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Relation	



# Structural Characterization of Cerium-encapsulated Preyssler-type Phosphotungstate: Additional Evidence of Ce(III) in the Cavity

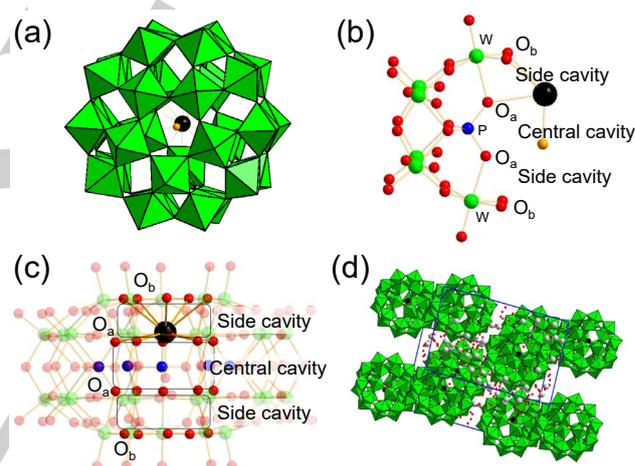
Kota Shitamatsu,<sup>[a]</sup> Tatsuhiro Kojima,<sup>[b]</sup> Paul G. Waddell,<sup>[c]</sup> Sugiarto,<sup>[a]</sup> Haruka Egawa Ooyama,<sup>[a]</sup> R. John Errington,<sup>[c]</sup> and Masahiro Sadakane\*<sup>[a]</sup>

**Abstract:** Single-crystal X-ray structure analysis revealed the precise structure of a Ce-encapsulated Preyssler-type phosphotungstate which was first synthesized by Pope et al. Antonio et al. reported that encapsulated Ce has a 3+ oxidation state and is redox-inactive, which is unlike other Ce-containing phosphotungstates. Therefore, precise structural analysis about Ce position is needed. The encapsulated Ce was located in one of the side cavities, and was coordinated to one H<sub>2</sub>O molecule. The position of Ce was similar to that of Y<sup>3+</sup> and Eu<sup>3+</sup> in similar compounds. This result, together with the bond valence sum calculation, provides additional evidence that the oxidation state of the redox-inactive Ce in the Preyssler-type compound is 3+.

## Introduction

Polyoxometalates (POMs) are anionic multi-metal-oxide molecules containing early transition metals, such as W and Mo. Their properties—including acidity, multi-electron redox activity, and magnetism—can be tuned by changing their molecular structure and component elements. Therefore, POMs have been used as functional materials.<sup>[1-3]</sup> Among the various POM structures, Preyssler-type phosphotungstates, [P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>M<sup>n+</sup>(side)(H<sub>2</sub>O)]<sup>(15-n)-</sup> (M<sup>n+</sup> = encapsulated cation),<sup>[4]</sup> have recently attracted significant attention because they are applicable as acid catalysts,<sup>[5]</sup> antibacterial materials,<sup>[6]</sup> liposome collapse reagents,<sup>[7]</sup> proton-conductive materials,<sup>[8, 9]</sup> single-molecule magnetic materials<sup>[10]</sup>, and single-molecule electret materials.<sup>[11]</sup>

Preyssler-type molecules have a doughnut-shaped structure consisting of five PO<sub>4</sub> tetrahedra surrounded by 30 WO<sub>6</sub> octahedra, and an internal cavity (Figure 1). The cavity has two side cavities surrounded by five O atoms (O<sub>a</sub>) that bind to the P atoms and five bridging O atoms (O<sub>b</sub>) between the two cap W atoms. The side cavities are separated by a central cavity surrounded by ten O<sub>a</sub> (Figure 1 (b) and (c)).



**Figure 1.** (a) Polyhedral representation of a Preyssler-type phosphotungstate with one encapsulated Ce cation, [P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]<sup>12-</sup>; (b) ball-and-stick representation of one-fifth of the Preyssler molecule, [PW<sub>6</sub>O<sub>22</sub>Ce(H<sub>2</sub>O)] unit; (c) ball-and-stick representation of [P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]<sup>12-</sup>; and (d) polyhedral representation of packing of K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]. Green, blue, black, red, and orange balls represent W, P, Ce, O, and (H<sub>2</sub>O) O atoms, respectively.

