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The novel one-dimensional chain of europium(III) complex $[Eu_2(BTA)_6(4,4'\text{-bpdo})]_n$ containing dimers bridged by terminal oxygen atoms of 4,4′-bpdo molecules

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Abstract

A new europium ternary complex $[Eu_2(BTA)_6(4,4'\text{-bpdo})]_n$ (HBTA = benzoyltrifluoroacetone, 4,4′-bpdo = 4,4′-bipyridine dioxide) is prepared. Crystal analysis shows that it possesses infinite one-dimensional linear chains containing binuclear coordination moieties $Eu_2(BTA)_6(4,4'\text{-bpdo})$ in which two Eu(III) ions were bridged by two terminal oxygen atoms from two different 4,4′-bpdo molecules. There are two crystallographically distinct $Eu_2(BTA)_6(4,4'\text{-bpdo})$ units, in which all Eu(III) ions are in the similar EuO_8 environments but with different symmetries and twisting angles between pyridine rings. The inter-chain π–π stacking interactions between neighboring phenyl rings in Eu2 chains extend the 1D coordination chains to construct a novel 2D supramolecular architecture, which further stabilizes this structure.

Keywords: Europium(III) complex; Benzoyltrifluoroacetone; 4,4′-Bipyridine dioxide; Crystal structure; One-dimensional linear chain

1. Introduction

The construction of inorganic coordination networks and crystal engineering has developed rapidly in recent years. Crystal engineering assembled through bridging ligands such as 4,4′-bipyridine and its analogues containing two or more 4-pyridyl donor units has intensively been investigated and many promising structures were documented [1–4]. Based on the fact that lanthanide ions have a high affinity for hard oxygen-containing ligands, a few examples of poly-dimensional coordination networks of 4,4′-bpdo have been constructed by using the concept of crystal engineering [5–7]. Much work on the application of 4,4′-bpdo has revealed that it is an excellent candidate to construct different kinds of lanthanide metal coordination polymers, including infinite 1D chain, 2D layer, and 3D netlike compounds. Among these compounds, the low dimensional coordination polymers exhibit unique physical properties comparing to high dimensional compounds [8]. One-dimensional chain compounds are of attractive attention due to their ability to show novel magnetic, nonlinear optical and conductive properties [9,10]. For example, the 1D chain compounds might assist dipole alignment and conjugation to favor desirable non-linear optical and ferroelectric properties [11].

Ideal metal–ion complexes for the formation of 1D chains will possess only two binding sites such as β-diketone metal–ion complexes [12]. The introduction of the O-containing chelating ligand as β-diketone can ‘passivate’ metal centers thus taking up much of the coordination space of the lanthanide ions, which may inhibit the expansion of the polymeric framework. By this way, low dimensional polymers can be obtained. Whereas only a few 1D chain complexes of lanthanides with β-diketone and 4,4′-bpdo molecules have been reported. $[Eu(TTA)_3(4,4'\text{-bpdo})]\cdot CH_3OH$ (HTTA = thenoyltrifluoroacetone) [13] and $[La(TFA)_3(4,4'\text{-bpdo})]_n$ (HTFA = trifluoroacetylacetone) [14] both had infinite

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1D coordination chains. Recently, we prepared $\{[La_2(BTA)_6(4,4'\text{-bpdo})_{1.5}]\cdot 1.5H_2O\}_n$ (HBTA = benzoyltrifluoroacetone) [15], in which two La(III) ions were bridged by three terminal oxygen atoms from three different 4,4′-bpdo molecules forming the dimers and the latter then were linked by 4,4′-bpdo themselves to construct a 3D coordination network. The formation of the 3D framework may be due to the bigger radium of La(III) ion. Taking account of the smaller radium of Eu(III) ion, the 1D chain may be obtained, so we prepare the present complex of Eu(III) with BTA anions and 4,4′-bpdo, $[Eu_2(BTA)_6(4,4'\text{-bpdo})]_n$. To our surprise, the complex really exhibits the 1D linear chain structure also containing dimers bridged by terminal oxygen atoms of 4,4′-bpdo molecules.

