Determination of the protonation state of $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$ and the stability constant of $[\text{Ag(H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^3-$ in aqueous solution

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ABSTRACT
By employing elemental analysis, $^{31}$P NMR, pH, and conductivity measurements, the protonated state of lacunary heteropolyoxotungstophosphates in aqueous solution, $[\text{PW}_{11}\text{O}_{39}]^-$, is determined to be $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$. Using it as ligand, a complex of $[\text{Ag(H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^3-$ is formed. An electrochemical cell is designed as follows: $(-)$ Hg, $\text{Hg}_2\text{Cl}_2$ $| [\text{Ag(H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^3-$ (aq) $| \text{Ag(s)}$ $(+)$ (salt bridge is saturated KNO$_3$ solution). By measuring the electromotive force of the cell, the stability constant of $[\text{Ag(H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^3-$ in aqueous solution is determined to be $4.34 \times 10^3$ ($25^\circ\text{C}$).

1. Introduction
Lacunary polyoxometalates (POMs) are a class of inorganic oxygen-containing ligands which can form stable complexes with metal ions [1, 2]. In recent years, homogenous molecular water oxidation catalysts of cobalt and ruthenium-containing POM complexes have attracted attention because they possess high stability toward oxidative degradation [3]. Their stability in aqueous solution has been of concern, especially for cobalt ion complexes [4]. Usually, the stability of water oxidation catalysts has been studied through qualitative technologies such as NMR, UV, dynamic light scattering, and capillary electrophoresis [5]. Therefore, it is significant to study the stability quantitatively for understanding the catalytic oxidation mechanism.

In the 1960s, Baker and Pope reported a general structural category of heteropolyoxometalates, formulated as $[\text{H}_n\text{M}^{m+n}\text{O}_{6}^x\text{W}_{11}\text{O}_{30}]^{(14-x-m)-}$ [6], the structure of which is a modification of the well-known...
12-tungsto Keggin structure, where octahedrally coordinated $M^{m+}$ replaces just one of 12 octahedral $W$ atoms in the Keggin structure (scheme 1). This category of compounds can be considered as transition metal complexes formulated as \([M^{m+}(H_2O)(X^{xW_{11}O_{39}})]^{-}\)\((14-x-m)\), where the lacunary heteropolyoxometallate anion \(XW_{11}O_{39}\) is a ligand. A series of complexes have been reported \([7, 8]\). \(PW_{11}O_{39}\) is a classical lacunary heteropolyanion ligand, which are inorganic ligands to form stable complexes with transition metal \([9]\) and lanthanide ions \([10]\). However, the charge of the \(PW_{11}O_{39}^–\) anion in aqueous solution and solid state is inconsistent in the reported literature. As reported \([11]\), the solid sodium and potassium salts are formulated as $Na_7PW_{11}O_{39}$ and $K_7PW_{11}O_{39}$, in which the anion is considered as \([\alpha-PW_{11}O_{39}]^7−\). However, Beer et al. reported that the tetrabutylammonium salt is formulated as \((Bu_4N)_4H_3PW_{11}O_{39}\) in which the anion is \([\alpha-H_3PW_{11}O_{39}]^{4−}[12]\). In \((Bu_4N)_4[M(H_2O)(HPW_{11}O_{39})]\) \((M = Cu^{2+}, Co^{2+}, Mn^{2+}\) and \(Ni^{2+}\)) reported by Cavaleiro et al. \([13]\), the anion is \([HPW_{11}O_{39}]^6−\). In 2014, we determined accurately the protonated state of \([Ag(H_2O)(H_3PW_{11}O_{39})]^3−\) in aqueous solution, in which the ligand is \([\alpha-H_3PW_{11}O_{39}]^{4−}\) \([14]\). It is necessary to determine the state of the anion of \(K_4[H_3PW_{11}O_{39}]\cdot14H_2O\) in aqueous solution.

$Ag^+$ can catalyze water oxidation with $S_2O_8^{2−}$ efficiently \([15]\). In 2014, our group \([14]\) reported that \([Ag(H_2O)(H_3PW_{11}O_{39})]^3−\) (abbreviated as \([Ag(H_2O)L]^3−\)) is a better molecular catalyst than AgNO$_3$, in which the ligand \([H_3PW_{11}O_{39}]^{4−}\) plays important roles in both the transmission of electron and proton, and the redox performance of $Ag^+$ is improved. However, there was a concern about the stability of \([Ag(H_2O)L]^3−\) in the catalysis reaction. Although its stability has been investigated by NMR, UV–visible absorption spectra, dynamic light scattering, and cyclic voltammetry, it is still necessary to understand its stability quantitatively with the stability constant of complexes. Based on the work, the stability constant of \([Ag(H_2O)L]^3−\) in aqueous solution is studied.

