

# Effect of valence of lanthanide ion and molecular symmetry in polyoxotungstoborate on the molecular structure and spectrochemical properties



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## ABSTRACT

The compound  $K_9(NH_4)H[Ce^{IV}(\alpha-BW_{11}O_{39})(W_5O_{18})] \cdot 16H_2O$  (**1**) was successfully isolated and structurally characterized. The structural investigation revealed that **1** displayed a less molecular distortion, whereas  $Ln^{3+}$ -analogs exhibited a large molecular distortion. IR spectroscopy demonstrated that the spectral patterns of **1** and  $Ce^{3+}$ -analog were depending on each valence of Ce (IV/III). <sup>11</sup>B-NMR spectroscopy showed that a decrease in site symmetry of B atom in the polyoxotungstoborate was related with an increase in a half width of NMR peak. There is a difference in molecular distortion between **1** and  $Ce^{3+}$ -analog, but they have similar large half widths because of the same site symmetry of B atom. The 4f electron in Ce atom exhibited less effect on the chemical shift.

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## 1. Introduction

Polyoxometalates (POMs), metal oxide cluster polyanions constructed from corner and edge shared  $MO_n$  polyhedrons, have occupied important positions in inorganic and material chemistry owing to their unlimited structural diversity and abundant physicochemical and biological properties [1,2]. POMs can coordinate to lanthanide (Ln) ion(s) as ligands to form polyoxometalloylanthanoates (Ln-POMs), in addition, Ln plays a significant role not only in assembly of POM units into higher integrated molecule but also optical and magnetic function in Ln-POM [3–11]. In 1971, the report about  $[Ln^{III}(\alpha-XW_{11}O_{39})_2]^{n-}$  (X = Si, P),  $[Ln^{III}(P_2W_{17}O_{61})_2]^{17-}$  and  $[Ln^{III}(W_5O_{18})_2]^{9-}$  by Peacock and Weakley initiated the Ln-POM study [12]. To date, our group have developed structural, solution, and spectroscopic chemistry of  $Ln^{3+}$ -POMs such as  $[Ce^{III}_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$  [13],  $[Er^{III}_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})]^{15-}$  [14], and  $[Ln^{III}(\alpha-BW_{11}O_{39})(W_5O_{18})]^{12-}$  (Ln = Ce, Eu) [15]. Recently, we have been focusing on  $Ln^{4+}$ -POMs because of their unique POM assembly patterns [16,17] and properties [18,19]. In fact, we reported spontaneous resolution of dimethylammonium salt of  $[Ce^{IV}(\alpha-$

$PW_{11}O_{39})_2]^{10-}$ , and full structural characterization of  $[Ce^{IV}(\alpha_2-P_2W_{17}O_{61})_2]^{16-}$  in crystal and in aqueous solution in 2010 and 2013, respectively [18,20]. Additionally, it is pointed out that POM is effective for chemical extraction and waste processing of radioactive actinide ion ( $Ac^{4+}$ ). The chemical similarity between  $Ac^{4+}$  and  $Ln^{4+}$  will allow us to use  $Ln^{4+}$  in ‘cold run’ experiment in  $Ac^{4+}$ -POM study. Besides,  $Ce^{4+}$  is easy to be available and handle in a series of  $Ln^{4+}$  ions. Hence, it is important to study the  $Ce^{4+}$ -POM in regard to synthesis and physicochemical properties. In this paper, we report an isolation and structural characterization of  $[Ce^{IV}(\alpha-BW_{11}O_{39})(W_5O_{18})]^{11-}$ . Effects of valence of Ln ion and molecular symmetry in polyoxotungstoborate on the molecular structure and spectrochemical properties are examined.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were analytical grade and used without further purification. IR spectra were recorded on a Jasco FT/IR-410 using KBr disc method. Elemental analysis of C, H, N was performed on a Yanaco MT5 CHN CORDER. The contents of Ce, B, W, and K were determined by inductively coupled plasma (ICP) atomic emission spectroscopy on an ICPS-8100 spectrometer. Thermogravimetric

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and differential thermal analyses (TG-DTA) were conducted with an ULVAC MTS9000 + TGD9600 system.  $^{11}\text{B}$ -NMR spectra were measured on Bruker Biospin AVANCE III (400 MHz) at a frequency of 128.38 MHz. All of the  $^{11}\text{B}$ -NMR spectra consist of parent peaks and weak single peaks of  $\text{H}_3\text{BO}_3$  (probably be dissociated from the parent compounds). So, chemical shifts were standardized using these  $\text{H}_3\text{BO}_3$  peaks as internal references ( $\delta = 0$ ).

