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Hydrothermal Synthesis and Crystal Structure of $[Tb(H_2O)_2(C_6NO_2H_4)_2Cl]_n$ with a Novel Three-Dimensional Motif

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A novel isonicotinic acid complex of terbium with the composition $[Tb(H_2O)_2(C_6NO_2H_4)_2Cl]_n$ (**1**), was obtained from a hydrothermal reaction and structurally characterized by a single-crystal X-ray diffraction. It is the first 3-D structure of terbium chloride with isonicotinic acid as a ligand. The terbuim complex is characteristic of a novel three-dimensional (3-D) motif with the terbium atoms locating at an environment of a square antiprism.

Key Words: Crystal, Hydrothermal, Isonicotinic, Terbium, X-ray.

INTRODUCTION

In recent years, lanthanide complexes have gained more and more attention because of their interesting properties and wide applications in many areas such as magnetic materials, catalysis and luminescent probes in biological systems, *etc.*[1-3]. Isonicotinic acid has also attracted increasing interest due to its common character-delocalized π-electrons of the pyridyl rings, which allows it to be a good candidate in producing light emitting complexes whose potential applications in various technical fields[4]. Moreover, isonicotinic acid is a useful building block in constructing an extended motif because it is an unsymmetrical divergent ligand. I deem that lanthanide complexes with an aromatic carboxylic acid (like isonicotinic acid or nicotinic acid) as a ligand might have novel structural topologies and physical properties, such as magnetism, luminescence, photochemistry and so on. Therefore, I recently became interested in the crystal engineering of lanthanide complexes with isonicotinic/nicotinic acid as a ligand. In this paper, the synthesis and crystal structure of $[Tb(H_2O)_2(C_6NO_2H_4)_2Cl]_n$ (**1**) are reported, which is the first 3-D structure of terbium chloride with isonicotinic acid as a ligand.

EXPERIMENTAL

Synthesis: The title complex was synthesized by mixing $TbCl_3 \cdot 6H_2O$ (1 mmol, 0.373 g), isonicotinic acid (2 mmol, 0.246 g) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 180 ºC for 10 days. After being slowly cooled to room temperature at 6 ºC/h, colourless crystals suitable for X-ray analysis were obtained. The yield was 43 %.

X-ray structure determination: X-ray single diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromatic MoK_α radiation (λ = 0.71073 Å) using a ω scanning technique. Crystal clear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTLTM Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yielded all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table-1. The selected bond lengths and bond angles are listed in Table-2.

RESULTS AND DISCUSSION

X-ray single diffraction analysis reveals that the structure of the title complex consists of $Tb(H_2O)_2(C_6NO_2H_4)_2Cl$ molecules (Fig. 1). The terbium ion is bound by two chlorine atoms and six oxygen atoms, among which two are from two coordinating water molecules and four from two isonicotinic acid ligands, yielding a distorted square anti-prism. The bond lengths of $Tb\text{-}O_{isonicotinic\ acid}$ range from 2.308(2) to 2.342(2) Å with an average value of 2.325(2) Å, which is obviously shorter than that of $Tb\text{-}O_{water}$ being of 2.417(2) Å, suggesting that isonicotinic acid ligand displays a stronger affinity to terbium

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC DATA AND STRUCTURE ANALYSIS FOR **1**

Empirical formula	$C_{12}H_{12}N_2O_6TbCl$
Formula weight	474.62
Crystal system	Orthorhombic
Space group	Pbcm
Unit cell dimensions	a = 9.793(3) Å; b = 9.995(3) Å c = 8.864(3) Å
Z	4
V	867.6(5) Å^3
D_c	3.633 Mg/m^3
Absorption coefficient	8.510 mm^{-1}
Crystal size	0.23 × 0.08 × 0.07 mm^3
No. of reflections collected/unique	5114/822 [$R_{(int)}$ = 0.0337]
Goodness-of-fit on F^2	1.005
Final R indices	R_1 = 0.0379, wR_2 = 0.1255
R indices (all data)	R_1 = 0.0390, wR_2 = 0.1276

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Bond lengths (Å)	
Tb(1A)-O(2)#1	2.308(2)
Tb(1A)-O(2)#2	2.308(2)
Tb(1A)-O(1)	2.342(2)
Tb(1A)-O(1)#3	2.342(2)
Tb(1A)-O(1W)#3	2.417(2)
Tb(1A)-O(1W)	2.417(2)
Tb(1A)-Cl(1)	2.4981(9)
Tb(1A)-Cl(1)#3	2.4981(9)
Bond angles (º)	
O(2)#1-Tb(1A)-O(2)#2	96.74(9)
O(2)#1-Tb(1A)-O(1)	146.72(7)
O(2)#2-Tb(1A)-O(1)	99.36(7)
O(1)-Tb(1A)-O(1)#3	82.53(9)
O(2)#1-Tb(1A)-O(1W)#3	70.17(6)
O(2)#2-Tb(1A)-O(1W)#3	77.81(6)
O(1)-Tb(1A)-O(1W)#3	141.86(6)
O(1)#3-Tb(1A)-O(1W)#3	80.57(7)