2. Experimental

2.1. General methods and materials

All reagents and chemicals were purchased from commercial sources and used without purification. The elemental analyses of K, P, and W were performed on an ICP-PRODIGY analyzer. The IR spectrum was recorded using KBr pellets on a TENSOR27 Bruker AXS spectrometer from 4000 to 400 cm$^{-1}$. TG analysis was performed on a Pyris Diamond TG/DTA thermal analyzer at a heating rate of 10 °C min$^{-1}$ in air. X-ray powder diffraction data were collected on a D8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). $^{31}P$ NMR was performed in a Bruker AVANCE500 spectrometer with a heavy water lock. Conductivity was measured in a DDS-11A conductivity meter. The pH was determined in a pHS-3C precise pH meter. Electromotive force (E.M.F.) measurement was carried out in a UJ-25 type potential difference meter with saturated calomel electrode and silver electrode as negative and positive electrodes, respectively. All experiments were carried out in ultrapure water with conductivity of 1.6 us cm$^{-1}$.

2.2. Determination of $[H_3PW_{11}O_{39}]^{4−}$ in aqueous solution

Potassium 11-tungstophosphate was prepared as reported \([11]\) and recrystallized three times to further improve the purity of the product. IR (KBr, cm$^{-1}$): 1084, 1043 (P–O$\equiv$), 953 (W=O$\equiv$), 900, 856 (W–O–W), 800,

\[\text{Scheme 1. Schematic diagram of } \alpha-PW_{11}O_{39}^7− \text{ formation by } [WO] \text{ departure from saturated Keggin structure } \alpha-PW_{12}O_{40}^3−.\]
730 (W–Oc–W) (figure S1). Anal. Calcd for K₄[H₃PW₁₁O₃₉]·14H₂O: K, 5.02%; P, 0.99%; W, 65.48%. Found: K, 4.92%; P, 0.97%; W, 67.11%. TG: The weight loss was 8.03% from 30 to 470 °C (theoretical value: 8.16%) (figure S2). Therefore, the composition was determined to be K₄[H₃PW₁₁O₃₉]·14H₂O.

For K₄[H₃PW₁₁O₃₉]·14H₂O solution with concentrations of 1.0, 0.8, 0.6, 0.4, and 0.2 mM, the pH values were measured by a pH5-3C precise pH meter. For K₄[H₃PW₁₁O₃₉]·14H₂O solution with concentrations of 10.0, 8.0, 6.0, 4.0, and 2.0 mM, conductivities were determined at 19 °C by a DDS-11A meter that was adjusted with 0.1 mol L⁻¹ KCl solution with the standard conductivity of 114 S cm⁻¹. The experimental data are listed in tables 1 and 2.

2.3. The stability constant of [Ag(H₂O)L]³⁻ in aqueous solution

K₃[H₃AgPW₁₁O₃₉]·12H₂O was synthesized and characterized according to our published work [14].

For K₃[H₃AgPW₁₁O₃₉]·12H₂O solution with concentrations of 1.0, 0.8, 0.6, 0.4, and 0.2 mM, pH values were measured by a pH5-3C precise pH meter and the experimental data are listed in table 3.

KI solution (2.5 mL of 10 mM) was added to 20 mL of 1.0 mM [Ag(H₂O)L]³⁻ solution dropwise, forming a yellow AgI precipitate. The pH before and after the reaction was measured with a pH5-3C precise pH meter and the experimental data are listed in table 4.

As shown in scheme 2, the galvanic cell with the configuration of (−) Hg, Hg₂Cl₂ [Ag(H₂O)L]³⁻ (aq) | Ag(s) (+) (salt bridge is saturated KNO₃ solution) was designed to determine the E.M.F. The experimental data of [Ag(H₂O)L]³⁻ solution with concentrations of 1.6, 1.2, 1.0, 0.8, 0.6, 0.4, and 0.2 mM at 25 °C are listed in table 5.

