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Introduction

Water oxidation into O_2 , as a half-reaction, is the key step to sustainable energy systems, including water splitting into H_2 or the direct conversion of carbon dioxide into methanol. In the last few decades, a robust, fast, and inexpensive water oxidation catalyst (WOC) has been sought.¹⁻⁴ Since Meyer and coworkers reported the 'blue dimer'⁵ *cis*, *cis*-[(bpy)₂(H₂O)Ru^{III}ORu^{III}(H₂O)(bpy)₂]⁴⁺, a range of homogeneous molecular catalysts of metal–organic complexes containing manganese, iron, cobalt, ruthenium, iridium, *etc.* have been successively reported,⁶⁻¹⁶ and the catalytic activity and the chemical stability have been increased dramatically. In 2012, Sun *et al.*¹⁷ reported a mononuclear ruthenium complex [Ru(bda)(isoq)₂] with high catalytic activity (TOF > 300 s⁻¹) and chemical

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A 1D chain-like Ag(i)-substituted Keggin polyoxotungstophosphate, K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O, has been synthesized in a high yield and characterized by single-crystal X-ray diffraction, XRD, IR, TG/DTA and elemental analysis. When the polyoxotungstophosphate is dissolved in aqueous solutions, ³¹P NMR, MS and conductivity analyses indicate that a Ag(i) anion-complex formulated as $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is formed and is stable in a solution of pH 3.5–7.0. The oxidation of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ by S₂O₈²⁻ has been studied by ESR, UV-Visible spectroscopy, ³¹P NMR and UV-Raman spectroscopy. It was found that $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ can be oxidized to dominantly generate a dark green Ag(II) anion-complex $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ and a small amount of Ag(III) complex $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, simultaneously evolving O₂. Compared with $[Ag^I(2,2'-bpy)NO_3]$ and AgNO₃, $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ has the higher activity in chemical water oxidation. This illustrates that the $[PW_{11}O_{39}]^{7-}$ ligand plays important roles in both the transmission of electrons and protons, and in the improvement of the redox performance of silver ions. The rate of O₂ evolution is a first-order law with respect to the concentrations of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is proposed, in which the $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ and $[H_3Ag^{II}(PW_{11}O_{39}]^{3-}$ intermediates are determined and the rate-determining step is $[H_3Ag^{III}OPW_{11}O_{39}]^{2-}$ oxidizing water into H_2O_2 .

stability (TON = 8360 ± 91) for water oxidation, which is moderately comparable with the reaction rate of the oxygen-evolving complex of photosystem II *in vivo*.

However, for all the homogenous WOCs with organic ligands reported to date, one fatal flaw is that they are all oxidatively deactivated. In recent years, polyoxometalates have been selected as inorganic ligands for assembly into the catalysts, because they possess higher stability toward oxidative degradation.¹⁸ As homogenous molecular WOCs, a series of ruthenium- and cobalt-polyoxometalate complexes, including $[\{Ru_4O_4(OH)_2-(H_2O)_4\}(\gamma-SiW_{10}O_{36})_2]^{10-,19-25}$ $[Ru^{III}(H_2O)-(H_2O)_4](\gamma-SiW_{10}O_{36})_2]^{10-,19-25}$ $XW_{11}O_{39}^{5-}$ (X = Si and Ge),²⁶ [{Ru₃O₃(H₂O)Cl₂}(SiW₉O₃₄)],²⁷ $[Co_4(H_2O)_2(\alpha-B-PW_9O_{34})_2]^{10-28-30}$ $[CoMo_6O_{24}H_6]^{3-,31}$ $[Co_2Mo_{10}O_{38}H_4]^{6-,31}$ $[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]^{7-,32}$ and $Cs_{15}K^{-1}$ $[Co_9(H_2O)_6(OH)_3-(HPO_4)_2(PW_9O_{34})_3]$ (a heterogeneous catalyst),³³ have been reported. They exhibit high catalytic activity for water oxidation into O2 in photoinduced chemical oxidation and in electrocatalytic oxidation systems. For example, $[{Ru_4O_4(OH)_2(H_2O)_4}(\gamma-SiW_{10}O_{36})_2]^{10-}$ exhibits a peak catalytic performance of TOF > 450 h^{-1} in chemical oxidation²⁰ and 306 h⁻¹ at $\eta = 0.60$ V in electrochemical oxidation,²⁵ which exceed the values for Co- and Mn-systems based on organic ligands.^{34,35} [Co₄(H₂O)₂(α-B-PW₉O₃₄)₂]^{10-,30} a sandwich tetracobalt complex based on the [\alpha-B-PW9O34]9- ligand, has received significant attention because it consists of the earth



