



Communication

Preparation and characterization of a novel single crystal of Th(IV) with cucurbit[6]uril



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ABSTRACT

One single crystal based on Th⁴⁺ and cucurbit[6]uril (CB6) in nitric acid aqueous solutions was synthesized by slow evaporation method. The single crystal was characterized by elemental analysis, single crystal X-ray diffraction, XRD, FT-IR and TGA. The complexed cation of Th⁴⁺ is a ten coordinated structure, in which the central thorium ion is coordinated by six monodentate water molecules and two bidentate nitrates. While CB6, as a second-sphere ligand, coordinates with the water molecules of [Th(NO₃)₂(H₂O)₆]²⁺ through the formation of hydrogen bonding. Two other nitrate ions act as the counter anions. Besides, there are two free water molecules in the crystal system. The formation of the Th⁴⁺-CB6 complex can contribute to the study of the coordination of CB6 and the extraction of Th⁴⁺ in HNO₃ system. © 2017 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

Cucurbit[n]uril, abbreviated as CBn, is the condensation product of glycoluril and formaldehyde in acid aqueous solution [1]. Due to a rigid hydrophobic cavity of low polarity accessible through two open polar portals rimmed with carbonyl groups [2,3], CBn could be used as a macrocyclic polydentate ligand to coordinate with various metal ions, e.g., alkali and alkaline earth metals [4,5], transition metals [6], lanthanides [7,8] and uranyl [9,10]. Besides, CBn can coordinate with metals through second-sphere hydrogen bonding interactions [11,12]. Therefore, CBn could be used to isolate kinetically labile lanthanide(III) complexes and to remove uranium [13,14] from aqueous solution efficiently. Now, CBn-based coordination chemistry becomes an important area in CBn chemistry.

Thorium is a very important nuclear fuel element. With respect to the Th⁴⁺-CBn based complexes, there are only a few reports [12,15]. Samsonenko *et al.* [15] got a single crystal [Th(H₂O)₅Cl]₂(C₃₆H₃₆N₂₄O₁₂)]Cl₆·13H₂O in hydrochloric acid. The coordination number of Th⁴⁺ is nine and one CB6 molecule serves as a hexadentate ligand coordinated with two thorium cations. Thuery [12] obtained a complex [Th(NO₃)(H₂O)₈][(ReO₄)(CB6)](ReO₄)₂·3H₂O by the reaction between thorium(IV) nitrate and CB6 in the presence of perhenic acid by hydrothermal method. In the complex, one Th⁴⁺ cation coordinates with eight monodentate

water molecules and one bidentate nitrate ion. Then, one [Th(NO₃)(H₂O)₈]³⁺ cation is located close to each CB6 portal, and the water ligands are hydrogen-bonded to carbonyl groups, i.e., CB6 acts as a second-sphere ligand. It is worthwhile that nitric acid is always used in the extraction of thorium from natural ores and spent nuclear fuel. Thus, the interaction between CB6 and Th⁴⁺ in nitric acid is of great importance. However, to the best of our knowledge, there is seldom report in the literature.

Herein, we report the synthesis and crystal structure of a new supramolecular adduct of thorium nitrate and macrocyclic cavitand CB6 in HNO₃ aqueous solutions, which is helpful for understanding the extraction mechanism of Th⁴⁺ from nitric acid solution.

Cucurbit[6]uril (CB6) was synthesized according to the reference [16]. All other reagents were purchased from commercial sources and used without further purification. The organic element analysis was performed on an elemental analyzer, vario EL (Elementar Analyse systeme GmbH, Germany). FT-IR spectrum of the complex was recorded on a NICOLET iN10 MX spectrometer. The thermogravimetric analysis (TGA) was measured on a Q600 SDT thermoanalyzer under air atmosphere with the temperature ranging from room temperature to 700 °C at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data was measured on a DMAX-2400 diffractometer Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and the simulated data was carried out by the crystal analytic software 'Mercury'. A suitable crystal was selected and was measured on a Bruker APEX-II CCD diffractometer, where monochromated MoK α