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It is possible to encapsulate one or two cations in the cavity,<sup>[12]</sup> such as Na<sup>+</sup>,<sup>[13, 14]</sup> Ag<sup>+</sup>,<sup>[15-17]</sup> K<sup>+</sup>,<sup>[18-21]</sup> Ca<sup>2+</sup>,<sup>[14]</sup> Y<sup>3+</sup>,<sup>[14]</sup> Bi<sup>3+</sup>,<sup>[22]</sup> and lanthanide<sup>[23]</sup> and actinide cations.<sup>[14, 23, 24]</sup> Selection of the encapsulated cation(s) is one of the most commonly used methods to adjust the properties of Preyssler molecules.<sup>[25, 26]</sup> Uchida et al. reported that the selection of an appropriate cation improved the proton conductivity of their Preyssler-polymer hybrid systems.<sup>[8, 27]</sup> We have reported that the acid catalytic activity for ester hydration was affected by the selection of encapsulated cations.<sup>[18]</sup> Yin et al. reported that the release of Ag<sup>+</sup> from the Ag<sup>+</sup>-encapsulated complex is one reason for high and long-lasting antibacterial properties.<sup>[6]</sup>

Cerium cations (Ce<sup>3+</sup> and Ce<sup>4+</sup>) are some of the most important metals used in POM structures. Several giant POM

molecules have been synthesized using Ce as linkers of building blocks<sup>[28-31]</sup>. Furthermore, Ce-containing POMs exhibit interesting properties such as interactions with amino acids<sup>[32, 33]</sup>, catalysis of protein hydrolysis<sup>[34]</sup>, catalysis for photochemical reactions,<sup>[35]</sup> and oxidation catalysis.<sup>[36]</sup>

Pope et al. reported the creation a Ce-encapsulated POM by reacting a Na-encapsulated Preyssler compound with cerium ammonium nitrate,  $(\text{NH}_4)_2\text{Ce}^{4+}(\text{NO}_3)_6$ .<sup>[12]</sup> Antonio et al. reported that the oxidation state of the encapsulated Ce was 3+ by analyzing the X-ray absorption fine structure<sup>[37]</sup>, and that  $\text{Ce}^{3+}$  was not redox-active in the Preyssler molecule.<sup>[38]</sup> This is unlike other Ce-containing POMs, such as  $[\text{Ce}(\text{PW}_{11}\text{O}_{39})_2]^n$ <sup>[39]</sup> and  $[\text{Ce}(\text{P}_2\text{W}_{17}\text{O}_{61})]^n$ <sup>[33]</sup> where a redox couple corresponding to  $\text{Ce}^{4+/3+}$  is observed in aqueous solution.

In all reported single-crystal X-ray structure analyses of lanthanide cation-encapsulated Preyssler compounds, one cation is located in one of the side cavities. However DFT calculations done by López et al. indicated that the most stable position of Ce is approximately 0.55 Å from the center of the molecule, which is in the central cavity.<sup>[26]</sup> It has been reported that  $\text{Na}^+$  and  $\text{K}^+$  can also be encapsulated in the central cavity.<sup>[13, 19]</sup> Recently, Stroppa et al. reported that the most stable position for an encapsulated cation in the absence of coordinating  $\text{H}_2\text{O}$  is in the central cavity.<sup>[40]</sup> However, the precise location of Ce cations has not yet been clarified.

Here, we present single-crystal structure analysis of  $\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ce}(\text{H}_2\text{O})]$  and a comparison of the position of Ce with other Preyssler-type phosphotungstates to provide additional evidence that the valence of the encapsulated Ce is 3+ by comparing the Ce position with metal positions in other metal-encapsulated Preyssler molecules. Pope et al. reported that the distance between the equatorial plane of the molecule and the encapsulated cation ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{U}^{4+}$ ) increases with increasing cation valence.<sup>[14, 23]</sup>

## Results and Discussion

The K salt of the Ce-encapsulated compound was synthesized by the reaction of  $\text{K}_{14}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}]$  with  $(\text{NH}_4)_2\text{Ce}^{4+}(\text{NO}_3)_6$ , under hydrothermal reaction conditions; this method was first reported by Pope et al.<sup>[12]</sup> Our elemental analysis results indicated that the P:W:K:Ce:Cl ratio was 5:30:12:1:0,<sup>[41]</sup> indicating that the formula is  $\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ce}]$ . From the formula, the valence of Ce was confirmed to be 3+. The  $^{31}\text{P}$  NMR chemical shift of the synthesized  $\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ce}]$  was similar to that reported by Pope et al.

To confirm the position of Ce in the cavity, we performed single-crystal structure analysis several times on different crystals using two different radiation sources: synchrotron ( $\lambda = 0.4126 \text{ \AA}$ ) and Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystallographic data are summarized in Table 1. All analyses revealed that the encapsulated Ce ion was crystallographically disordered over two equivalent positions with 50% occupancies for each, and one Ce was located in one of the side cavities, and was coordinated by five  $\text{O}_a$  with Ce-O bond lengths between 2.62 (1) and 2.67 (1) Å, five  $\text{O}_b$  with Ce-O bond lengths between 2.79 (1) and 2.87 (2) Å,

and one  $\text{H}_2\text{O}$  O with a Ce-O bond length of 2.33 (3) Å. López et al. reported that the most stable position of Ce in the Preyssler molecule is in the central cavity where no  $\text{H}_2\text{O}$  molecule coordinates to  $\text{Ce}^{3+}$ .<sup>[26]</sup> However, the distance between Ce and the equatorial plane is 1.73 Å, which is in one of the side cavities. They also reported that the most stable position of  $\text{Na}^+$  in the Preyssler molecule is in the central cavity without coordinating  $\text{H}_2\text{O}$ . However, in most cases,  $\text{Na}^+$  is located in the side cavity with one coordinating  $\text{H}_2\text{O}$  molecule (Table 2). Recently, we reported that  $\text{Na}^+$  moved from the side to the central cavity after heating at 300 °C.<sup>[13]</sup> We believe that the coordinating  $\text{H}_2\text{O}$  stabilizes Ce in the side cavity.

