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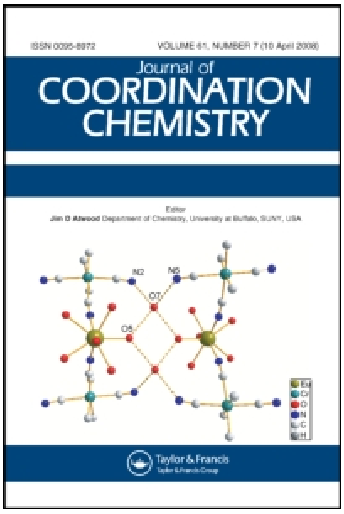

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Synthesis and structure of a three-dimensional lanthanide complex $[Tm_2(C_5H_3N(COO)_2)_3(H_2O)_3)]\cdot H_2O$

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SYNTHESIS AND STRUCTURE OF A THREE-DIMENSIONAL LANTHANIDE COMPLEX $[TM_2(C_5H_3N(COO)_2)_3(H_2O)_3)]\cdot H_2O$

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A new three-dimensional complex $[Tm_2(C_5H_3N(COO)_2)_3(H_2O)_3)]\cdot H_2O$ (PDC = 3,5-pyridinedicarboxylate), has been synthesized and its structure determined by x-ray single crystal diffraction methods. Complex **1** crystallizes in the monoclinic space group P2(1)/*n* with $a = 14.579(4)$, $b = 11.193(3)$, $c = 14.839(5)$ Å, $\beta = 94.009(6)^\circ$, $U = 2415.5(13)$ Å^3. Two independent PDC ligands bridge Tm^{III} ions from different orientations to form a network. Thermogravimetric analyses on compound **1** show its high structural stability to 410°C.

Keywords: Crystal structure; Thulium; Oxalates; TGA

INTRODUCTION

Due to their potential applications as promising materials in catalysis, separation, gas storage and molecular recognition, the design and synthesis of metal-organic complexes has received intense attention in recent years [1–3]. Despite the established role of lanthanide compounds in sensor technology, design of lanthanide compounds was rarely considered since f-elements have high and variable coordination number and a wide variety of coordination environments [4], these characteristics may lead to unusual molecular architectures [5,6]. Work on 1, 3-benzenedicarboxylate (BDC) was reported [7], so modification of BDC may allow preparation of more metal-organic analogues [8,9]. For the reason that affinity of oxygen of pyridine carboxylic groups to lanthanides is higher than nitrogen such that nitrogen would not coordinate with metal ions, but provide functionality in channel leading to interesting properties. 3, 5-pyridinedicarboxylate (PDC) was reacted with lanthanides through hydrothermal methods. In this paper, a new coordination polymer of $[Tm_2(C_5H_3N(COO)_2)_3(H_2O)_3)]\cdot H_2O$ **1** is reported.

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EXPERIMENTAL

Preparation of Compound 1

Aqueous NaOH was added to an aqueous solution of H_2PDC (3,5-pyridinedicarboxylic acid 0.50 g, 3.0 mmol) to adjust the pH value of the mixture to approximately 6, Aqueous solution of $Tm(ClO_4)_3 \cdot 6H_2O$ (0.84 g, 1.5 mmol) was added. The resulting mixture was placed into a Parr Teflon-lined autoclave. The autoclave was then sealed and heated at 140°C for two days. Colorless crystals of **1** suitable for x-ray crystallography were obtained with a yield of 35% according to the quality of thulium perchlorate added. Elemental analysis calcd. (%) $C_{21}H_{17}N_3O_{16}Tm_2$: C 27.83, H 1.91, N 4.57; found: C 27.86, H 1.89, N 4.64. IR (KBr, cm^{-1}): 3340(m), 2975(w), 1635(vs), 1580(vs), 1432(s), 1320(w), 916(w), 785(w), 730(w).

Caution: Perchlorate salts are potentially explosive and should only be handled in small quantities.