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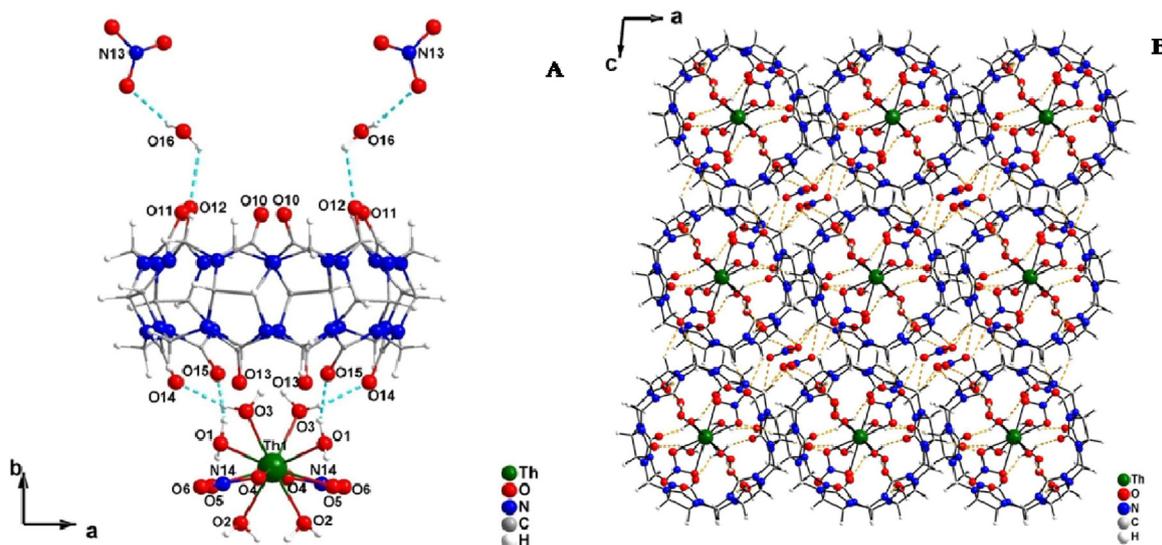


Fig. 1. (A) Ellipsoid representation of the molecular structure of $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Selected bond lengths: Th1–O1 2.426(3); Th1–O2 2.457(3); Th1–O3 2.469(3); Th1–O4 2.642(3); Th1–O5 2.546(3) Å. (B) Packing of $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ molecules in the crystal structure, viewed along b direction.

($\lambda = 0.71073 \text{ \AA}$) radiation was used. The crystal was kept at 300 K during data collection. The structure was solved with the SIR2004 structure solution program using Direct Methods and refined with the olex².

In a glass vessel, 11 mg CB6 and 5 mL water were added. After increasing the temperature to 80 °C, HNO_3 was added with stirring until CB6 was dissolved. $\text{Th}(\text{NO}_3)_4$ (ten-fold of CB6) aqueous solution was added. The mixed solution was left in the room temperature. Over a period of 3 days, the X-ray quality crystal was obtained from the solution. **Caution!** Thorium is a radioactive element. Suitable precautions and protection should be taken, and all operations should follow the criteria while handling the thorium ion in the experiment. According to the result of X-ray diffraction, the components of the crystal is $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ($\text{ThC}_{36}\text{H}_{52}\text{N}_{28}\text{O}_{32}$). There exist Q peaks resulting from solvent molecules in the cavity of the CB6, which is highly disorder with the shielding of CB6. It is difficult to ascertain the orientation of the water molecules in the cavity of CB6. After three water molecules were added into a crystal cell, *i.e.*, $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6]$

$(\text{CB6})(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, the result of elemental analysis was identical to the theoretical value. Elemental analysis: calcd. (%) for $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$: C, 25.81%; H, 3.49%; N, 23.41%; found (%): C, 25.55%; H, 3.09%; N, 23.78%.

The structure of $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is presented in Fig. 1A. Single crystal analysis revealed that the central Th^{4+} cation is coordinated with six monodentate water molecules and two bidentate nitrates. The two bidentate nitrates coordinate with Th^{4+} in a symmetrical way. While the six oxygen atoms of water molecules are coordinated to Th^{4+} asymmetrically. Meanwhile, four water ligands adjoin CB6, while the other two water ligands coordinate with Th^{4+} on the opposite position, which connect with other NO_3^- ions *via* hydrogen bonding. There is no direct bonding between CB6 and Th^{4+} . However, one $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6]^{2+}$ cation is located close to one portal of CB6, and water ligands in a suitable position can bond to the carbonyl groups of CB6 through hydrogen bonding. From the selected bond lengths data, the average bond distances of Th–O3(H) and Th–O1(H) are 2.469(3) and 2.426(3) Å, respectively. The bond length of Th–O2(H)