**Table 1.** Crystallographic data.

Radiation	Synchrotron ( $\lambda = 0.4126 \text{ \AA}$ )	Mo $K\alpha$ ( $\lambda = 0.71073 \text{ \AA}$ )
Empirical formula	$\text{CeK}_{12}\text{O}_{142}\text{P}_5\text{W}_{30}$	$\text{CeK}_{10}\text{O}_{128.89}\text{P}_5\text{W}_{30}$
Formula weight, g/mol	8551.67	8551.67
Temperature (K)	100 (2)	100 (2)
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	28.5524 (5)	28.616 (2)
<i>b</i> (Å)	21.4607 (4)	21.505 (1)
<i>c</i> (Å)	20.8379 (4)	20.846 (1)
<i>V</i> (Å <sup>3</sup> )	12768.5 (4)	12827.9
<i>Z</i>	4	4
<i>D</i> <sub>calcd.</sub> (g/cm <sup>-3</sup> )	4.449	4.279
$\mu$ (mm <sup>-1</sup> )	6.652	27.708
F(000)	14868	14868
Crystal size (mm <sup>3</sup> )	0.04 x 0.03 x 0.03	0.10 x 0.09 x 0.07
2 $\theta$ range	1.582–28.784°	2.418–55.820°
Index ranges	-34 ≤ <i>h</i> ≤ 34 -25 ≤ <i>k</i> ≤ 25 -25 ≤ <i>l</i> ≤ 25	-37 ≤ <i>h</i> ≤ 37 -28 ≤ <i>k</i> ≤ 28 -27 ≤ <i>l</i> ≤ 27
No. of reflections collected	229364	149785
No. of unique reflections	12022	15740
Data/restraints/parameters	12022/108/963	15740/30/590
G.O.F.	1.268	1.310
R indexes [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0373 <i>wR</i> <sub>2</sub> = 0.0813	<i>R</i> <sub>1</sub> = 0.0661 <i>wR</i> <sub>2</sub> = 0.1401
R indexes [all data]	<i>R</i> <sub>1</sub> = 0.0407 <i>wR</i> <sub>2</sub> = 0.0825	<i>R</i> <sub>1</sub> = 0.0774 <i>wR</i> <sub>2</sub> = 0.1363
( $\Delta\sigma$ ) <sub>max</sub>	0.002	0.001

$(\Delta\rho)_{\max/\min}$  (e  $\text{\AA}^{-3}$ )      3.307/–2.804      4.088/–4.092

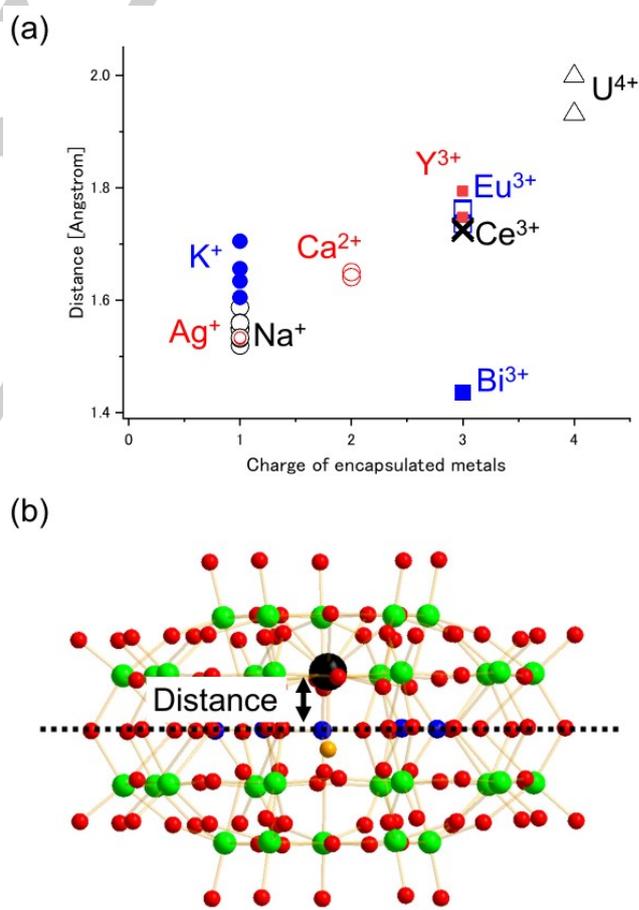
Pope et al. reported that the distance between the equatorial plane of the molecule and the encapsulated cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{U}^{4+}$ ) increases with increasing molecule valence.<sup>[14, 23]</sup> In these cases, one cation was encapsulated in one of the side cavities with one coordinating  $\text{H}_2\text{O}$  molecule. We summarize these distances for many Preyssler compounds based on reported single-crystal structure data in Table 2 and Figure 2. Only structures with one encapsulated cation and a coordinated  $\text{H}_2\text{O}$  molecule were included. The distance between the equatorial plane and the encapsulated cation in the side cavity increased with increasing cation valence, with the exception of  $\text{K}^+$  and  $\text{Bi}^{3+}$ . The distance between Ce and the equatorial plane was close to that of other cations with a valence of 3+. Furthermore, the oxidation state of Ce estimated by the bond valence sum (BVS) calculation is +2.73. These results indicate that Ce has a valence of 3+.