Physical Measurements

Elemental analyses of carbon, hydrogen and nitrogen were carried out with a *Perkin-Elmer* analyzer model *240*. The infrared spectroscopy on KBr pellets was performed on a *Magma IR 560* infrared spectrophotometer in the 4000–600 cm^{-1} region. Thermal gravimetric analyses (TGA) were carried out in N_2 with 10°C per minute heating in the temperature range of 25–700°C.

Crystallographic Studies

Determination of the unit cell and data collection was performed at room temperature on a BRUKER SMART 1000, using graphite-monochromated *Mo-Kα* radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined by least-squares procedures on Fo^2 with SHELXL-97 by minimizing the function $w(Fo^2 – Fc^2)^2$, where *Fo* and *Fc* are, respectively, the observed and calculated structure factors [10]. The hydrogen atoms of solvent molecules were not added, and the other hydrogen atoms were located geometrically and refined isotropically. Information concerning crystallographic data collection and refinement of the structure is compiled in Table I.

RESULTS AND DISCUSSION

The Structure of Complex 1

The projection of the structure of complex **1** is shown in Figure 1, and selected bonds and angles are listed in Table II. Complex **1** consists of the neutral dinuclear unit $[Tm_2(C_5H_3N(COO)_2)_3(H_2O)_3)]$ and one uncoordinated water. There are two independent Tm^{III} ions. As for Tm_1, it is coordinated with seven oxygen atoms from six PDC ligands in which one carboxylate group chelates with Tm_1 ion, and two waters. So the $Tm^{III}O_9$ part forms a nine-coordinate, square-face capped square antiprism

TABLE I Data collection and processing parameters for **1**

Empirical formula	$[Tm_2(C_5H_3N(COO)_2)_3(H_2O)_3)] \cdot H_2O$
Formula weight	905.24
Temperature	293(2) K
Crystal system	Monoclinic
Space group	P2(1)/*n*
Unit cell dimensions	$a = 14.579(4)$ Å $\alpha = 90°$ $b = 11.193(3)$ Å $\beta = 94.009(6)°$ $c = 14.839(5)$ Å $\gamma = 90°$
Volume	2415.5(13) $Å^3$
Z, Calculated density	4, 2.489 Mg/m^3
Absorption coefficient	7.391 mm^{-1}
F(000)	1720
Crystal size	$0.12 \times 0.06 \times 0.04$ mm
θ range for data collection	2.03 to 26.45°
Limiting indices	$-18 \leq h \leq 8$, $-12 \leq k \leq 14$, $-18 \leq l \leq 18$
Reflections collected	11005
Independent reflections	4867 [$R(\text{int}) = 0.0526$]
Data/restraints/parameters	4867/240/379
Goodness-of-fit on F^2	0.967
Final *R* indices [$I > 2\theta(I)$]	$R_1 = 0.0628$, $wR_2 = 0.0994$
R indices (all data)	$R_1 = 0.1170$, $wR_2 = 0.1150$
Largest diff. peak and hole	-1.465 to 1.327 $eÅ^{-3}$

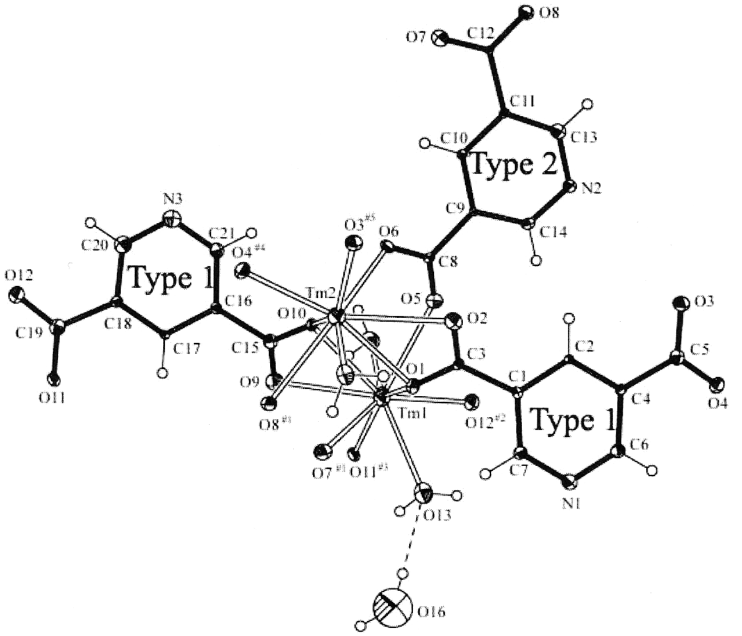

FIGURE 1 ORTEP drawing of the complex with 35 % probability ellipsoids, showing the atomic numbering scheme.