### 2.2. Synthesis of $\text{K}_9(\text{NH}_4)\text{H}[\text{Ce}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 16\text{H}_2\text{O}$ (**1**)

Solid  $\text{H}_3\text{BO}_3$  (0.1 g, 0.2 mmol) was dissolved into a boiling aqueous solution (60 ml) containing  $\text{WO}_3$  (4.0 g, 17 mmol) and  $\text{KOH}$  (2.5 g, 45 mmol). Then, an aqueous solution (10 ml) of  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4\cdot 4\text{H}_2\text{O}$  (1.0 g, 1.5 mmol) was added dropwise into the hot solution with vigorous stirring, and the pH of the solution was adjusted to *c.a.* 5.0 by  $\text{H}_2\text{SO}_4$ . The resulting solution was boiled for 1 h and then cooled to room temperature. The residual powders were filtered off, and the filtrate was kept for several days. Yellow block crystals of  $\text{K}_9(\text{NH}_4)\text{H}[\text{Ce}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 16\text{H}_2\text{O}$  (**1**) were obtained (0.88 g, 17.4% based on W). Anal. Calcd for  $\text{H}_3\text{7BCE-K}_9\text{NO}_7\text{3W}_{16}$ : H, 0.80; N, 0.30; K, 7.55; B, 0.23; W, 63.1; Ce, 3.00. Found: H, 0.57; N, 0.26; K, 7.35; B, 0.23; W, 60.8; Ce, 3.04. IR (KBr disc): 996(w), 950(s), 892(m), 836(w), 816(s), 776(w), 745(w), 679(w). The number of waters of crystallization calculated from the thermogravimetric analysis (Fig. S1) was *c.a.* 15.

The compounds  $\text{K}_{8.5}\text{H}_{3.5}[\text{Ce}^{\text{III}}(\text{BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 25\text{H}_2\text{O}$  (**Ce-III**),  $\text{K}_5[\text{BW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  (**BW<sub>12</sub>**), and  $\text{K}_9[\text{BW}_{11}\text{O}_{39}]\cdot n\text{H}_2\text{O}$  (**BW<sub>11</sub>**) were prepared according to the literature [15,22,23] for comparison in molecular structure, IR and  $^{11}\text{B}$ -NMR study.

### 2.3. X-ray crystallography

The reflection data for single crystal X-ray diffraction analysis of the compound **1** were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) at 173 K. A numerical absorption correction was made using SHAPE [24] and NUMABS [25]. The structure was solved by the direct method SHELXS-97 [26] and refined by the full-matrix least-squares program SHELXL-97 [27] on  $F^2$  using the CrystalStructure [28]. The Ce, W, B, and K atoms were refined anisotropically, and the other atoms were refined isotropically. The H atoms were not included in the refinements. The crystal data and refinement results are summarized in Table 1. Sixteen waters of crystallization were found, which slightly differs from the thermogravimetric analysis (*c.a.* 15). It is presumed that overall number of water molecules is variable depending on the dryness condition of the sample.

## 3. Results and discussion

### 3.1. Molecular structure of **1**

Single crystal X-ray diffraction analysis revealed that the compound **1** consists of  $[\text{Ce}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]^{11-}$  polyanion, 9  $\text{K}^+$  ions, one  $\text{H}^+$ , one  $\text{NH}_4^+$ , and 16 waters of crystallization. The compound **1** is isomorphous with  $\text{K}_{10.5}\text{H}_{0.5}[\text{Np}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 15\text{H}_2\text{O}$  (**Np-IV**) [29], and has a different molecular packing compared with  $\text{Ce}^{\text{III}}$ -analog of  $\text{K}_{8.5}\text{H}_{3.5}[\text{Ce}^{\text{III}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 25\text{H}_2\text{O}$  (**Ce-III**) and  $\text{Eu}^{\text{III}}$ -analog of  $\text{K}_{9.5}\text{H}_{2.5}[\text{Eu}^{\text{III}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]\cdot 25\text{H}_2\text{O}$  (**Eu-III**) [15]. As shown in Fig. 1, the  $[\text{Ce}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]^{11-}$  polyanion is composed of a  $\text{Ce}^{4+}$  ion sandwiched by  $[\alpha\text{-BW}_{11}\text{O}_{39}]^{9-}$  and  $[\text{W}_5\text{O}_{18}]^{6-}$  units as O-tetradentate ligands. Eight O atoms coordinating to  $\text{Ce}^{4+}$  are arranged in a square-antiprismatic geometry. The Ce–O bond lengths are in the range of 2.280(8) to 2.445(9)  $\text{Å}$  (average, 2.362  $\text{Å}$ ), which are

