å] and angles [°] for complex 2.

Tb(1)–O(6)#1 ^[a]	2.470(4)	Tb(1)–O(3)	2.476(4)
Tb(1)–O(5)	2.487(4)	Tb(1)–O(1)	2.504(4)
Tb(1)–O(2)#2	2.504(4)	Tb(1)–O(4)#2	2.513(4)
Tb(1)–O(7)	2.566(4)	Tb(1)–N(1)	2.851(5)
O(6)#1–Tb(1)–O(3)	99.78(15)	O(6)#1–Tb(1)–O(5)	83.05(14)
O(3)–Tb(1)–O(5)	143.71(14)	O(6)#1–Tb(1)–O(1)	142.84(14)
O(3)–Tb(1)–O(1)	75.50(15)	O(5)–Tb(1)–O(1)	80.72(14)
O(6)#1–Tb(1)–O(2)#2	78.13(14)	O(3)–Tb(1)–O(2)#2	71.70(14)
O(5)–Tb(1)–O(2)#2	142.85(14)	O(1)–Tb(1)–O(2)#2	131.55(14)
O(6)#1–Tb(1)–O(4)#2	133.69(15)	O(3)–Tb(1)–O(4)#2	122.08(14)
O(5)–Tb(1)–O(4)#2	74.71(15)	O(1)–Tb(1)–O(4)#2	72.77(16)
O(2)#2–Tb(1)–O(4)#2	95.84(16)	O(6)#1–Tb(1)–O(7)	71.31(15)
O(3)–Tb(1)–O(7)	72.88(14)	O(5)–Tb(1)–O(7)	73.95(15)
O(1)–Tb(1)–O(7)	72.15(15)	O(2)#2–Tb(1)–O(7)	127.62(16)
O(4)#2–Tb(1)–O(7)	135.85(17)	O(6)#1–Tb(1)–N(1)	68.34(15)
O(3)–Tb(1)–N(1)	142.93(15)	O(5)–Tb(1)–N(1)	71.85(15)
O(1)–Tb(1)–N(1)	135.20(15)	O(2)#2–Tb(1)–N(1)	71.50(15)
O(4)#2–Tb(1)–N(1)	66.29(15)	O(7)–Tb(1)–N(1)	129.25(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x, -y + 1, -z + 1$.

Structural Description of $[\text{Tb}(\text{2-FBA})_3 \cdot (2,2'\text{-bpy})]_2$ (3)

The structure of complex 3 is shown in Figure 3 (a, b and c). It is dimeric and, interestingly, there are three independent molecules in the asymmetric unit, in which each molecular unit is dimeric with an inversion center. Each Tb^{3+} ion is coordinated by nine atoms, seven oxygen atoms from five 2-FBA groups and two nitrogen atoms of one 2,2'-bpy ligand (Figure 3, part a). They adopt a distorted monocapped square-antiprism arrangement, with atoms O3, O5, O4A, and O6A forming the upper and O1, O2, N1, and N2 the lower square-planes with a dihedral angle between them of 4.4°; atom O4 caps the upper plane. The 2-FBA ligands act in chelating, bridging, and chelating-bridging modes. Two Tb1 ions are held together by four 2-FBA groups, with two of them in a bidentate bridging mode, and the other two in a chelating-bridging mode. In addition, each terbium ion is also chelated by one 2-FBA group and one 2,2'-bpy ligand. The Tb1...Tb1A distance is 4.137 Å (Table 3). The Tb1–O bond lengths range from 2.28(8) to 2.91(9) Å, with an average length of 2.459 Å. It is reasonable that the Tb1–O4 distance, 2.91 Å, of the tridentate bridging carboxylato group is the largest due to O3–C18–O4–Tb1 being an unstable four-membered ring. This feature has been observed in other lanthanide carboxylate complexes. The O–Tb1–O angles vary considerably in the range 53.00(3)–150.00(3)°, but they are not uncommon