Table 1
Crystal data and structure refinement of $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Chemical formula	$\text{ThC}_{36}\text{H}_{52}\text{N}_{28}\text{O}_{32}$
Formula weight	1621.02
Temperature/K	300
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$, $b/\text{\AA}$, $c/\text{\AA}$	21.087(15), 12.303(8), 22.041(15)
$\alpha/^\circ$, $\beta/^\circ$, $\gamma/^\circ$	90.00, 95.80(3), 90.00
Volume/ \AA^3	5689(7)
Z	4
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.8924
μ/mm^{-1}	2.745
F000	3240.0
Crystal size/ mm^3	0.919 × 0.148 × 0.098
2θ range for data collection	5.48° to 54.92°
Index ranges	$-27 \leq h \leq 27$, $-15 \leq k \leq 15$, $-28 \leq l \leq 28$
Reflections collected	48453
Independent reflections	6487 [$R_{\text{int}} = 0.0312$, $R_{\text{sigma}} = 0.0190$]
Data/restraints/parameters	6487/0/444
Goodness-of-fit on F^2	1.020
Final R indexes [$I > 2\sigma(I)$ <i>i.e.</i> , $F_o > 4\sigma(F_o)$]	$R_1 = 0.0273$, $wR_2 = 0.0797$
Final R indexes [all data]	$R_1 = 0.0303$, $wR_2 = 0.0816$
Largest diff. peak/hole/ $e\text{\AA}^{-3}$	3.08/−0.70
Completeness	0.997

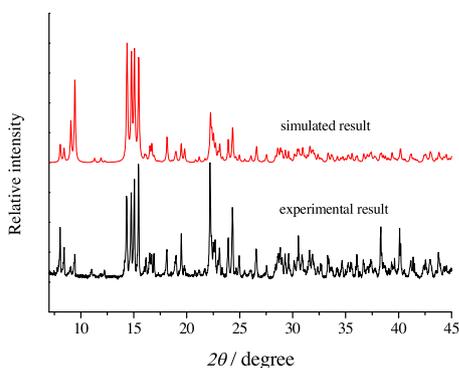


Fig. 2. Simulated and experimental PXRD result of single crystal $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

is 2.457(3) Å, while those of Th-O4(N14) and Th-O5(N14) are 2.642(3) and 2.546(3) Å, respectively. There also exist two free water molecules and two NO_3^- ions. Meanwhile, every water molecule connected one free NO_3^- and carbonyl groups of CB6 through hydrogen bonding.

The coordination interaction between Cl^- and Th^{4+} is weak in aqueous solution, so CB6 acts as a hexadentate ligand coordinated to Th^{4+} ion in HCl solutions [15]. However, in the presence of NO_3^- , which could coordinate with Th^{4+} more strongly, the bonding cannot be formed between Th^{4+} and carbonyl in HReO_4 [12] and HNO_3 solutions, the thorium cation is prone to coordinate with nitrate ion and water molecules, while CB6 serves as a second-sphere ligand bonding to thorium through hydrogen bonding. The differences of the ligand affinity can lead to the formation of Th^{4+} -CB6 based crystals with different coordination modes and structures. In addition, with respect to $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ crystal, the Th^{4+} ion is coordinated by four bidentate nitrate ions and four monodentate water molecules, and the coordination number of Th^{4+} is 12 [17], obviously different from the CB6-based crystals. In other words, the addition of CB6 could affect the coordination interaction between Th^{4+} and NO_3^- although CB6 only act as a second-sphere ligand. This will be helpful for synthesizing the CB6 based crystals with different structures and components.

The crystal data and structure refinement of the Th^{4+} -CB6 based complex are shown in Table 1. The Th^{4+} -CB6 complex is a monoclinic system with space group C2/c. In the crystal lattice (Fig. 1B), the $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ molecules arranged to tubular structure along *b* direction. The crystal was also investigated by powder X-ray diffraction. In the XRD pattern of the crystal, there appear ten main peaks at the 2θ values of 8.08°, 14.43°, 14.80°, 15.00°, 15.43°, 18.21°, 22.21°, 24.36°, 26.64° and 28.78°, agree well with the simulated result (Fig. 2). This means that the purity of the crystal is high enough.