**Table 2.** Distances between encapsulated metal cations and equatorial plane of Preyssler-type phosphotungstates.

Preyssler compounds (encapsulated cation)	Distances [Å] <sup>[a]</sup>	Ref.
$(\text{NH}_4)_{14}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]$ ( $\text{Na}^+$ )	1.552	[14]
$\text{Na}_2(\text{Ce}(\text{H}_2\text{O})_6)_4[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]$ ( $\text{Na}^+$ )	1.5505	[42]
$\text{K}_2\text{Na}_6\text{Fe}_2(\text{H}_2\text{O})_8[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]$ ( $\text{Na}^+$ )	1.5875	[43]
$[\text{Cu}(\text{H}_2\text{biim})_2][\text{Cu}(\text{H}_2\text{biim})_2(\mu\text{-H}_2\text{O})_2][\text{Cu}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2]\text{H}[(\text{Cu}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2)_{0.5}]_2[\mu\text{-C}_3\text{HN}_2\text{Cl}_2(\text{Cu}(\text{H}_2\text{biim}))_2][\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]$ ( $\text{Na}^+$ )	1.5475	[44]
$\text{K}_{11.1}\text{H}_{2.9}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]\cdot 0.3\text{PEG400}$ ( $\text{Na}^+$ )	1.56	[27]
$\text{K}_{13}\text{H}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]\cdot 0.03\text{PAA5000}$ ( $\text{Na}^+$ )	1.5195	[27]
$\text{Na}(\text{K}(\text{H}_2\text{O})_6)(\text{Eu}_4(\text{H}_2\text{O})_{12}(\text{Hina})_6)[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Na}(\text{H}_2\text{O})]$ ( $\text{Na}^+$ )	1.5595	[45]
$\text{Ag}_{19}(\text{ptz})_8(\text{H}_2\text{ptz})(\text{H}_3\text{ptz})\cdot [\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ag}(\text{H}_2\text{O})]$ ( $\text{Ag}^+$ )	1.532	[17]
$[\text{Cu}(\text{H}_2\text{biim})_2][\text{Cu}(\text{H}_2\text{biim})_2(\mu\text{-H}_2\text{O})_2][\text{Cu}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2]\text{H}[(\text{Cu}(\text{H}_2\text{biim})(\text{H}_2\text{O})_2)_{0.5}]_2[\mu\text{-C}_3\text{HN}_2\text{Cl}_2(\text{Cu}(\text{H}_2\text{biim}))_2][\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ag}(\text{H}_2\text{O})]$ ( $\text{Ag}^+$ )	1.5335	[44]
$\text{Co}_4(\text{dimb})_4(\text{H}_2\text{O})_8\text{H}_6[\text{P}_5\text{W}_{30}\text{O}_{110}\text{K}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.656	[21]
$\text{Co}_4(\text{dimb})_4(\text{H}_2\text{O})_8\text{H}_6[\text{P}_5\text{W}_{30}\text{O}_{110}\text{K}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.634	[21]
$\text{Cu}_{10}(\text{ttbz})_2(\text{Httbz})_4(\text{OH})_6(\text{H}_2\text{O})_8[\text{P}_5\text{W}_{30}\text{O}_{110}\text{K}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.605	[20]
$\text{Co}_4(\text{bpz})_2(\text{H}_2\text{O})_5[\text{P}_5\text{W}_{30}\text{O}_{110}\text{K}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.705	[20]
$(\text{NH}_4)_{13}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ca}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.650	[14]
$\text{K}_5\text{H}_6[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ca}(\text{H}_2\text{O})]$ ( $\text{K}^+$ )	1.641	[14]
$\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Bi}(\text{H}_2\text{O})]$ ( $\text{Bi}^{3+}$ )	1.436	[22]
$(\text{NH}_4)_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Y}(\text{H}_2\text{O})]$ ( $\text{Y}^{3+}$ )	1.747	[14]