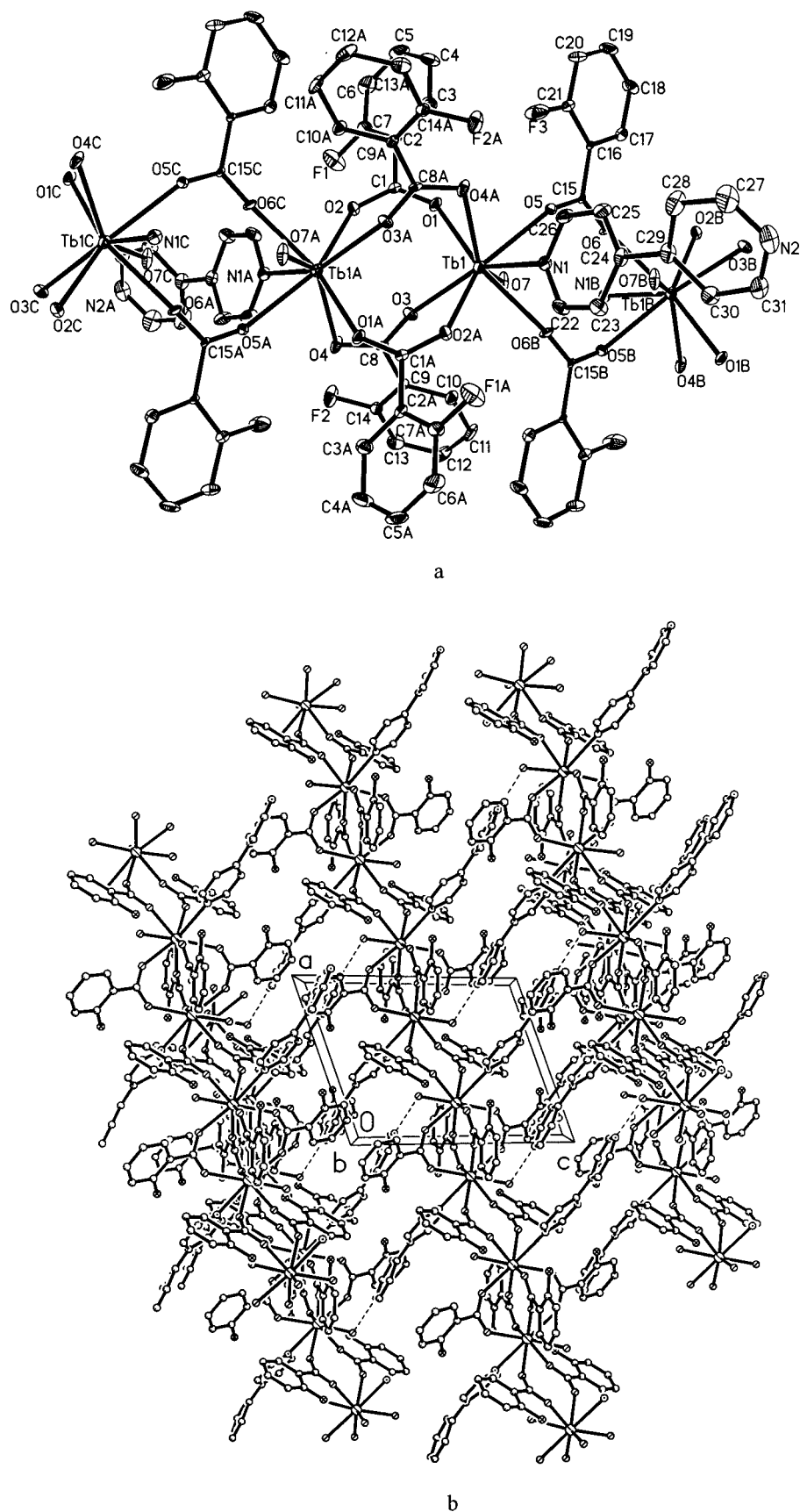


Figure 2. Molecular structure of complex **2** (a) and the packing diagram (b). All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

for lanthanide carboxylate complexes. The 2,2'-bpy ligand coordinates to the Tb^{3+} ion in a conventional chelation mode with two N atoms, forming a five-membered ring. The two pyridyl rings of the 2,2'-bpy ligand are not coplanar and form a dihedral angle of 12.2° in the dimer. The Tb1–N bond lengths are similar, with an average value of $2.56 \text{ \AA}$, and the N–Tb1–N bond angle is $62(3)^\circ$.

Each Tb^{3+} ion is eight-coordinate, with six oxygen atoms from five 2-FBA groups and two nitrogen atoms from one chelating 2,2'-bpy ligand (Figure 3, part b). The two terbiums in the dimer are held together by four 2-FBA groups, all with a bidentate-bridging coordination mode, and each terbium ion is further bonded to one chelating 2-FBA group and one 2,2'-bpy molecule. Thus, each terbium ion has a distorted square-antiprism coordination geometry with O7, O8, N3, and N4 forming one square face and O9, O11, O10A, and O12A the other. The dihedral angle between the two faces is 4.6° . The 2-FBA ligands coordinate

the terbium ion in chelating and bidentate-bridging coordination modes. Obviously, the structures given in Figure 3 (part b) and Figure 3 (part a) are different with respect to the different linking modes of the four 2-FBA groups to the two terbium ions. The Tb2...Tb2A distance is $4.260 \text{ \AA}$. The Tb2–O distances vary in the range $2.35(7)$ to $2.48(8) \text{ \AA}$, with an average value of $2.372 \text{ \AA}$, and the O–Tb2–O angles range from $53.00(3)$ to $149.00(3)^\circ$. The average Tb2–N distance is $2.53 \text{ \AA}$ and the N–Tb2–N angle is $62(4)^\circ$. The dihedral angle between the two pyridyl rings of the 2,2'-bpy molecule is 6.0° .

As shown in Figure 3 (part c), the Tb^{3+} ion is coordinated by nine atoms, seven oxygen atoms from five 2-FBA groups and two nitrogen atoms of one 2,2'-bpy ligand. The coordination polyhedron of the Tb^{3+} ion is a distorted monocapped square-antiprism, which is quite similar to that of the Tb^{3+} ion in Figure 3 (part a) but differs from that of the Tb2 ion in Figure 3 (part b). The distance be-

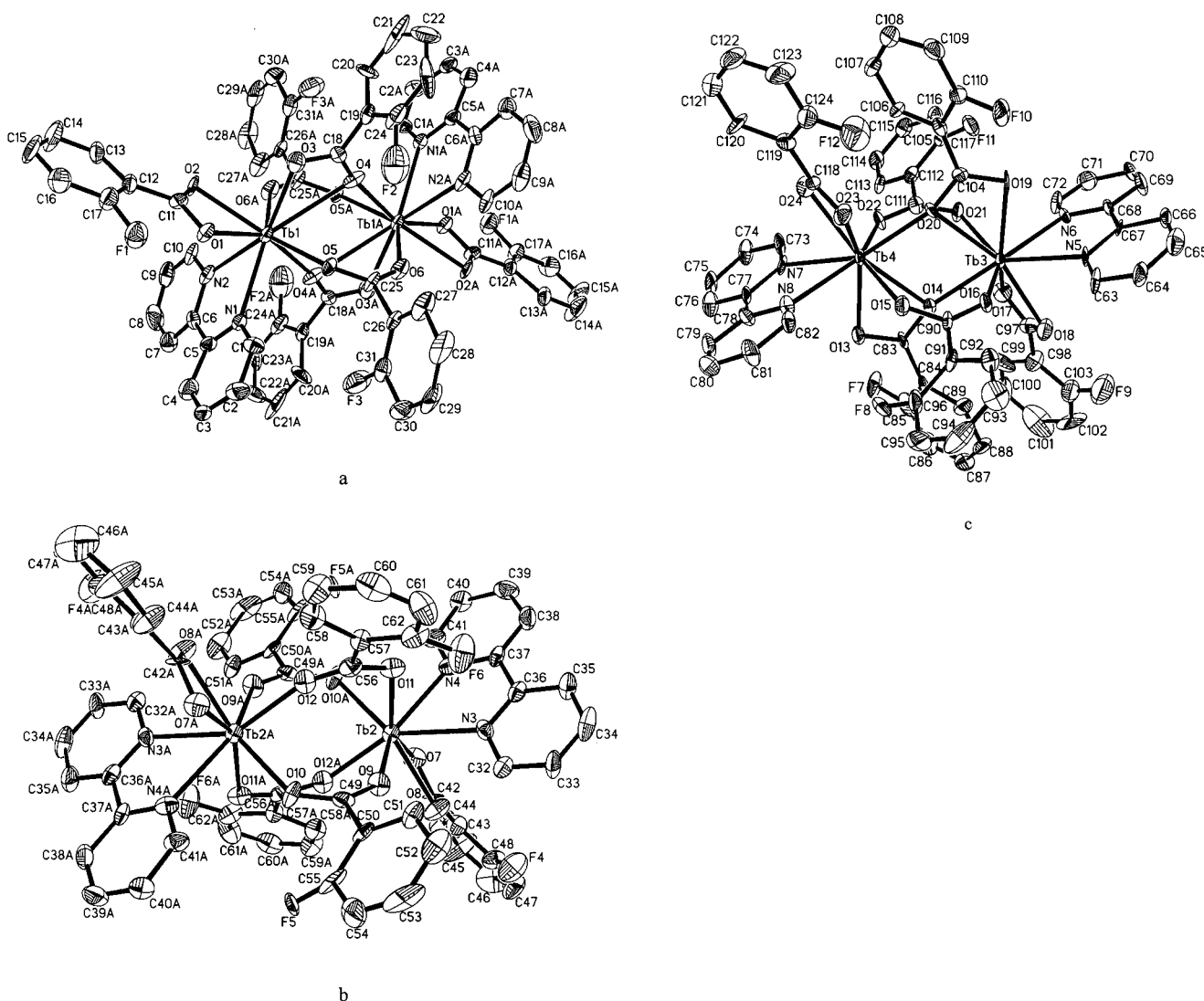


Figure 3. Molecular structures of the complex 3. (a), (b), and (c) show three different structures. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

Table 3. Bond lengths [Å] and angles [°] for complex 3.