Table 1. pH values of K₄[H₃PW₁₁O₃₉]·14H₂O solution.

| C × 10⁻³ (mol L⁻¹) | pH | 1st | 2nd | 3rd | Mean pH | RSD (n = 3, %) |
|-------------------|----|-----|-----|-----|---------|---------------|
| 1.0               | 5.57 | 5.57 | 5.59 | 5.58 | 1.22    |
| 0.8               | 5.63 | 5.60 | 5.62 | 5.62 | 1.72    |
| 0.6               | 5.72 | 5.71 | 5.71 | 5.71 | 0.71    |
| 0.4               | 5.85 | 5.83 | 5.81 | 5.83 | 1.41    |
| 0.2               | 5.95 | 5.91 | 5.93 | 5.93 | 1.41    |

Table 2. Conductivity of K₄[H₃PW₁₁O₃₉]·14H₂O solution.

| C × 10⁻³ (mol L⁻¹) | Conductivity (S cm⁻¹) | Molar conductivity(∧)m (S m² mol⁻¹) |
|-------------------|------------------------|----------------------------------|
| 10                | 4.78 × 10⁻¹            | 478                              |
| 8.0               | 3.93 × 10⁻¹            | 491                              |
| 6.0               | 3.10 × 10⁻¹            | 517                              |
| 4.0               | 2.21 × 10⁻¹            | 553                              |
| 2.0               | 1.22 × 10⁻¹            | 610                              |

Table 3. pH values of [Ag(H₂O)L]³⁻ solution.

| C × 10⁻³ (mol L⁻¹) | pH | 1st | 2nd | 3rd | Mean pH | RSD (n = 3, %) | Dissociation degree of H⁺ (%) |
|-------------------|----|-----|-----|-----|---------|---------------|-----------------------------|
| 1.0               | 5.60 | 5.60 | 5.59 | 5.60 | 0.71    | 0.25           |
| 0.80              | 5.66 | 5.66 | 5.65 | 5.66 | 1.58    | 0.27           |
| 0.60              | 5.76 | 5.73 | 5.72 | 5.74 | 1.73    | 0.30           |
| 0.40              | 5.88 | 5.84 | 5.84 | 5.85 | 2.35    | 0.35           |
| 0.20              | 5.96 | 5.97 | 5.96 | 5.96 | 0.71    | 0.55           |
3. Results and discussion

3.1. Determination of α-[H₃PW₁₁O₃₉]⁴⁻ in aqueous solution

We first investigated the protonated state of K₄[H₃PW₁₁O₃₉]·14H₂O. Elemental analysis shows that the molar ratio of K and P is 4.08:1 for the synthesized solid potassium salt of lacunary Keggin phosphotungstate, indicating that three hydrogen protons have to be introduced to balance the charge. Therefore, the solid is formulated as K₄[H₃PW₁₁O₃₉]·14H₂O. When dissolved in water, the pH values are 5.58–5.93 for the solutions with concentrations of 0.2–1.0 mM (table 1), indicating that the lacunary POM anion is a very weak acid, or that H⁺ ions are hardly dissociated from the POM anion. Therefore, the main state in aqueous solution is deduced to be [H₃PW₁₁O₃₉]⁴⁻. As listed in table 2, the molar conductivities of K₄[H₃PW₁₁O₃₉]·14H₂O solutions are 478–610 s m² mol⁻¹. According to the literature [16], this indicates a complex of M₄A type, demonstrating that the existing state of {PW₁₁O₃₉} in aqueous solution is [H₃PW₁₁O₃₉]⁴⁻.

As shown in figure 1(a), only a single ³¹P NMR signal at 10.67 ppm is observed for [H₃PW₁₁O₃₉]⁴⁻ aqueous solution, which suggests that [H₃PW₁₁O₃₉]⁴⁻ is stable in aqueous solution, and the dominant species for the lacunary Keggin tungstophosphate anions.