$\text{K}_5\text{H}_7[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Y}(\text{H}_2\text{O})]$ ( $\text{Y}^{3+}$ )	1.794	[14]
$\text{K}_{0.5}(\text{NH}_4)_{11.5}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Eu}(\text{H}_2\text{O})]$ ( $\text{Eu}^{3+}$ )	1.763	[23]
$\text{K}_6\text{H}_6[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Eu}(\text{H}_2\text{O})]$ ( $\text{Eu}^{3+}$ )	1.760	[23]
$\text{K}_2\text{NaEu}_3(\text{H}_2\text{O})_{14}(\text{HNA})_5[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Eu}(\text{H}_2\text{O})]$ ( $\text{Eu}^{3+}$ )	1.736	[42]
$\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ce}(\text{H}_2\text{O})]$ ( $\text{Ce}^{3+}$ ) Synchrotron	1.728	This work
$\text{K}_{12}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{Ce}(\text{H}_2\text{O})]$ ( $\text{Ce}^{3+}$ ) MoKa	1.723	This work
$(\text{NH}_4)_{11}[\text{P}_5\text{W}_{30}\text{O}_{110}\text{U}(\text{H}_2\text{O})]$ ( $\text{U}^{4+}$ )	1.931	[23]
$\text{K}_3\text{H}_8[\text{P}_5\text{W}_{30}\text{O}_{110}\text{U}(\text{H}_2\text{O})]$ ( $\text{U}^{4+}$ )	1.998	[23]

[a] Distances between the encapsulated metal cation and equatorial plane through five P atoms. [b]  $\text{H}_2\text{biim}$ : 2,2'-biimidazole. [c] PEG400: polyethylene glycol. [d] PAA5000: poly(allylamine). [e] Hina: isonicotinic acid. [f] Hptz: 5-phenyl-1H-tetrazole. [g] dimb: 1,3-di(1H-imidazol-1-yl)benzene. [h] Httbz: 1-(tetrazo-5-yl)-4-(triazol-1-yl)benzene. [i] bpz: 3,3',5,5'-tetramethyl-4,4'-bipyrazole. [j] HNA: Protonated nicotinate.

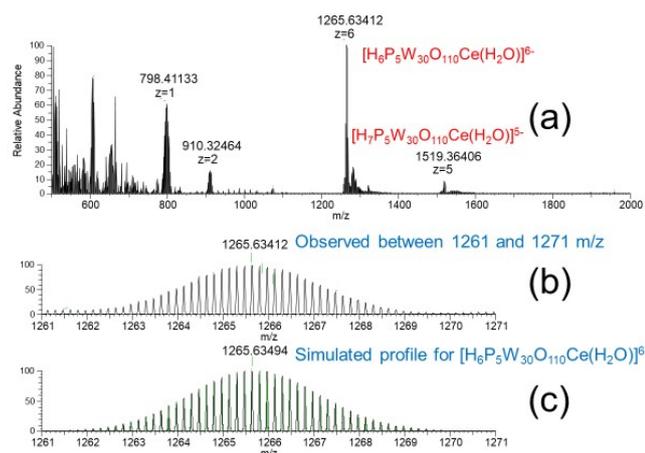


**Figure 2.** (a) Distances between encapsulated cations and equatorial plane vs. charge of encapsulated cations and (b) ball-and-stick representation of mono-

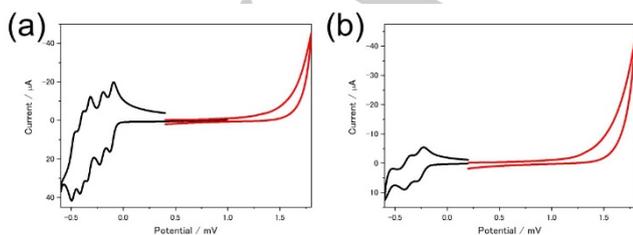
cation-encapsulated Preyssler-type phosphotungstate. Green, blue, black, red, and orange balls indicate W, P, encapsulated cation, O, and (H<sub>2</sub>O) O, respectively. Dotted line indicates equatorial plane of the Preyssler ion through five P atoms. Data are listed in Table 2.

In order to confirm the stability of the Preyssler structure in solution, ESI-MS was performed after the K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)] was dissolved in CH<sub>3</sub>CN-H<sub>2</sub>O mixed solution. The ESI-MS profile assignable to H<sub>6</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce<sup>3+</sup>(H<sub>2</sub>O)]<sup>6-</sup> was observed (Figure 3), indicating that [P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce<sup>3+</sup>(H<sub>2</sub>O)]<sup>12-</sup> was present in the solution.