Tb(1)–O(4)#1 ^[a]	2.28(8)	Tb(1)–O(6)#1	2.36(8)
Tb(1)–O(5)	2.37(7)	Tb(1)–O(3)	2.41(9)
Tb(1)–O(1)	2.42(7)	Tb(1)–O(2)	2.46(7)
Tb(1)–N(2)	2.55(11)	Tb(1)–N(1)	2.58(9)
Tb(1)–O(4)	2.91(9)	Tb(2)–O(12)#2	2.27(9)
Tb(2)–O(10)#2	2.32(8)	Tb(2)–O(9)	2.35(8)
Tb(2)–O(11)	2.37(8)	Tb(2)–O(8)	2.44(8)
Tb(2)–O(7)	2.48(7)	Tb(2)–N(4)	2.52(11)
Tb(2)–N(3)	2.54(10)	Tb(3)–O(21)	2.35(7)
Tb(3)–O(16)	2.36(7)	Tb(3)–O(14)	2.37(7)
Tb(3)–O(18)	2.44(9)	Tb(3)–O(17)	2.45(8)
Tb(3)–O(19)	2.48(8)	Tb(3)–N(6)	2.56(8)
Tb(3)–N(5)	2.57(8)	Tb(3)–O(20)	2.60(8)
Tb(4)–O(22)	2.34(7)	Tb(4)–O(15)	2.35(8)
Tb(4)–O(20)	2.37(7)	Tb(4)–O(23)	2.43(8)
Tb(4)–O(24)	2.44(8)	Tb(4)–O(13)	2.48(8)
Tb(4)–N(8)	2.56(9)	Tb(4)–N(7)	2.58(8)
Tb(4)–O(14)	2.58(7)		
O(4)#1–Tb(1)–O(6)#1	76(3)	O(4)#1–Tb(1)–O(5)	75(3)
O(6)#1–Tb(1)–O(5)	131(3)	O(4)#1–Tb(1)–O(3)	121(3)
O(6)#1–Tb(1)–O(3)	85(3)	O(5)–Tb(1)–O(3)	77(3)
O(4)#1–Tb(1)–O(1)	150(3)	O(6)#1–Tb(1)–O(1)	129(3)
O(5)–Tb(1)–O(1)	93(3)	O(3)–Tb(1)–O(1)	82(3)
O(4)#1–Tb(1)–O(2)	144(3)	O(6)#1–Tb(1)–O(2)	77(3)
O(5)–Tb(1)–O(2)	140(3)	O(3)–Tb(1)–O(2)	79(3)
O(1)–Tb(1)–O(2)	53(3)	O(4)#1–Tb(1)–N(2)	79(3)
O(6)#1–Tb(1)–N(2)	78(3)	O(5)–Tb(1)–N(2)	132(3)
O(3)–Tb(1)–N(2)	150(3)	O(1)–Tb(1)–N(2)	90(3)
O(2)–Tb(1)–N(2)	74(3)	O(4)#1–Tb(1)–N(1)	81(3)
O(6)#1–Tb(1)–N(1)	137(3)	O(5)–Tb(1)–N(1)	74(3)
O(3)–Tb(1)–N(1)	138(3)	O(1)–Tb(1)–N(1)	70(3)
O(2)–Tb(1)–N(1)	105(3)	N(2)–Tb(1)–N(1)	62(3)
O(4)#1–Tb(1)–O(4)	75(3)	O(6)#1–Tb(1)–O(4)	68(3)
O(5)–Tb(1)–O(4)	68(2)	O(3)–Tb(1)–O(4)	46(2)
O(1)–Tb(1)–O(4)	126(3)	O(2)–Tb(1)–O(4)	114(2)
N(2)–Tb(1)–O(4)	141(3)	N(1)–Tb(1)–O(4)	139(3)
O(12)#2–Tb(2)–O(10)#2	76(3)	O(12)#2–Tb(2)–O(9)	78(3)
O(10)#2–Tb(2)–O(9)	127(3)	O(12)#2–Tb(2)–O(11)	125(3)
O(10)#2–Tb(2)–O(11)	82(3)	O(9)–Tb(2)–O(11)	76(3)
O(12)#2–Tb(2)–O(8)	82(3)	O(10)#2–Tb(2)–O(8)	138(3)
O(9)–Tb(2)–O(8)	81(3)	O(11)–Tb(2)–O(8)	139(3)
O(12)#2–Tb(2)–O(7)	81(3)	O(10)#2–Tb(2)–O(7)	88(3)
O(9)–Tb(2)–O(7)	132(3)	O(11)–Tb(2)–O(7)	149(3)
O(8)–Tb(2)–O(7)	53(3)	O(12)#2–Tb(2)–N(4)	144(3)
O(10)#2–Tb(2)–N(4)	79(3)	O(9)–Tb(2)–N(4)	138(3)
O(11)–Tb(2)–N(4)	75(3)	O(8)–Tb(2)–N(4)	101(3)
O(7)–Tb(2)–N(4)	74(3)	O(12)#2–Tb(2)–N(3)	147(3)
O(10)#2–Tb(2)–N(3)	136(3)	O(9)–Tb(2)–N(3)	80(3)
O(11)–Tb(2)–N(3)	72(3)	O(8)–Tb(2)–N(3)	71(3)
O(7)–Tb(2)–N(3)	97(3)	N(4)–Tb(2)–N(3)	62(4)
O(21)–Tb(3)–O(16)	137(3)	O(21)–Tb(3)–O(14)	80(3)
O(16)–Tb(3)–O(14)	72(2)	O(21)–Tb(3)–O(18)	124(3)
O(16)–Tb(3)–O(18)	88(3)	O(14)–Tb(3)–O(18)	88(3)
O(21)–Tb(3)–O(17)	71(3)	O(16)–Tb(3)–O(17)	128(3)
O(14)–Tb(3)–O(17)	74(3)	O(18)–Tb(3)–O(17)	53(3)
O(21)–Tb(3)–O(19)	80(3)	O(16)–Tb(3)–O(19)	90(3)
O(14)–Tb(3)–O(19)	125(2)	O(18)–Tb(3)–O(19)	144(3)
O(17)–Tb(3)–O(19)	142(3)	O(21)–Tb(3)–N(6)	78(3)
O(16)–Tb(3)–N(6)	140(3)	O(14)–Tb(3)–N(6)	145(3)
O(18)–Tb(3)–N(6)	83(3)	O(17)–Tb(3)–N(6)	74(3)
O(19)–Tb(3)–N(6)	76(3)	O(21)–Tb(3)–N(5)	136(3)
O(16)–Tb(3)–N(5)	77(3)	O(14)–Tb(3)–N(5)	145(3)
O(18)–Tb(3)–N(5)	73(3)	O(17)–Tb(3)–N(5)	114(3)
O(19)–Tb(3)–N(5)	71(3)	N(6)–Tb(3)–N(5)	63(3)
O(21)–Tb(3)–O(20)	66(3)	O(16)–Tb(3)–O(20)	74(3)
O(14)–Tb(3)–O(20)	74(2)	O(18)–Tb(3)–O(20)	158(3)
O(17)–Tb(3)–O(20)	130(3)	O(19)–Tb(3)–O(20)	51(2)
N(6)–Tb(3)–O(20)	119(3)	N(5)–Tb(3)–O(20)	114(3)
O(22)–Tb(4)–O(15)	137(3)	O(22)–Tb(4)–O(20)	74(3)
O(15)–Tb(4)–O(20)	76(3)	O(22)–Tb(4)–O(23)	126(3)
O(15)–Tb(4)–O(23)	74(3)	O(20)–Tb(4)–O(23)	74(3)
O(22)–Tb(4)–O(24)	85(3)	O(15)–Tb(4)–O(24)	128(3)
O(20)–Tb(4)–O(24)	92(3)	O(23)–Tb(4)–O(24)	54(3)
O(22)–Tb(4)–O(13)	90(3)	O(15)–Tb(4)–O(13)	81(3)
O(20)–Tb(4)–O(13)	125(3)	O(23)–Tb(4)–O(13)	144(3)
O(24)–Tb(4)–O(13)	139(3)	O(22)–Tb(4)–N(8)	141(3)
O(15)–Tb(4)–N(8)	78(3)	O(20)–Tb(4)–N(8)	143(3)
O(23)–Tb(4)–N(8)	74(3)	O(24)–Tb(4)–N(8)	84(3)
O(13)–Tb(4)–N(8)	75(3)	O(22)–Tb(4)–N(7)	78(3)
O(15)–Tb(4)–N(7)	136(3)	O(20)–Tb(4)–N(7)	147(3)
O(23)–Tb(4)–N(7)	110(3)	O(24)–Tb(4)–N(7)	68(3)
O(13)–Tb(4)–N(7)	70(3)	N(8)–Tb(4)–N(7)	63(3)
O(22)–Tb(4)–O(14)	74(3)	O(15)–Tb(4)–O(14)	67(3)
O(20)–Tb(4)–O(14)	75(3)	O(23)–Tb(4)–O(14)	135(3)
O(24)–Tb(4)–O(14)	158(3)	O(13)–Tb(4)–O(14)	51(2)
N(8)–Tb(4)–O(14)	117(3)	N(7)–Tb(4)–O(14)	113(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z$; #2 $-x + 1, -y + 1, -z + 1$.