The infrared spectra of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and Th^{4+} -CB6 complex contain some typical features of water and nitrate (Fig. 3A). The asymmetric stretching vibrations (ν_1), the symmetric stretching vibrations (ν_2) and the N—O stretching vibrations (ν_3) of the NO_3^- in $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ appear at 1479, 1307 and 1047 cm^{-1} , respectively, indicating the presence of bidentate nitrates [18,19]. The Th^{4+} -CB6 complex also contains similar vibrations, which means the existence of bidentate nitrates. Besides, vibrations at 806 and 759 cm^{-1} of the Th^{4+} -CB6 complex can be assigned to the bending out-of-plane (ν_4) and in-of-plane (ν_5) of NO_3^- , respectively. Compared with the crystal of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, the IR spectrum of water in the Th^{4+} -CB6 based single crystal gets more broader. The vibrations of the carbonyl groups in CB6 appear at 1747 cm^{-1} (weak peak) and 1723 cm^{-1} (Fig. S1 in Supporting information), while the vibrations of the carbonyl groups in Th^{4+} -CB6 complex

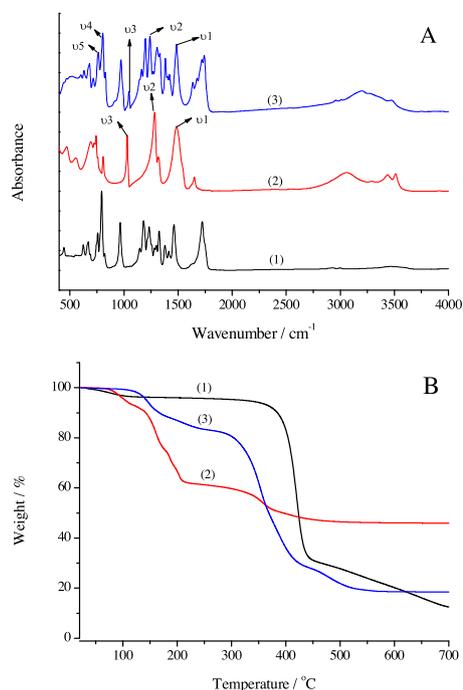


Fig. 3. IR spectra (A) and TGA curves (B) of CB6 (1), $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (2) and $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (3).

are slightly red shifted to 1742 and 1720 cm^{-1} , respectively. Besides the vibration frequency of the C=O in Th^{4+} -CB6 complex partly shifts down to a new peak at 1675 cm^{-1} compared with CB6 due to the splitting of the carbonyl groups of CB6. This also means that there exist two kinds of carbonyl groups with different environments in the Th^{4+} -CB6 complex and the formation of hydrogen bonding.

In order to assess the thermal stabilities and the phase behaviors of the precursors as well as the Th^{4+} -CB6 complex, the decomposition temperature was determined using TGA (Fig. 3B). CB6 starts to decompose at 360 °C. The weight percent of the Th^{4+} -CB6 complex decrease by 9.86% at 167 °C, which is attributed to the loss of the water molecules [20]. The complex decreased to 83.27% at 253 °C due to the decomposition of NO_3^- [20]. The last stage is mainly the decomposition of CB6 of the crystal. The possible final residue of the crystal is thorium dioxide [20].

In summary, the single crystal $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{CB6})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was synthesized and characterized. The single crystal is a second-sphere complex of $[\text{Th}(\text{NO}_3)_2(\text{H}_2\text{O})_6]^{2+}$ with CB6 through hydrogen bonding. Meanwhile, the thorium ion is coordinated by six water molecules and two bidentate nitrates, and two NO_3^- act as the counterion anions. Besides, there are also two free water molecules in the crystal system. The infrared spectrum of the compound exhibited some typical features of water molecules and bidentate nitrates of the complex. The TGA curve of the crystal shows a three-step decomposition process. The weight loss of the crystal is mainly the loss of water molecules, and then the removal of nitrogen oxides and carbon dioxides at high temperature. Eventually, the crystal decomposed to thorium dioxide. The structural differences of thorium with CB6 in hydrochloric acid, perchloric acid and nitric acid aqueous solutions can be helpful to understand the differences of coordination abilities of Cl^- , ReO_4^- and NO_3^- . Besides, the formation of Th^{4+} -CB6 based crystal can contribute to explore the recycle and separation of thorium in HNO_3 system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ccllet.2017.09.030>.

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