We also performed cyclic voltammetry measurements in several solutions. Well-defined reversible redox couples corresponding to the reduction of W in the molecule were observed in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH 4.5) (Figure 4). No oxidation peaks of Ce<sup>3+</sup> were observed in either solution. In 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH 4.5) solution, the redox couple Ce<sup>4+/3+</sup> in Ce-containing polyoxotungstates such as [Ce(SiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>n-</sup> (0.323 V), [Ce(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>n-</sup> (0.424 V), [Ce(P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>]<sup>n-</sup> (0.365 V), [Ce(SiW<sub>11</sub>O<sub>39</sub>)]<sup>n-</sup> (0.581 V), [Ce(PW<sub>11</sub>O<sub>39</sub>)]<sup>n-</sup> (0.747 V), and [Ce(P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)]<sup>n-</sup> (0.654 V), has been observed.<sup>[33, 39]</sup> However, we did not observe any redox couple corresponding to Ce<sup>4+/3+</sup> until 1.80 V.



**Figure 3.** High-resolution ESI-MS of K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]. (a)  $m/z = 500$ – $2000$ . (b) enlarged  $m/z = 1261$ – $1271$ , and (c) simulated profile for [H<sub>6</sub>P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]<sup>6-</sup>.



**Figure 4.** Cyclic voltammograms of K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)] dissolved in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and (b) 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH 4.5) solution. Black and red lines represent the reduction and oxidation regions, respectively.

## Conclusions

We performed single-crystal X-ray structure analysis of the K salt of Ce-encapsulated Preyssler-type phosphotungstate, K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)] for the first time and showed that the encapsulated Ce is located in one of the side cavities with one coordinating H<sub>2</sub>O molecule. Through BVS calculations and comparison of the encapsulated position with other metal-encapsulated derivatives, we provide evidence that the oxidation state of the redox-inactive Ce is 3+.

## Experimental Section

**Materials:** All chemicals were of reagent grade and were used as obtained. Deionized H<sub>2</sub>O was prepared using a water purification system (Millipore, Elix). The compound, K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]·23H<sub>2</sub>O, was prepared according to a previously reported method<sup>[41]</sup> and the structure was confirmed by <sup>31</sup>P NMR and IR spectroscopy.

**Recrystallization:** K<sub>12</sub>[P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>Ce(H<sub>2</sub>O)]·23H<sub>2</sub>O (0.30 g) was dissolved in H<sub>2</sub>O (1.0 mL) and heated at 80 °C using a metal bath. Single crystals were obtained after the compound had been cooled to room temperature.

### X-ray crystallography.

Single crystals suitable for X-ray diffraction were selected using a microscope and mounted on a goniometer head using a LithoLoop. Intensity data were collected at 100 K on a Rigaku 1/4χ goniometer with a PILATUS3 X CdTe 1M detector using synchrotron radiation ( $\lambda = 0.4126$  Å) monochromated by a Si (311) double crystal. Data reduction was performed using RAPID AUTO. Absorption correction was applied using ABCOR. The structure was solved by a direct method and was refined using the SHELXL program<sup>[46]</sup> on WinGX.<sup>[47]</sup> All atoms in the POM framework, except for the O atom of the coordinating H<sub>2</sub>O molecule and K counter-cations, were refined anisotropically. Hydrogen atoms on water molecules were not located. Only three K cations in the asymmetric unit were found with a site occupancy of 1.0 the other three were severely disordered between six positions with a site occupancy of 0.5. Further details of the crystal structure investigation can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de; [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-2063590.

In addition single crystal structure analysis using a common single-crystal X-ray analysis equipment was performed. Single crystals suitable for X-ray diffraction were mounted on a goniometer head using a MiTeGen MicroMount. Intensity data were collected at 100 K on a Bruker SMART APEXII diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) monochromated by a multilayered confocal mirror. Data reduction and space group determination were carried out using the Bruker APEXIII suite. Absorption correction was applied using SADABS (Bruker). The structure was solved by a direct method<sup>[48]</sup> and was refined using the SHELXL<sup>[46]</sup> program running on the ShelXle<sup>[49]</sup> interface. W, Ce, and P atoms in the POM framework, as well as K counter-cations, were refined anisotropically. All O atoms, including crystal H<sub>2</sub>O molecules, were refined isotropically. Hydrogen atoms on water molecules were not located. The positions of K cations and crystal H<sub>2</sub>O were determined based on single-crystal data collected with synchrotron radiation. Further details of the crystal structure analysis can be found in the Supporting Information.