tween the two central terbium ions (Tb3...Tb4) is 3.951 Å. The average Tb3–O and Tb3–N bond lengths are 2.436 Å and 2.56 Å, respectively. The O–Tb3–O angles range from 53.00(3) to 144.00(3)°; the N–Tb3–N angle is 63(3)°. The two pyridyl rings of 2,2'-bpy in the dimer are not coplanar, and have a dihedral angle of 10.1°.

The structure of complex 3 contains three independent centrosymmetric units [Figure 3, parts a–c]. Figure 3 (part b) is different from Figure 3 (part a) or Figure 3 (part c) owing to the different bonding mode of the carboxyl groups, similar to the previously reported complex [Eu₂(*p*-CH₃C₆H₄COO)(phen)₂], which contains two nonequivalent binuclear molecules.^[9] The mean Tb1–O distance (2.459 Å) in Figure 3 (part a) is longer than that of Tb2–O (2.372 Å) in Figure 3 (part b), and the distance between the central metal ions Tb1...Tb1A (4.137 Å) in Figure 3 (part a) is shorter than that of Tb2...Tb2A (4.260 Å) in Figure 3 (part b). A similar feature in the following discussion for complex 4 can be found due to the different bonding mode of the carboxyl groups. The Tb1–O mean distance in Figure 3 (part a) is close to that of Tb3–O (2.436 Å) in Figure 3 (part c), and the distance between the central metal ions Tb1...Tb1A in Figure 3 (part a) is close to that of Tb3...Tb4 (3.951 Å) in Figure 3 (part c) due to the similar coordination environments of Tb1³⁺ and Tb3³⁺. The corresponding O–Tb–O bond angles for the three molecules are in agreement with each other. For coordinated 2,2'-bpy, the two pyridyl rings are not coplanar in the complex, although the Tb–N bond lengths and the N–Tb–N bond angles for the three molecules are in good agreement.

Structural Description of a phen-Containing Terbium 2-Fluorobenzoate Complex with Two Different Compositions, [Tb(2-FBA)₃·phen·CH₃CH₂OH]₂ and [Tb(2-FBA)₃·phen]₂ (4)

The structure of complex 4 is shown in Figure 4 (parts a and b). Obviously, the structure of complex 4 contains two nonequivalent binuclear molecules, namely [Tb(2-FBA)₃·phen·CH₃CH₂OH]₂ (Figure 4, part a) and [Tb(2-FBA)₃·phen]₂ (Figure 4, part b); both dimers are centrosymmetric.