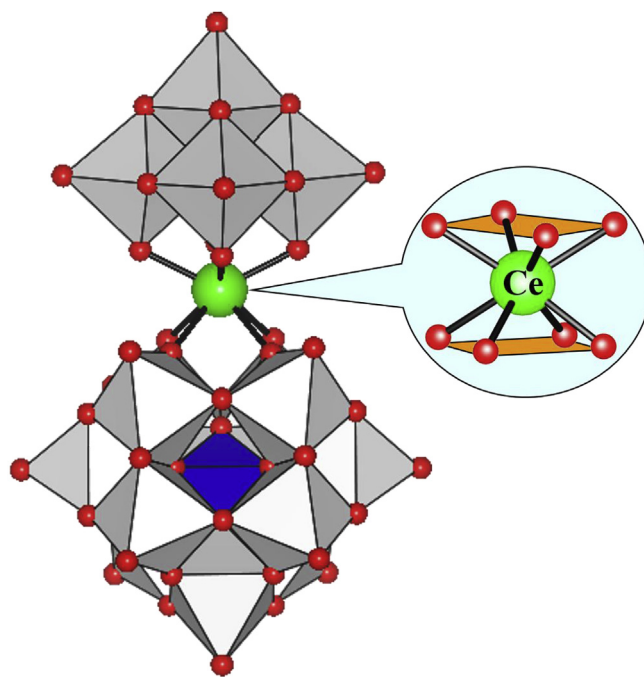
**Table 1**  
Crystal data and refinement result of **1**.

Compound <b>1</b>	
Empirical formula	$\text{H}_3\text{7BCEK}_9\text{NO}_7\text{3W}_{16}$
Formula weight	4663.67
Crystal system	Triclinic
Space group	$P\bar{1}$
a ( $\text{Å}$ )	12.6979 (3)
b ( $\text{Å}$ )	17.4517 (4)
c ( $\text{Å}$ )	17.5078 (4)
$\alpha$ ( $^\circ$ )	111.3222 (8)
$\beta$ ( $^\circ$ )	93.3235 (7)
$\gamma$ ( $^\circ$ )	96.6068 (7)
V ( $\text{Å}^3$ )	3569.2 (2)
Z	2
$\theta$ range ( $^\circ$ )	3.0–30.0
Limiting indices reflections	$-17 \leq h \leq 17$ $-24 \leq k \leq 22$ $-22 \leq l \leq 24$
Crystal size ( $\text{mm}^3$ )	$0.31 \times 0.25 \times 0.10$
$D_c$ ( $\text{g cm}^{-3}$ )	4.339
$F(000)$	4092.00
$\mu$ ( $\text{mm}^{-1}$ )	26.960
Total data collected	70,696
Unique data	20,747
$ R_{\text{int}} $	0.1173
Goodness-of-fit (GOF)	1.055
$R_1$ [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0575
$wR_2$ <sup>b</sup>	0.1461

$w$  (for **1**) =  $1/[\sigma^2(F_0^2) + (0.0409 P)^2 + 132.9845 P]$ , where  $P = (\text{Max}(F_0^2, 0) + 2F_c^2)/3$ .

<sup>a</sup>  $R_1 = (\sum |F_0| - |F_c|) / (\sum |F_c|)$ .

<sup>b</sup>  $wR_2 = \sqrt{[\sum (w(F_0^2 - F_c^2)^2) / \sum (w(F_0^2)^2)]^{1/2}}$ .



**Fig. 1.** Combined polyhedral and ball-and-stick model of  $[\text{Ce}^{\text{IV}}(\alpha\text{-BW}_{11}\text{O}_{39})(\text{W}_5\text{O}_{18})]^{11-}$  polyanion in compound **1**. The close view represents the  $\text{Ce}^{4+}$  center in square-antiprismatic (SA) coordination environment. Color codes; white octahedron:  $\text{WO}_6$ , blue tetrahedron:  $\text{PO}_4$ , green sphere: Ce. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

comparable to those in  $[\text{Ce}^{\text{IV}}(\text{W}_5\text{O}_{18})]^{8-}$  (2.34(1)–2.38(1)  $\text{Å}$ , average, 2.361  $\text{Å}$ ) [30],  $[\text{Ce}^{\text{IV}}(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$  (2.30(2)–2.38(2)  $\text{Å}$ , average, 2.357  $\text{Å}$ ) [18],  $[\text{Ce}^{\text{IV}}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{16-}$  (2.30(2)–2.38(4)  $\text{Å}$ , average, 2.348  $\text{Å}$ ) [20]. Whereas, they are shorter than those in **Ce-III**

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