Symmetry code: #1 -x+1, y-1/2, z; #2 -x+1, -y, -z+1; #3 x, -y-1/2, -z+1

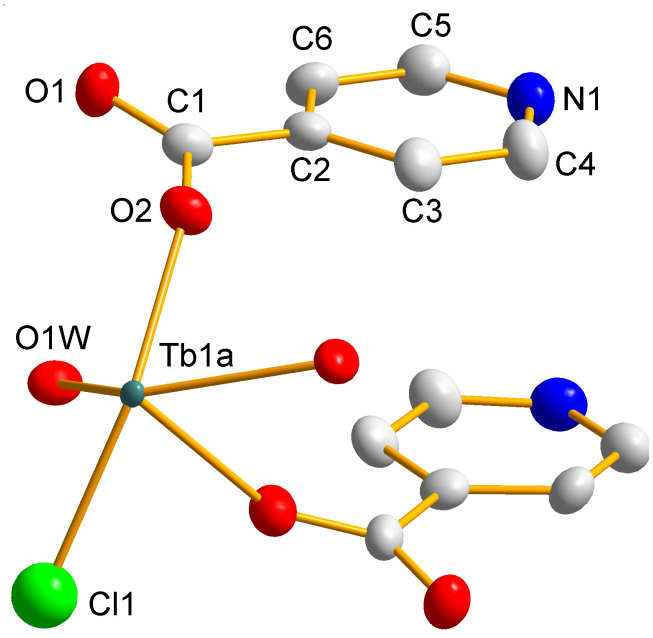

Fig. 1. Molecular structure of **1** with 50 % thermal ellipsoids. Hydrogen atoms and disordered Tb1b atom were omitted for clarity

ions than that of water. For the carboxyl group, the bond lengths of O(1)-C(1) and O(2)-C(1) are very close with the values being of 1.241(3) and 1.260(3) Å, respectively, suggesting the de-localization of COO^- group. The neighboring terbium ions are linked by one μ_2-chlorine atom to construct a 1-D infinite chain running along the *c*-axis, with the Tb···Tb distance being of *ca*. 4.432 Å, as shown in Fig. 2. The chains are further interconnected by the isonicotinic acid ligands to yield a 2-D layer parallel to bc plane (Fig. 3). These layers stack along the a-axis, forming a 3-D framework, as shown in Fig. 4. In complex **1**, there is no π···π stacking interactions between the adjacent isonicotinic acid ligands.

Fig. 2. 1-D chain-like structure of **1**

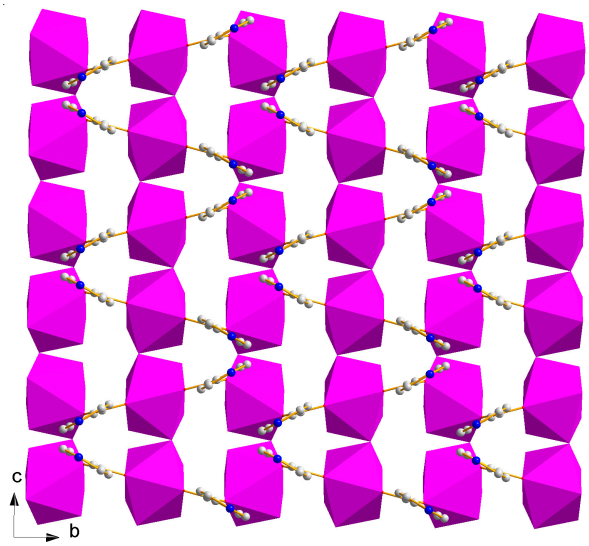

Fig. 3. 2-D layer of **1**

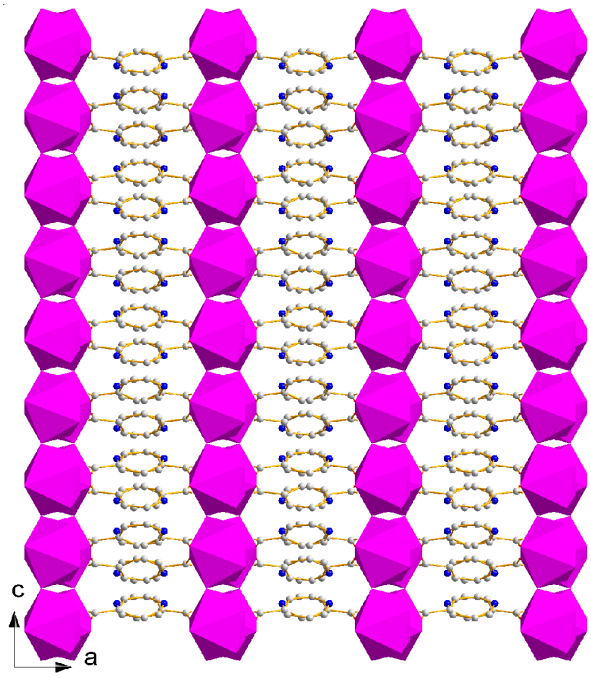

Fig. 4. Crystal packing diagram of **1**

A search from the Cambridge crystallographic data centre (CCDC) shows that there are several terbium-isonicotinic acid complexes[5-8]. However, in these complexes only one is chloride[8]. Furthermore, this complex is a 1-D structure, different from the 3-D motif of the title complex. Therefore, complex **1** is the first 3-D structure of terbium chloride with isonicotinic acid as a ligand.

In summary, I have prepared and characterized a novel terbium-isonicotinic acid complex, $[Tb(H_2O)_2(C_6NO_2H_4)_2Cl]_n$ (**1**), which is the first 3-D structure of terbium chloride with isonicotinic acid as a ligand.

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