Figure 4 (part a) shows that four 2-FBA groups function as a bridge and connect two terbium ions to form a dimeric molecule with a Tb1...Tb1A separation of 4.423 Å. Each Tb1³⁺ ion is further bonded to a monodentate 2-FBA group, one chelated phen, and one ethanol molecule to give a coordination number of eight. The Tb1³⁺ ion is in a distorted square-antiprism arrangement in which the dihedral angle between the top (atoms O1, O5, O2A, O6A) and bottom (atoms O3, O7, N1, N2) planes is 3.0°. The 2-FBA groups link the Tb1³⁺ ion in monodentate and bidentate-bridging coordination modes. The Tb1–O(carboxyl) distances are in the range 2.30(4) to 2.43(4) Å, with an average distance of 2.348 Å, and the O–Tb1–O(carboxyl) angles range from 72.90(13) to 144.9(13)° (Table 4). The bond length for the oxygen atom of the ethanol molecule to the terbium ion is 2.575 Å. The coordinated ethanol molecules

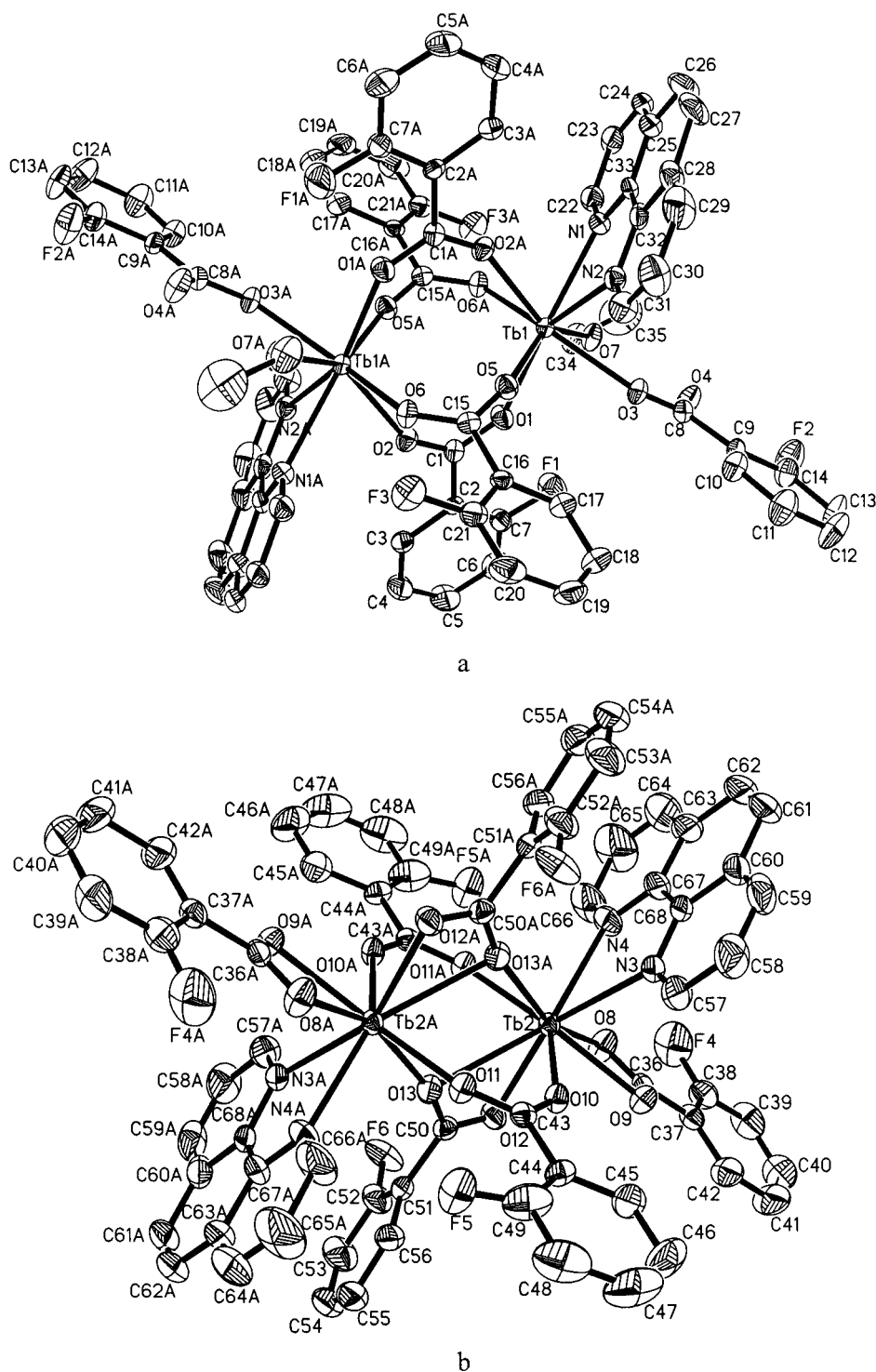


Figure 4. Molecular structures of complex 4. (a) and (b) show two different structures. All hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level.

form hydrogen bonds with uncoordinated carboxyl oxygen atoms ($O7-H7\cdots O4$, with an $O7\cdots O4$ distance of 2.578 Å and $O7-H7\cdots O4$ angle of 136.18°). The phen ligand acts as a typical chelating ligand coordinating to the terbium ion, with an average $Tb1-N$ distance of 2.43 Å and $N-Tb1-N$ angle of 63.7(16)°.

Figure 4 (part b) shows that the $Tb2^{3+}$ ion is surrounded by nine atoms, seven oxygen atoms from five 2-FBA groups and two nitrogen atoms from one phen molecule. The $Tb2^{3+}$ ion is in a distorted monocapped square-antiprism configuration. Atoms $O10$, $O12$, $O11A$, and $O13A$ and $O8$, $O9$, $N3$, and $N4$ form the upper and lower square-planes,

Table 4. Bond lengths [Å] and angles [°] for complex 4.