in which O_9, O_{13}, $O_7^{\#1}$, $O_{11}^{\#3}$ and O_1, O_{10}, O_{14}, $O_{12}^{\#2}$ form two approximate squares (Fig. 2(a)). The bond distances of Tm_1-O are from 2.340 to 2.646 Å and the mean distance is about 2.484 Å. Tm_2 ion is also coordinated with seven oxygen atoms from six PDC ligands but only one oxygen atom from water. The $Tm^{III}O_8$

TABLE II Selected bond lengths(Å) and angles (°) of **1**

Tm_1–O_1	2.446(8)	Tm_2–O_1	2.496(7)
Tm_1–O_5	2.641(7)	Tm_2–O_2	2.623(8)
Tm_1–O_9	2.646(8)	Tm_2–O_6	2.372(7)
Tm_1–O_{10}	2.543(7)	Tm_2–O_{10}	2.399(7)
Tm_1–O_{13}	2.540(8)	Tm_2–O_{15}	2.412(8)
Tm_1–O_{14}	2.439(8)	Tm_2–$O_8^{\#1}$	2.489(7)
Tm_1–$O_7^{\#1}$	2.340(8)	Tm_2–$O_4^{\#4}$	2.316(8)
Tm_1–$O_{12}^{\#2}$	2.364(8)	Tm_2–$O_5^{\#3}$	2.371(7)
Tm_1–$O_{11}^{\#3}$	2.395(7)	O_{16}–H···O_{13}	2.864
$O_7^{\#1}$–Tm_1–$O_{12}^{\#2}$	137.3(3)	O_1–Tm_1–O_9	116.6(3)
$O_7^{\#1}$–Tm_1–$O_{11}^{\#3}$	87.3(3)	O_{13}–Tm_1–O_9	122.4(2)
$O_{12}^{\#2}$–Tm_1–$O_{11}^{\#3}$	87.1(3)	O_{10}–Tm_1–O_9	50.2(2)
$O_7^{\#1}$–Tm_1–O_{14}	137.6(3)	O_5–Tm_1–O_9	112.0(2)
$O_{12}^{\#2}$–Tm_1–O_{14}	80.1(3)	$O_4^{\#4}$–Tm_2–$O_5^{\#3}$	78.6(3)
$O_{11}^{\#3}$–Tm_1–O_{14}	73.3(2)	$O_4^{\#4}$–Tm_2–O_6	99.9(3)
$O_7^{\#1}$–Tm_1–O_1	68.8(3)	$O_5^{\#3}$–Tm_2–O_6	82.8(3)
$O_{12}^{\#2}$–Tm_1–O_1	96.4(3)	$O_4^{\#4}$–Tm_2–O_{10}	83.0(3)
$O_{11}^{\#3}$–Tm_1–O_1	148.3(2)	$O_5^{\#3}$–Tm_2–O_{10}	143.1(2)
O_{14}–Tm_1–O_1	138.4(2)	O_6–Tm_2–O_{10}	69.1(2)
$O_7^{\#1}$–Tm_1–O_{13}	67.0(3)	$O_4^{\#4}$–Tm_2–O_{15}	104.5(3)
$O_{12}^{\#2}$–Tm_1–O_{13}	70.8(3)	$O_5^{\#3}$–Tm_2–O_{15}	73.3(3)
$O_{11}^{\#3}$–Tm_1–O_{13}	73.4(3)	O_6–Tm_2–O_{15}	141.3(3)
O_{14}–Tm_1–O_{13}	136.3(3)	O_{10}–Tm_2–O_{15}	142.9(2)
O_1–Tm_1–O_{13}	78.1(3)	$O_4^{\#4}$–Tm_2–$O_8^{\#1}$	79.2(3)
$O_7^{\#1}$–Tm_1–O_{10}	76.4(2)	$O_5^{\#3}$–Tm_2–$O_8^{\#1}$	134.5(3)
$O_{12}^{\#2}$–Tm_1–O_{10}	140.7(2)	O_6–Tm_2–$O_8^{\#1}$	140.2(3)
$O_{11}^{\#3}$–Tm_1–O_{10}	119.7(2)	O_{10}–Tm_2–$O_8^{\#1}$	71.3(2)
O_{14}–Tm_1–O_{10}	81.1(2)	O_{15}–Tm_2–$O_8^{\#1}$	74.6(3)
O_1–Tm_1–O_{10}	75.8(2)	$O_4^{\#4}$–Tm_2–O_1	156.8(3)
O_{13}–Tm_1–O_{10}	140.8(2)	$O_5^{\#3}$–Tm_2–O_1	124.5(3)
$O_7^{\#1}$–Tm_1–O_5	128.6(3)	O_6–Tm_2–O_1	85.0(2)
$O_{12}^{\#2}$–Tm_1–O_5	71.9(2)	O_{10}–Tm_2–O_1	77.6(2)
$O_{11}^{\#3}$–Tm_1–O_5	143.1(2)	O_{15}–Tm_2–O_1	84.2(3)
O_{14}–Tm_1–O_5	73.4(3)	$O_8^{\#1}$–Tm_2–O_1	82.6(2)
O_1–Tm_1–O_5	66.3(2)	$O_4^{\#4}$–Tm_2–O_2	152.2(3)
O_{13}–Tm_1–O_5	124.0(3)	$O_5^{\#3}$–Tm_2–O_2	74.4(3)
O_{10}–Tm_1–O_5	69.7(2)	O_6–Tm_2–O_2	70.3(3)
$O(7)^{\#1}$–Tm_1–O_9	68.6(3)	O_10–Tm_2–O_2	115.2(3)
$O_{12}^{\#2}$–Tm_1–O_9	145.8(3)	O_15–Tm_2–O_2	74.2(3)
$O_{11}^{\#3}$–Tm_1–O_9	9.7(2)	$O_8^{\#1}$–Tm_2–O_2	125.3(2)
O_{14}–Tm_1–O_9	69.4(3)	O_1–Tm_2–O_2	50.6(2)