Table 4. pH values of [Ag(H₂O)L]³⁻ solution before and after KI titration.

| Group | V[Ag(H₂O)L]³⁻ (mL) | Vₛ (mL) | pH before titration | pH after titration |
|-------|------------------|---------|---------------------|-------------------|
| 1st   | 20.00            | 2.50    | 5.62                | 5.65              |
| 2nd   | 20.00            | 2.50    | 5.58                | 5.60              |
| 3rd   | 20.00            | 2.50    | 5.61                | 5.63              |

Table 5. The E.M.F. of (−) Hg, Hg₂Cl₂ [Ag(H₂O)L]³⁻ (aq) | Ag(s) (+) and K₀ of [Ag(H₂O)L]³⁻ for the different concentrations and ionic strengths.

| C × 10⁻³ (mol L⁻¹) | E(V) | Mean E(V) | I × 10⁻³ (mol L⁻¹) | ⁰[Ag⁺] × 10⁻³ (mol L⁻¹) | bₙ | K₀ × 10³ |
|-------------------|------|-----------|-------------------|-------------------------|----|---------|
| 1.6               | 0.3678 | 0.3659   | 0.3697            | 0.3678                  | 9.6 | 0.85    | 0.75 | 0.75 | 1.04 |
| 1.2               | 0.3606 | 0.3606   | 0.3612            | 0.3606                  | 7.2 | 0.60    | 0.76 | 0.60 | 1.67 |
| 1.0               | 0.3565 | 0.3560   | 0.3558            | 0.3561                  | 6.0 | 0.50    | 0.78 | 0.50 | 2.00 |
| 0.8               | 0.3510 | 0.3522   | 0.3522            | 0.3518                  | 4.8 | 0.42    | 0.79 | 0.38 | 2.15 |
| 0.6               | 0.3458 | 0.3461   | 0.3461            | 0.3460                  | 3.6 | 0.32    | 0.82 | 0.28 | 2.73 |
| 0.4               | 0.3370 | 0.3372   | 0.3368            | 0.3370                  | 2.4 | 0.22    | 0.85 | 0.18 | 3.71 |
| 0.2               | 0.3256 | 0.3256   | 0.3250            | 0.3254                  | 1.2 | 0.13    | 0.89 | 0.07 | 4.14 |

<sup>a</sup>⁰[Ag⁺] can be obtained according to \( E = 0.5579 + 0.05915 \log{[Ag⁺]} + 0.05915 \log{[Ag⁺]} \)

<sup>b</sup>\( b_n \) can be obtained according to \( \log{b_n} = -\frac{4[Ag⁺][Ag⁺]}{1 + [Ag⁺]} \).

<sup>c</sup>\( K₀ = \frac{C[Ag⁺][Ag⁺]}{[Ag(H₂O)]³⁻} \).
3.2. Determination of the stability constant of \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) with E.M.F.

As reported \cite{14}, the following ionization reaction occurs when \(\text{K}_3[\text{H}_3\text{AgPW}_{11}\text{O}_{39}] \cdot 12\text{H}_2\text{O}\) is dissolved in water:

\[
\text{K}_3[\text{H}_3\text{AgPW}_{11}\text{O}_{39}] \cdot 12\text{H}_2\text{O} \rightarrow [\text{Ag(H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^{3−} + 3\text{K}^+ + 11\text{H}_2\text{O}
\]

(1)

As shown in figure 1(b), one \(^{31}\text{P}\) NMR signal at \(δ = −11.00 \text{ ppm}\) is observed for \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) solution, illustrating that \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) is the main state in aqueous solution. The pH values of \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) solutions with concentrations of 0.2–1.0 \(\text{mM}\) are 5.60–5.96, from which the dissociation degree of \(\text{H}^+\) in \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) is deduced to be 0.25–0.55\% (table 3). Further, after adding KI into \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) solution to precipitate \(\text{Ag}^+\) as \(\text{AgI}\), the pH of the filtrate is hardly changed (table 4), which shows that dissociation of \(\text{Ag}^+\) from the complex does not lead to dissociation of \(\text{H}^+\) ions in \([\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4−}\). Thus, it is deduced that the \([\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4−}\) ligand remains in its state in aqueous solution after \(\text{Ag}^+\) dissociated from \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\).