Tb(1)–O(5)	2.30(4)	Tb(1)–O(1)	2.34(4)
Tb(1)–O(6)#1 ^[a]	2.36(4)	Tb(1)–O(2)#1	2.37(4)
Tb(1)–O(3)	2.37(4)	Tb(1)–O(7)	2.43(4)
Tb(1)–N(1)	2.55(5)	Tb(1)–N(2)	2.60(5)
Tb(2)–O(13)#2	2.30(4)	Tb(2)–O(10)	2.34(4)
Tb(2)–O(11)#2	2.36(4)	Tb(2)–O(9)	2.42(4)
Tb(2)–O(12)	2.44(4)	Tb(2)–O(8)	2.50(4)
Tb(2)–N(4)	2.55(5)	Tb(2)–N(3)	2.65(5)
Tb(2)–O(13)	2.71(4)		
O(5)–Tb(1)–O(1)	74.5(14)	O(5)–Tb(1)–O(6)#1	121.5(13)
O(1)–Tb(1)–O(6)#1	80.2(14)	O(5)–Tb(1)–O(2)#1	78.3(13)
O(1)–Tb(1)–O(2)#1	122.9(14)	O(6)#1–Tb(1)–O(2)#1	72.9(13)
O(5)–Tb(1)–O(3)	83.6(13)	O(1)–Tb(1)–O(3)	84.3(14)
O(6)#1–Tb(1)–O(3)	144.9(13)	O(2)#1–Tb(1)–O(3)	140.6(13)
O(5)–Tb(1)–O(7)	143.4(14)	O(1)–Tb(1)–O(7)	75.3(14)
O(6)#1–Tb(1)–O(7)	72.5(13)	O(2)#1–Tb(1)–O(7)	136.6(13)
O(3)–Tb(1)–O(7)	73.2(13)	O(5)–Tb(1)–N(1)	138.6(15)
O(1)–Tb(1)–N(1)	146.9(15)	O(6)#1–Tb(1)–N(1)	79.0(15)
O(2)#1–Tb(1)–N(1)	74.4(14)	O(3)–Tb(1)–N(1)	98.4(14)
O(7)–Tb(1)–N(1)	73.9(15)	O(5)–Tb(1)–N(2)	78.2(15)
O(1)–Tb(1)–N(2)	145.2(15)	O(6)#1–Tb(1)–N(2)	133.3(15)
O(2)#1–Tb(1)–N(2)	70.7(14)	O(3)–Tb(1)–N(2)	71.5(14)
O(7)–Tb(1)–N(2)	118.6(14)	N(1)–Tb(1)–N(2)	63.7(16)
O(13)#2–Tb(2)–O(10)	77.7(14)	O(13)#2–Tb(2)–O(11)#2	74.3(14)
O(10)–Tb(2)–O(11)#2	135.2(13)	O(13)#2–Tb(2)–O(9)	143.5(14)
O(10)–Tb(2)–O(9)	75.0(13)	O(11)#2–Tb(2)–O(9)	141.9(13)
O(13)#2–Tb(2)–O(12)	123.9(14)	O(10)–Tb(2)–O(12)	87.5(15)
O(11)#2–Tb(2)–O(12)	80.2(15)	O(9)–Tb(2)–O(12)	78.7(14)
O(13)#2–Tb(2)–O(8)	155.7(16)	O(10)–Tb(2)–O(8)	125.3(15)
O(11)#2–Tb(2)–O(8)	90.5(14)	O(9)–Tb(2)–O(8)	52.5(14)
O(12)–Tb(2)–O(8)	70.1(15)	O(13)#2–Tb(2)–N(4)	90.0(18)
O(10)–Tb(2)–N(4)	138.1(18)	O(11)#2–Tb(2)–N(4)	76.2(17)
O(9)–Tb(2)–N(4)	94.4(17)	O(12)–Tb(2)–N(4)	130.9(19)
O(8)–Tb(2)–N(4)	67.7(19)	O(13)#2–Tb(2)–N(3)	72.9(15)
O(10)–Tb(2)–N(3)	75.7(16)	O(11)#2–Tb(2)–N(3)	126.2(16)
O(9)–Tb(2)–N(3)	77.2(15)	O(12)–Tb(2)–N(3)	153.5(16)
O(8)–Tb(2)–N(3)	103.1(16)	N(4)–Tb(2)–N(3)	62(2)
O(13)#2–Tb(2)–O(13)	74.7(14)	O(10)–Tb(2)–O(13)	66.3(13)
O(11)#2–Tb(2)–O(13)	73.0(13)	O(9)–Tb(2)–O(13)	114.5(13)
O(12)–Tb(2)–O(13)	50.0(13)	O(8)–Tb(2)–O(13)	119.4(14)
N(4)–Tb(2)–O(13)	148.3(17)	N(3)–Tb(2)–O(13)	134.1(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 2, -z$; #2 $-x + 1, -y, -z + 1$.

respectively, with a dihedral angle between them of 8.2°; atom O13 caps the upper plane. The 2-FBA ligands act in chelating, bidentate-bridging, and chelating-bridging modes. Two terbium ions are connected by four 2-FBA groups – two bidentate-bridging and two chelating-bridging – to give a Tb2...Tb2A distance of 3.985 Å. In addition, each terbium ion is chelated by one 2-FBA group and one phen ligand. Obviously, Figure 4 (part b) is unlike Figure 4 (part a) but quite similar to Figure 3 (part a) and Figure 3 (part c). The Tb2–O bond lengths range from 2.30(4) to 2.71(4) Å, with an average distance of 2.439 Å, and the O–Tb2–O angles range from 52.5(14) to 155.7(16)°. The phen molecule chelates the terbium ion with an average Tb2–N bond length of 2.60 Å and N–Tb2–N angle of 62(2)°.

However, there are very few cases where two molecules with two different compositions and structures exist in an asymmetric unit. By comparing Figure 4 (part b) with Figure 4 (part a), their formulas, the coordination environment

of central ion and coordination mode of carboxylato groups are different. The differences result in different distances of Tb–O(carboxyl) and Tb...Tb. The mean Tb2–O(carboxyl) distance of 2.439 Å in Figure 4 (part b) is longer than that of Tb1–O(carboxyl) (2.348 Å) in Figure 4 (part a), and the distance between the central metal ions (Tb2...Tb2A) (3.985 Å) in Figure 4 (part b) is shorter than that between Tb1 and Tb1A (4.423 Å) in Figure 4 (part a). A similar feature was observed in complex 3. The fact that Ln³⁺ ions are bridged by chelating-bridging carboxylato groups results in a larger Ln–O distance and a smaller Ln–Ln distance.

Figure 3 (parts a, b and c) and Figure 4 (part b) exhibit common structures of lanthanide carboxylate complexes with 2,2'-bpy or phen, in which the carboxylate groups coordinate to lanthanide in different modes, such as monodentate, chelating-bidentate, bidentate-bridging, and tridentate-bridging. Generally, ternary lanthanide complexes containing a monoacid and 2,2'-bpy or phen are centrosymmetric dimers with a coordination number at the metal of eight or nine. The structure of eight-coordinate complexes is the same as that in Figure 3b, where two metal ions are linked together by four carboxylato groups with a bidentate-bridging coordination mode, and each metal ion is also chelated by one carboxylato group and one 2,2'-bpy or phen molecule, such as in [Sm₂(4-CH₃C₆H₄COO)₆(2,2'-bpy)₂]^[10] [Eu(*m*-CH₃C₆H₄COO)₃(phen)](H₂O)^[11] and [Eu₂(3,4-DMBA)₆(phen)₂]^[12]. The structure of nine-coordinate complexes is the same as those in Figure 3 (parts a and c) and Figure 4 (part b), where two metal ions are linked together by four carboxylato groups with bidentate-bridging and chelating-bridging modes, and each metal ion is also chelated by one carboxylato group and one 2,2'-bpy or phen ligand, such as in [Eu(2,3-DMOBA)₃·bpy]₂ (2,3-DMOBA = 2,3-dimethoxybenzoate)^[15] [Ln₂(O₂CCH₃)₆(phen)₂] (Ln = Ce, Gd)^[16] and [La₂(propionato)₆(2,2'-bpy)₂]^[17]. Eight- or nine-coordinate complexes are formed depending on the different bridges over the two central metal ions of the four carboxyl groups, namely whether the four carboxylato groups are all in a bidentate-bridging mode or two of them are in a bidentate-bridging mode and the other two in a chelating-bridging mode. The phen or 2,2'-bpy molecule coordinates to the metal in conventional chelation through two N atoms to form a five-membered ring. However, although the two phenyl rings are coplanar in the phen complexes since this molecule is rigid, the two pyridyl rings are not coplanar in 2,2'-bpy complexes since this is a flexible ligand.