**Other analytical techniques.** High-resolution ESI-MS spectra were recorded on a LTQ Orbitrap XL (Thermo Fisher Scientific) with an accuracy of 3 ppm. Each sample (5 mg) was dissolved in 5 ml of H<sub>2</sub>O, and the solutions were diluted by CH<sub>3</sub>CN (final concentration: ~10 µg/ml). Cyclic voltammetry was performed on a CHI620D system (BAS Inc.) at ambient temperature. A glassy carbon working electrode (diameter, 3 mm), a platinum wire counter electrode, and an Ag/AgCl reference electrode (203 mV vs NHE at 25 °C) (3M NaCl, BAS Inc.) were used. Approximate formal potential values ( $E_{1/2}$  values) were calculated from the CVs as the average of cathodic and anodic peak potentials for corresponding oxidation and reduction waves.

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**Keywords:** Polyoxometalate • Preyssler-type phosphotungstate • Oxidation state • Ce • Single crystal X-ray structure analysis

- [1] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, **1983**.
- [2] C. L. Hill ed., *Chem. Rev.* **1998**, *98*, 1-390.
- [3] L. Cronin ed., *Chem. Soc. Rev.* **2012**, *41*, 7325-7648.
- [4] M. H. Alizadeh, S. P. Harmalkar, Y. Jeannin, J. Martin-Frère, M. T. Pope, *J. Am. Chem. Soc.* **1985**, *107*, 2662-2669.
- [5] O. H. Pardo Cuervo, G. P. Romanelli, J. A. Cubillos, H. A. Rojas, J. J. Martínez, *ChemistrySelect* **2020**, *5*, 4186-4193.
- [6] Z. Xu, K. Chen, M. Li, H. C., P. Yin, *Chem. Commun.* **2020**, *56*, 5287-5290.
- [7] D. Kobayashi, Y. Ouchi, M. Sadakane, K. Unoura, H. Nabika, *Chem. Lett.* **2017**, *46*, 533-535.
- [8] T. Iwano, S. Miyazawa, R. Osuga, J. N. Kondo, K. Honjo, T. Kitao, T. Uemura, S. Uchida, *Commun. Chem.* **2019**, *2*, 1-8.
- [9] L. Chen, K. A. San, M. J. Turo, M. Gembicky, S. Fereidouni, M. Kalaj, A. M. Schimph, *J. Am. Chem. Soc.* **2019**, *141*, 20261-20268.
- [10] S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Arino, A. Camon, M. Evangelisti, F. Luis, M. J. Martínez-Perez, J. Sese, *J. Am. Chem. Soc.* **2012**, *134*, 14982-14990.
- [11] C. Kato, R. Machida, R. Maruyama, R. Tsunashima, X. M. Ren, M. Kurmoo, K. Inoue, S. Nishihara, *Angew. Chem. Int. Ed.* **2018**, *57*, 13429-13432.
- [12] I. Creaser, M. C. Heckel, R. J. Neitz, M. T. Pope, *Inorg. Chem.* **1993**, *32*, 1573-1578.
- [13] M. N. K. Wihadi, A. Hayashi, T. Ozeki, K. Ichihashi, H. Ota, M. Fujibayashi, S. Nishihara, K. Inoue, N. Tsunoji, T. Sano, M. Sadakane, *Bull. Chem. Soc. Jpn* **2020**, *93*, 461-466.
- [14] K.-C. Kim, M. T. Pope, G. J. Gama, M. H. Dickman, *J. Am. Chem. Soc.* **1999**, *121*, 11164-11170.
- [15] A. Haider, K. Zarschler, S. A. Joshi, R. M. Smith, Z. G. Lin, A. S. Mougharbel, U. Herzog, C. E. Muller, H. Stephan, U. Kortz, *Z. anorg. allgem. Chem.* **2018**, *644*, 752-758.
- [16] C. Kato, K. Y. Maryunina, K. Inoue, S. Yamaguchi, H. Miyaoka, A. Hayashi, M. Sadakane, R. Tsunashima, S. Nishihara, *Chem. Lett.* **2017**, *46*, 602-604.
- [17] M.-X. Liang, C.-Z. Ruan, D. Sun, X.-J. Kong, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng, *Inorg. Chem.* **2014**, *53*, 897-902.
- [18] A. Hayashi, H. Ota, X. López, N. Hiyoshi, N. Tsunoji, T. Sano, M. Sadakane, *Inorg. Chem.* **2016**, *55*, 11583-11592.
- [19] A. Hayashi, M. N. K. Wihadi, H. Ota, X. López, K. Ichihashi, S. Nishihara, K. Inoue, N. Tsunoji, T. Sano, M. Sadakane, *ACS Omega* **2018**, *3*, 2363-2373.
- [20] T.-P. Hu, Y.-Q. Zhao, Z. Jagličić, K. Yu, X.-P. Wang, D. Sun, *Inorg. Chem.* **2015**, *54*, 7415-7423.