Symmetry code: $^{\#1}x-1/2, -y+1/2, z-1/2$; $^{\#2}x, y+1, z$; $^{\#3}-x+1, -y, -z$; $^{\#4}x, y-1, z$; $^{\#5}-x+2, -y+1, -z$.

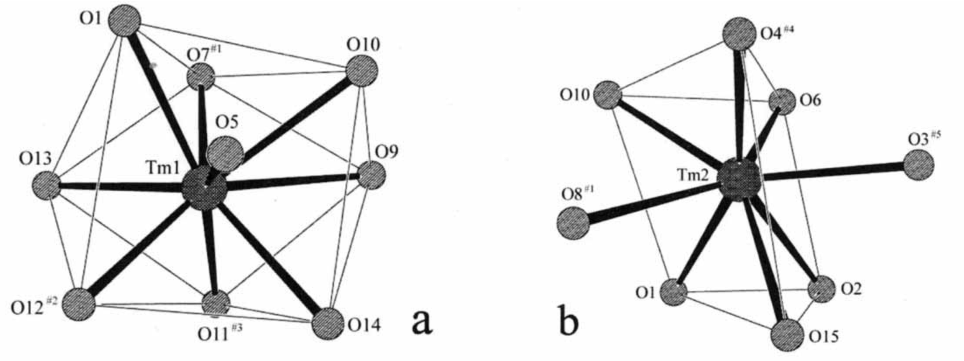

FIGURE 2 View of the coordination environment around thulium atoms: (a) around Tm_1, (b) around Tm_2.