Fluorescence Spectra

The complexes 1, 3, and 4 emit a bright-green light in the solid state under UV light. Fluorescence was observed in the range of 400–700 nm by selective excitation at 353 nm, as shown in Figure 5 (parts a, b, and c). There are four main emission peaks in the luminescence spectra at

488, 543, 584, and 618 nm, corresponding to the transition between the first excited state (5D_4) and the ground-state multiplet ($^7F_{6-3}$) of the Tb^{3+} ion, namely $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$, respectively. The most intense emission band is at 543 nm. The luminescence spectra of complexes **1** and **3** are similar to that of complex **4**. The splits observed in the emission bands correspond to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$. Shoulder peaks at 486 nm, 542 and 548 nm were observed. The nonluminescence of complex **2** may be due to 4,4'-bpy coordinating in a monodentate manner, which means that the ligand-to-metal energy transfer processes are not effective.

Conclusion

The complexes discussed above were constructed based on terbium and 2-fluorobenzoic acid, with 4,4'-bpy, 2,2'-bpy, or phen acting as co-ligands to generate terbium complexes with various structures. Complex **1** is a dimeric molecule, unlike the majority of known lanthanide complexes containing a monoacid, which are one-dimensional polymers. Complex **2** is one of the very few lanthanide complexes containing a coordinated 4,4'-bpy molecule, complex **3** contains three independent binuclear molecules, and complex **4** contains two different binuclear molecules. Several other structural features of these complexes are of particular importance. In particular, complexes **1**, **3**, and **4** exhibit good fluorescence properties.

Experimental Section

Fluorescence Spectroscopy: Fluorescence spectra were measured on an F-4500 FL spectrophotometer in the solid state at room temperature.

[Tb(2-FBA)₃·(2-HFBA)·H₂O]₂ (1): 2-Fluorobenzoic acid (1.5 mmol) was dissolved in the appropriate amount of ethanol. The pH of the solution was controlled in the range 6–7 by addition of 2 M NaOH solution. An ethanolic solution of TbCl₃·6H₂O (0.5 mmol) was then added dropwise. The mixture was heated under reflux with stirring for 3 h. Single crystals were obtained from the mother liquor after a month at room temperature. Yield: 0.0969 g (26.39%). C₅₆H₃₈F₈O₁₈Tb₂ (1468.7): calcd. C 45.80, H 2.61; found C 45.39, H 3.00.

[Tb(2-FBA)₃·(4,4'-bpy)·H₂O]_n (2): 2-Fluorobenzoic acid (1.5 mmol) was dissolved in the appropriate amount of ethanol. The pH of the solution was controlled in the range 6–7 by addition of 2 M NaOH solution. An ethanolic solution of 4,4'-bipyridine (0.5 mmol) and an ethanolic solution of TbCl₃·6H₂O (0.5 mmol) were then added dropwise, successively. The mixture was heated under reflux with stirring for 2 h. Single crystals were obtained from the mother liquor after seven weeks at room temperature. Yield: 0.1200 g (31.98%). C₆₂H₄₄F₆N₄O₁₄Tb₂ (1500.9): calcd. C 49.62, H 2.96, N 3.73; found C 51.18, H 3.06, N 4.32.

[Tb(2-FBA)₃·(2,2'-bpy)]₂ (3): When 2,2'-bpy was used instead of 4,4'-bpy, complex **3** was obtained. Yield: 0.1959 g (53.50%). C₁₂₄H₈₀F₁₂N₈O₂₄Tb₄ (2929.64): calcd. C 50.84, H 2.75, N 3.82; found C 50.82, H 3.06, N 3.80.

[Tb(2-FBA)₃·phen]₂ and [Tb(2-FBA)₃·phen·CH₃CH₂OH]₂ (4): When phen was used instead of 4,4'-bpy, complex **4** was obtained. Yield: 0.1983 g (50.89%). C₁₃₆H₉₂F₁₂N₈O₂₆Tb₄ (3117.9): calcd. C 52.39, H 2.97, N 3.59; found C 52.75, H 2.69, N 3.61.

X-ray Crystallographic Study: X-ray crystal data collection for the complexes was performed on a Bruker Smart 1000 CCD diffractometer with monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K (Table 5). Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out with SHELXS-97 and SHELXL-97.^[18,19] The structures were solved by direct methods and refined on $|F|^2$ by full-matrix least-squares methods.

CCDC-250512, -250511, -250513, and -250514 (for **1–4**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

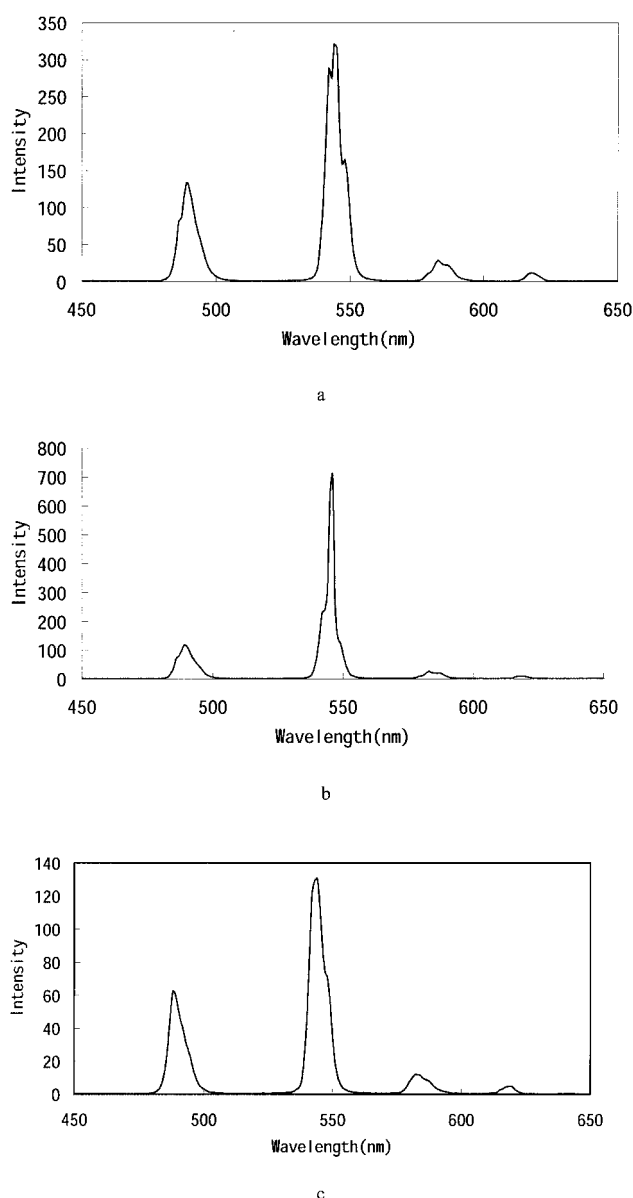


Figure 5. The fluorescence spectra of complexes **1** (a; $\lambda_{exc} = 353$ nm), **3** (b; $\lambda_{exc} = 353$ nm), and **4** (c; $\lambda_{exc} = 353$ nm).