- [21] Y.-Q. Zhao, K. Yu, L.-W. Wang, Y. Wang, X.-P. Wang, D. Sun, *Inorg. Chem.* **2014**, *53*, 11046-11050.
- [22] A. Hayashi, T. Haioka, K. Takahashi, B. S. Bassil, U. Kortz, T. Sano, M. Sadakane, *Z. anorg. allg. Chem.* **2015**, *641*, 2670-2676.
- [23] M. H. Dickman, G. J. Gama, K.-C. Kim, M. T. Pope, *J. Cluster Sci.* **1996**, *7*, 567-583.
- [24] M. R. Antonio, M.-H. Chiang, *Inorg. Chem.* **2008**, *47*, 8278-8285.
- [25] M.-H. Chiang, M. R. Antonio, L. Soderholm, *Dalton Trans.* **2004**, 3562-3567.
- [26] J. A. Fernández, X. López, C. Bo, C. de Graaf, E. J. Baerends, J. M. Poblet, *J. Am. Chem. Soc.* **2007**, *129*, 12244-12253.
- [27] K. Niinomi, S. Miyazawa, M. Hibino, N. Mizuno, S. Uchida, *Inorg. Chem.* **2017**, *56*, 15187-15913.
- [28] K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed.* **1997**, *36*, 1445-1448.
- [29] M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed.* **2000**, *39*, 2914-2916.
- [30] J. C. Liu, Q. Han, L.-J. Chen, J.-W. Zhao, C. Streb, Y.-F. Song, *Angew. Chem. Int. Ed.* **2018**, *57*, 8416-8420.
- [31] B. S. Bassil, M. H. Dickman, I. Römer, B. v. d. Kammer, U. Kortz, *Angew. Chem. Int. Ed.* **2007**, *46*, 6192-6195.
- [32] M. Sadakane, A. Ostuni, M. T. Pope, *J. Chem. Soc., Dalton Trans.* **2002**, 63-67.
- [33] M. Sadakane, M. H. Dickman, M. T. Pope, *Inorg. Chem.* **2001**, *40*, 2715-2719.
- [34] K. Stroobants, E. Moelants, H. G. T. Ly, P. Proot, K. Bartik, T. N. Parac-Vogt, *Chem. Eur. J.* **2013**, *19*, 2848-2858.
- [35] K. Suzuki, J. Jeong, K. Yamaguchi, N. Mizuno, *New J. Chem.* **2016**, *40*, 1014-1021.
- [36] H. M. Qasim, W. W. Ayass, P. Donfack, A. S. Mougharbel, S. Bhattacharya, T. Nisar, T. Balster, A. Solé-Daura, I. Römer, J. Goura, A. Materny, V. Wagner, J. M. Poblet, B. S. Bassil, U. Kortz, *Inorg. Chem.* **2019**, *58*, 11300-11307.
- [37] M. R. Antonio, L. Soderholm, *Inorg. Chem.* **1994**, *33*, 5988-5993.
- [38] M. R. Antonio, L. Soderholm, C. W. Williams, N. Ullah, L. C. Francesconi, *J. Chem. Soc., Dalton Trans.* **1999**, 3825-3830.
- [39] N. Haraguchi, Y. Okaue, T. Isobe, Y. Matsuda, *Inorg. Chem.* **1994**, *33*, 1015-1020.
- [40] F. Wang, Z. Lang, L. Yan, A. Stroppa, J. M. Poblet, C. de Graaf, *APL Materials* **2021**, *9*.
- [41] K. Takahashi, T. Sano, M. Sadakane, *Z. anorg. allg. Chem.* **2014**, *640*, 1314-1321.
- [42] Y. Lu, Y. Li, E. Wang, X. Xu, Y. Ma, *Inorg. Chim. Acta*, **2007**, *360*, 2063-2070.
- [43] Z. Zhang, S. Yao, Y. Li, Q. Shi, E. Wang, *J. Coord. Chem.* **2009**, *62*, 3259-3267.
- [44] J. Du, M.-D. Cao, S.-L. Feng, F. Su, X.-J. Sang, L.-C. Zhang, W.-S. You, M. Yang, Z.-M. Zhu, *Chem. Eur. J.* **2017**, *23*, 14614-14622.
- [45] H.-M. Zhao, H.-M. Gan, L. Zhao, Z.-M. Su, *Inorg. Chem. Commun.* **2020**, *113*.

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- [46] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3-8.  
[47] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849-854.  
[48] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.
- [49] C. B. Hubschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.

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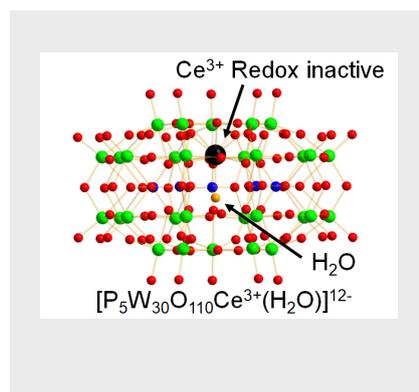
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*K. Shitamatsu, T. Kojima, P. G. Waddell, Sugiarto, H. E. Ooyama, R. J. Errington, M. Sadakane\**

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