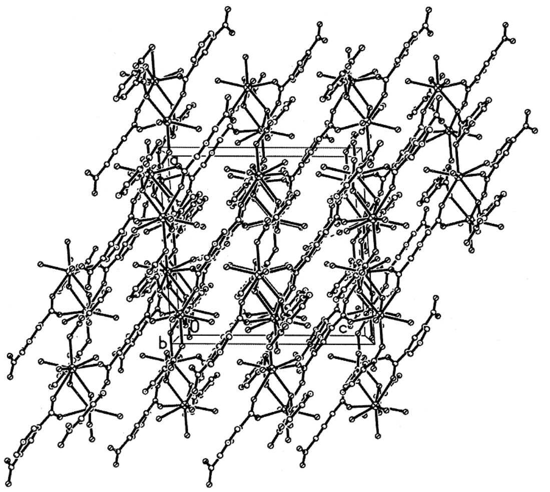

FIGURE 3 A packing view on the *ac* plane.

forms a eight-coordinate 4, 4′-bicapped trigonal prism in which O_1, O_2, O_{15} and O_6, O_{10}, $O_4^{\#4}$ form two triangles (Fig. 2(b)). The bond distances of Tm_2-O are from 2.316 to 2.623 Å and the mean distance is about 2.435 Å.

Two independent PDC ligands discovered in this three dimensional complex act as bridges from different orientations. One carboxylate group of the PDC ligand (Type 1) chelates with one metal ion and one oxygen atom coordinates with another metal (for example, O_1 and O_2 chelate with Tm_2 and O_1 coordinates with Tm_1 also); two oxygen atoms of another carboxylate group of the PDC ligand coordinate with two different metals (for example, O_3 coordinates with Tm_2 $(2-x, 1-x, 1-z)$, O_4 with Tm_2 $(x, 1+y, z)$). Each binuclear unit was bridged with other units by four PDC ligands (Type 1) to construct a 2-D layer parallel to the *ac* plane. On the other hand, the PDC ligand (Type 2) links adjacent layers to form a three dimension network. Two oxygen atoms of one carboxylate group (Type 2) coordinate two metal ions in one layer and two oxygen atoms of another carboxylate group to another layer (Fig. 3).

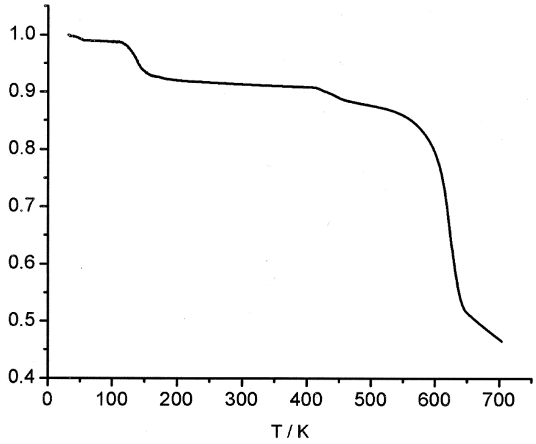

FIGURE 4 TGA curves for complex **1**.

There are three coordinated and one uncoordinated water molecules per Tm_2 unit of which two coordinate with Tm_1 ion and another with Tm_2 ion. Hydrogen bonds were formed between two water molecules.

In summary, the noticeable feature of the complex is the versatile coordination modes of the PDC groups and their strong bridging capability. In this complex, the PDC ligands display two kinds of coordination modes and serve as bridge ligands of different orientations. A second noticeable feature is that no nitrogen atoms of the ligands coordinate with lanthanide ions. This is not a surprise for their low affinity to lanthanide, but indicates a new approach in designing 3d-4f inorganic-organic materials.

Thermogravimetric Analyses

Thermal gravimetric analyses (TGA) were carried out in N_2 to examine the dehydration and stability (Fig. 4). For complex **1**, the first loss of 7.87% at 186°C corresponds to the loss of one uncoordinated and three coordinated waters per Ln_2 unit (cal. 7.96%). The following temperature platforms of these complexes from 180 to 410°C show their stablity. Above 410°C, the weight began to decrease slowly, which is thought to be the beginning of the decomposition of phenol ligands.

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