Table 5. Crystal data and structure refinement for complexes 1–4.

Compound	1	2	3	4
Empirical formula	C ₅₆ H ₃₈ F ₈ O ₁₈ Tb ₂	C ₆₂ H ₄₄ F ₆ N ₄ O ₁₄ Tb ₂	C ₁₂₄ H ₈₀ F ₁₂ N ₈ O ₂₄ Tb ₄	C ₁₃₆ H ₉₂ F ₁₂ N ₈ O ₂₆ Tb ₄
Formula mass	1468.70	1500.85	2929.64	3117.86
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit-cell dimensions	1	2	1	2
<i>a</i> [Å]	9.100(7)	9.745(3)	11.281(4)	11.261(3)
<i>b</i> [Å]	11.548(9)	12.770(4)	21.845(7)	12.627(4)
<i>c</i> [Å]	13.600(11)	13.312(4)	22.213(7)	22.746(7)
α [°]	110.625(12)	113.134(4)	93.142(6)	81.154(5)
β [°]	92.949(13)	104.747(5)	90.885(6)	78.244(5)
γ [°]	91.065(13)	97.008(5)	91.585(6)	80.697(5)
Volume [Å ³]	1334.8(18)	1426.6(8)	5463(3)	3100.3(16)
<i>Z</i>	1	1	2	1
<i>d</i> _{calcd.} [g cm ^{−3}]	1.827	1.747	1.781	1.670
<i>T</i> [K]	293(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm ^{−1}]	2.732	2.550	2.659	2.350
<i>F</i> (000)	720	740	2880	1540
Limiting indices	−7 ≤ <i>h</i> ≤ 10 −13 ≤ <i>k</i> ≤ 13 −15 ≤ <i>l</i> ≤ 16	−7 ≤ <i>h</i> ≤ 11 −14 ≤ <i>k</i> ≤ 15 −15 ≤ <i>l</i> ≤ 15	−12 ≤ <i>h</i> ≤ 13 −25 ≤ <i>k</i> ≤ 25 −20 ≤ <i>l</i> ≤ 26	−7 ≤ <i>h</i> ≤ 13 −14 ≤ <i>k</i> ≤ 15 −25 ≤ <i>l</i> ≤ 27
Reflections collected/unique	6908/4692 <i>R</i> (int.) = 0.0547	7414/4992 <i>R</i> (int.) = 0.0191	28575/19190 <i>R</i> (int.) = 0.173	16241/10893 <i>R</i> (int.) = 0.0283
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0688 <i>wR</i> ₂ = 0.1678	<i>R</i> ₁ = 0.0377 <i>wR</i> ₂ = 0.1123	<i>R</i> ₁ = 0.0790 <i>wR</i> ₂ = 0.1671	<i>R</i> ₁ = 0.0382 <i>wR</i> ₂ = 0.0778
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0980 <i>wR</i> ₂ = 0.1919	<i>R</i> ₁ = 0.0455 <i>wR</i> ₂ = 0.1223	<i>R</i> ₁ = 0.1686 <i>wR</i> ₂ = 0.2039	<i>R</i> ₁ = 0.0685 <i>wR</i> ₂ = 0.0982
Largest diff. peak and hole [e Å ^{−3}]	2.576 and −2.742	0.939 and −0.736	2.692 and −3.145	0.833 and −0.649

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- [1] C. Seward, N. X. Hu, S. Wang, *J. Chem. Soc., Dalton Trans.* **2001**, 134–137.
- [2] T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1999**, *121*, 1651–1657.
- [3] L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067.
- [4] Y. Wang, X. J. Zheng, W. J. Zhuang, L. P. Jin, *Eur. J. Inorg. Chem.* **2003**, 3572–3582.
- [5] J. F. Ma, Z. S. Jin, J. Z. Ni, *Acta Chim. Sinica* **1993**, *51*, 265–272.
- [6] T. N. Polynova, B. B. Smolyar, T. F. Filippova, M. A. Porai-Koshits, S. B. Pirkes, *Koord. Khim.* **1987**, *13*, 130–135.
- [7] Q. H. Jin, X. Li, Y. Q. Zou, *Acta Crystallogr., Sect. C* **2001**, *57*, 676–677.
- [8] X. Li, Y. Q. Zou, B. Zheng, H. M. Hu, *Acta Crystallogr., Sect. C* **2004**, *60*, m197–m199.
- [9] L. P. Jin, M. Z. Wang, G. L. Cai, *Sci. China, Ser. B* **1994**, *24*, 577–583.
- [10] X. Li, Y. Q. Zou, Z. Kristallogr. **2003**, *218*, 448–450.
- [11] L. P. Jin, R. F. Wang, M. Z. Wang, G. L. Cai, S. X. Liu, J. L. Huang, *Chem. J. Chin. Univ.* **1993**, *14*, 1195–1200.
- [12] L. Y. Wang, X. J. Zheng, L. P. Jin, S. Z. Lu, *Chem. J. Chin. Univ.* **1999**, *20*, 1110–1114.
- [13] X. Li, X. Zheng, L. Jin, S. Lu, W. Qin, *J. Mol. Struct.* **2000**, *519*, 85–91.
- [14] X. Li, X. Zheng, L. Jin, S. Lu, J. Zhang, *J. Mol. Struct.* **2001**, *559*, 341–346.
- [15] X. Li, L. P. Jin, X. J. Zheng, S. Z. Lu, J. H. Zhang, *J. Mol. Struct.* **2002**, *607*, 59–67.
- [16] A. Panagiotopoulos, T. F. Zafiroopoulos, S. P. Perlepes, E. Bakalbassis, I. Masson-Ramade, O. Kahn, A. Terzis, C. P. Raptopoulou, *Inorg. Chem.* **1995**, *34*, 4918–4920.
- [17] J. S. Brodtkin, B. M. Foxman, W. Clegg, J. T. Cressey, D. R. Harbron, P. A. Hunt, B. P. Straughan, *Chem. Mater.* **1996**, *8*, 242–247.
- [18] *Phase Annealing in SHELX-90: Direct Methods for Larger Structures*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
- [19] G. M. Sheldrick, *SHELXL97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

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