Accordingly, the ionization equilibrium of \([\text{Ag(H}_2\text{O})\text{L}]^{3−}\) is described as follows:

\[
[\text{Ag(H}_2\text{O})\text{L}]^{3−} \rightleftharpoons \text{Ag}^+ + \text{L}^{4−} + \text{H}_2\text{O}
\]

(2)

The stability constant \(K_a\) is deduced as follows:

\[
K_a = \frac{[\text{AgL}^{3−}] \cdot [\text{L}^{4−}]}{[\text{Ag}^+] \cdot [\text{L}^{4−}]} = \frac{[\text{AgL}^{3−}] \cdot [\text{L}^{4−}]}{[\text{Ag}^+] \cdot [\text{L}^{4−}]} = K_c \cdot \frac{[\text{AgL}^{3−}]}{[\text{Ag}^+] \cdot [\text{L}^{4−}]}
\]

(3)

\[
K_c = \frac{[\text{AgL}^{3−}]}{[\text{Ag}^+] \cdot [\text{L}^{4−}]} = \frac{C - [\text{Ag}^+]}{[\text{Ag}^+]^2}
\]

(4)

An electrochemical cell is designed (salt bridge is saturated KNO\textsubscript{3} solution) as follows:

\[
(−) \text{Hg}, \text{Hg}_2\text{Cl}_2 || [\text{Ag(H}_2\text{O})\text{L}]^{3−}(\text{aq}) | \text{Ag(s)} (+)
\]

(5)

The electrode reactions:

\[
(−) 2\text{Hg} + 2\text{Cl}^{−} = 2\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^{−}
\]

(6)

\[
(+) [\text{Ag(H}_2\text{O})\text{L}]^{3−} + \text{e}^{−} = \text{Ag(s)} + \text{L}^{4−} + \text{H}_2\text{O}
\]

(7)

Figure 1. \(^{31}\text{P}\) NMR spectra for (a) \(\text{K}_4[\text{H}_3\text{PW}_{11}\text{O}_{39}] \cdot 19\text{H}_2\text{O}\) aqueous solution (~30\% \(\text{D}_2\text{O}\)) and (b) \(\text{K}_3[\text{H}_3\text{AgPW}_{11}\text{O}_{39}] \cdot 12\text{H}_2\text{O}\) aqueous solution (~30\% \(\text{D}_2\text{O}\)).
The E.M.F. at 25 °C:

\[ E = \phi_e - \phi_i = \phi^0_{(Ag^+/Ag)} + 0.05915 \log \gamma_{Ag^+} - \phi_{calomel} \]

where \( \phi_{calomel} = 0.2412 \text{ V} \), \( \phi^0_{(Ag^+/Ag)} = 0.7991 \text{ V} \) [17], and \( \gamma_{Ag^+} = \gamma_{Ag^+} [Ag^+] \) (\( \gamma_{Ag^+} \) represents the activity coefficient of \( Ag^+ \)). Therefore,

\[ E = 0.5579 + 0.05915 \log \gamma_{Ag^+} + 0.05915 \log [Ag^+] \]

For \([Ag(H_2O)l]^{3-}\) solution, \( \gamma_\pm (\gamma_\pm \) represents the average activity coefficient in the dilute solution, the activity coefficient of silver ions \( \gamma_{Ag^+} \) can replace \( \gamma_\pm \) approximately) at concentrations of 1.6, 1.2, 1.0, 0.8, 0.6, 0.4, and 0.2 mM is calculated through the Debye–Hückel limiting equation (see table 5 and Supplemental Material). The E.M.F. of the cell was determined and the data are listed in table 5. The concentrations of dissociated \( Ag^+ \) can be obtained (see table 5) according to equation (9). Then, \( K_c \) can be obtained by formula (4).

To eliminate the influence of the ionic strength (\( I \)) on the stability constant and obtain the activity stability constant \( K_a \), a plot of \( K_c \) against \( I \) is drawn (figure 2). By extrapolating to the ionic strength of 0, \( K_a \) of \([Ag(H_2O)l]^{3-}\) can be obtained [18] as \( 4.34 \times 10^3 \) at 25 °C.

4. Conclusion

The protonated state of lacunary Keggin type \( \alpha-[PW_{11}O_{39}] \) in aqueous solution is \([H_3PW_{11}O_{39}]^{4-}\). Furthermore, the stability constant of \([Ag(H_2O)(H_3PW_{11}O_{39})]^{3-}\) is determined to be \( 4.34 \times 10^3 \) by E.M.F. measurement. This is the first example of determining the stability constant of complexes of POM ligands.

Supplementary material

FTIR spectra, TG curve of \( K_4[H_3PW_{11}O_{39}] \cdot 14H_2O \) and deriving the concentration of \( Ag^+ \) in the solution are available online.

Disclosure statement

No potential conflict of interest was reported by the authors.
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