2. Experimental

2.1. Reagents and physical measurements

4,4′-Bipyridine-dioxide was prepared according to the literature method [16]. Other chemicals were of analytical grade used without further purification. Elemental analyses of C, H and N were performed by an Elementar Vario EL elemental analyzer. The IR spectra were recorded on a NEXUS670 FTIR spectrometer using KBr pellets in the 400–4000 cm^{-1} region.

2.2. Synthesis of the complex

A solution of HBTA (0.324 g, 1.5 mmol) in 5 mL of MeOH was added to a solution of $EuCl_3\cdot 6H_2O$ (0.183 g, 0.5 mmol) in 5 mL MeOH with stirring. The reacting solution was adjusted to pH of 6.2 with dilute solution of NaOH. A solution of 4,4′-bpdo (0.0941 g, 0.5 mmol) in 5 mL of MeOH was added to the above reacting solution. Some white powder precipitated from the solution. The product was characterized to have a formula of $Eu_2(BTA)_6$ (4,4′-bpdo). The powder was recrystallized from $EtOH:CH_3CN:H_2O$ (8:4:1) solvent mixture giving colorless crystals over several days. Calc. for $C_{70}H_{44}Eu_2F_{18}N_2O_{14}$: C, 47.14; H, 2.469; N, 1.571. Found: C, 47.03; H, 2.311; N, 1.311.

2.3. X-ray crystallography

A crystal with dimensions $0.15\times0.10\times0.08$ mm^3 was selected for X-ray diffraction experiment. The measurements were performed on a Rigaku Raxis Rapid IP diffractometer at 293 K with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using program SHELXS 97 [17] and refined by full-matrix least-squares on F^2 using the SHELXL 97 program [18]. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and details of the structure refinements are listed in Table 1.

Table 1
Crystal data and structure refinements for the complex

Empirical formula	$C_{70}H_{44}Eu_2F_{18}N_2O_{14}$
Formula weight	1783.0
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	20.601(4)
b (Å)	12.201(2)
c (Å)	28.115(6)
β(deg)	90.08(3)
V (Å^3)	7067(2)
Z, calculated density (Mg/m^3)	8, 1.676
T (K)	293
Wavelength (Å)	0.71073
μ (mm^{-1})	1.871
Crystal size (mm)	$0.15\times0.10\times0.08$
θ range for data collection (deg)	1.67–23.26
Limiting indices	$-22\le h\le 22$, $-13\le k\le 13$, $-31\le l\le 31$
Reflections collected/unique	36931/10055 [R(int) = 0.0870]
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0672$, $wR_2 = 0.1526$

3. Results and discussion

3.1. Description of the structure

Single crystal analysis confirms that the complex contains two crystallographically independent molecular units as shown in Fig. 1. The complex has the alternative 1D chains (Fig. 2) based on two different binuclear coordination moieties with the metal–metal distance of 4.267 and 4.244 Å for Eu1–Eu1A and Eu2–Eu2A, respectively. Each Eu(III) ion is in the EuO_8 environment with the approximate square antiprism geometry defined by six oxygen atoms from three bidentate BTA anions and other two provided by the terminal oxygen atoms of two different 4,4′-bpdo molecules. Though all Eu(III) ions are eight-coordinate, there exist the differences on the symmetries and the relevant Eu–O distances (Table 2) and twisting angles between pyridine rings. Eu1 and Eu1A ions are centrosymmetric while the Eu2–Eu2A binuclear moiety has a two-fold rotation axis passing through O8, N2, C38, C39, N3 and O15 centers. The Eu–O distances for β-dik (2.25–2.39 Å) are shorter than those for 4,4′-bpdo (2.46–2.52 Å). This may be attributed to the extensive conjugation in β-diketonate anions and their chelating effect. In Eu1 chain, two pyridine rings of the 4,4′-bpdo molecule are completely coplanar because of the symmetry, while in Eu2 chain, the 4,4′-bpdo molecule is more bent, with two pyridine rings twisted at an angle of 27.6° (Fig. 2).

It is apparent from Fig. 1 that in one binuclear moiety three β-diketonate anions coordinate to one Eu(III) ion on one side, and other three coordinate to another Eu(III) ion on the other side, thus leaving the space occupied by 4,4′-bpdo molecules. Two terminal oxygen atoms from two 4,4′-bpdo molecules bridge two Eu(III) ions forming the dimer, while the remaining two terminal oxygen atoms of 4,4′-bpdo link