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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 Th^{4+} 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 Th^{4+} 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 $[Th(NO_3)_2(H_2O)_6]^{2+}$ 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 Th^{4+}-CB6 complex can contribute to the study of the coordination of CB6 and the extraction of Th^{4+} in HNO_3 system

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 Th^{4+}-CBn based complexes, there are only a few reports [12,15]. Samsonenko *et al.* [15] got a single crystal $[\{Th(H_2O)_5Cl\}_2(C_{36}H_{36}N_{24}O_{12})]Cl_6{\cdot}13H_2O$ in hydrochloric acid. The coordination number of Th^{4+} is nine and one CB6 molecule serves as a hexadentate ligand coordinated with two thorium cations. Thuery [12] obtained a complex $[Th(NO_3)(H_2O)_8][(ReO_4)(CB6)](ReO_4)_2{\cdot}3H_2O$ by the reaction between thorium(IV) nitrate and CB6 in the presence of perrhenic acid by hydrothermal method. In the complex, one Th^{4+} cation coordinates with eight monodentate water molecules and one bidentate nitrate ion. Then, one $[Th(NO_3)(H_2O)_8]^{3+}$ 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 Th^{4+} 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 HNO_3 aqueous solutions, which is helpful for understanding the extraction mechanism of Th^{4+} 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 Kα radiation (λ = 1.5406 Å) 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$_\alpha$

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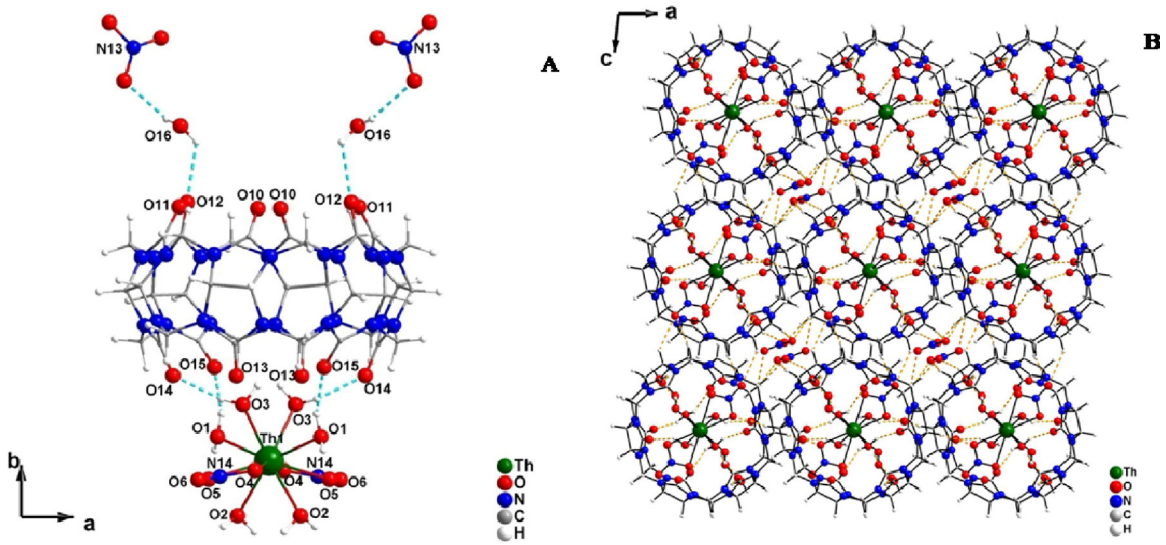

Fig. 1. (A) Ellipsoid representation of the molecular structure of $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}2H_2O$. Selected bond lengths: Th1-O1 2.426(3); Th1-O2 2.457(3); Th1-O3 2.469 (3); Th1-O4 2.642(3); Th1-O5 2.546(3) Å. (B) Packing of $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}2H_2O$ molecules in the crystal structure, viewed along *b* direction.

(λ = 0.71073 Å) 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 olex[2].

In a glass vessel, 11 mg CB6 and 5 mLwater were added. After increasing the temperature to 80 °C, HNO_3 was added with stirring until CB6 was dissolved. $Th(NO_3)_4$ (ten-folded 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 $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}2H_2O$ ($ThC_{36}H_{52}N_{28}O_{32}$). 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.*, $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}5H_2O$, the result of elemental analysis was identical to the theoretical value. Elemental analysis: calcd. (%) for $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}5H_2O$: C, 25.81%; H, 3.49%; N, 23.41%; found (%): C, 25.55%; H, 3.09%; N, 23.78%.

The structure of $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}2H_2O$ 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 $[Th(NO_3)_2(H_2O)_6]^{2+}$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 $[Th(NO_3)_2(H_2O)_6](CB6)(NO_3)_2{\cdot}2H_2O$.

Chemical formula	$ThC_{36}H_{52}N_{28}O_{32}$
Formula weight	1621.02
Temperature/K	300
Crystal system	monoclinic
Space group	C2/c
a/Å, *b*/Å, *c*/Å	21.087(15), 12.303(8), 22.041(15)
α/°, *β*/°, *γ*/°	90.00, 95.80(3), 90.00
Volume/Å^3	5689(7)
Z	4
ρ_{calc}/g cm^{-3}	1.8924
μ/mm^{-1}	2.745
*F*000	3240.0
Crystal size/mm^3	0.919 × 0.148 × 0.098
2*Θ* range for data collection	5.48° to 54.92°
Index ranges	$-27 \le h \le 27$, $-15 \le k \le 15$, $-28 \le l \le 28$
Reflections collected	48453
Independent reflections	6487 [R_{int} = 0.0312, R_{sigma} = 0.0190]
Data/restraints/parameters	6487/0/444
Goodness-of-fit on F^2	1.020
Final *R* indexes [I > 2*σ* (I) *i.e.* $F_o > 4\sigma(F_o)$]	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 Å^{-3}	3.08/−0.70
Completeness	0.997

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