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[†]Electronic supplementary information (ESI) available: Structural diagram of $[H_3AgPW_{11}O_{39}]^{3-}$; XRD patterns, IR, TG/DTA, crystallographic data and selected bond lengths and angles of $K_3[H_3AgPW_{11}O_{39}]$ ·12H₂O; the isotopic patterns at m/z = 935.3751 for MS analysis of $K_3[H_3AgPW_{11}O_{39}]$ ·12H₂O solution; UV-visible spectra of the $[H_3AgPW_{11}O_{39}]^{3-}$ and $S_2O_8^{2-}$ solution. See DOI: 10.1039/c4dt01538j

abundant elements. As homogenous molecular catalysts, the issue of the stability of polyoxometalate complexes are more evident in the dispute about $[Co_4(H_2O)_2(\alpha-B-PW_9O_{34})_2]^{10-1}$ between Hill³⁶ and Finke.^{37,38} Clearly, polyoxomelates are promising ligands for developing homogenous molecular catalysts. In addition, polyoxometalate complexes, as molecular catalysts, are suitable for elucidating the catalytic mechanism of water oxidation, because of their stability and defined structures. Fukuzumi et al.26 proposed a catalytic mechanism of $[Ru^{III}(H_2O)XW_{11}O_{39}]^{5-}$ (X = Si and Ge), involving the multistep oxidation of Ru atoms and the formation of O-O bonds. Employing DFT calculations on the mechanism of the single-Ru-substituted polyoxometalates, Su et al.³⁹ indicated that the polytungstate ligands act as the most favorable proton acceptor in the O-O bond formation, with an energy barrier of 28.43 kcal mol⁻¹. However, currently, WOCs based on polyoxometalate ligands are limited to Co(II) and Ru(III)/(IV) complexes, and it would be interesting to develop polyoxometalate complex catalysts of other metal ions.

The Ag(I) ion is often used as a powerful catalyst for most $S_2O_8^{2-}$ oxidation reactions.⁴⁰ The kinetics and mechanism of Ag(1)-catalyzed water oxidation into O_2 by $S_2O_8^{2-}$ in aqueous solution have even been reported.^{40,41} In 2012, Li et al.⁴² prepared a Ag-based electrode with favorable activity for O₂ evolution and a lower overpotential in mild conditions. To the best of our knowledge, Ag(I) salts are the best homogenous molecular catalyst among the simple inorganic salts, including Co²⁺, Mn²⁺, Ru³⁺, etc. Catalytic activity could be improved by decorating central metal ions effectively by suitable ligands. However, organic ligands would capture radicals, one of the efficient oxidizing agents, which would lead to a loss of catalytic activity of Ag(1).⁴¹ Therefore, it would be a good choice to develop efficient WOCs of Ag(1) complexes based on polyoxometalates as ligands. Based on the considerations above, our attention has thus been focused on WOCs based on Ag(1)-polyoxometalate complexes.

Results and discussion

Synthesis and crystal structure

Employing $Na_9[A-PW_9O_{34}]\cdot 7H_2O$ as the raw material, a Ag(1)substituted Keggin polyoxotungstophosphate, the crystal of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$, has been synthesized in high

Table 1 Conductivity and K_a of $K_3[H_3Ag^{I}PW_{11}O_{39}]$ ·12H₂O solutions^a

^{*a*} Solution temperature: 18 °C. ^{*b*} $\Lambda_{\rm m} = K \times 10^{-3}/{\rm C}$. ^{*c*} $K_{\rm a} = [{\rm H}^+]^2/{\rm C}$.

yield. As shown in Table S1,† this is isomorphic with $K_{3.67}Ag_{0.33}H_2[AgPW_{11}O_{39}]\cdot9.25H_2O\cdotCH_3OH$, as reported by Nogueira *et al.*⁴³ In the crystal structure, Ag(1) ions, exhibiting an eight-coordination fashion, bridge monolacunary α -Keggin, forming a one-dimensional anionic $[Ag^IPW_{11}O_{39}]_n^{6n-}$ chain (Fig. S1†).⁴³ K⁺ ions, as counterions, are six-coordinated to the oxygen atoms of $[Ag^IPW_{11}O_{39}]^{6-}$ units and water molecules. The experimental and simulated PXRD patterns of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot12H_2O$ are shown in Fig. S2.† The diffraction peaks match well in key positions, indicating the crystal phase purity. For some peaks, the difference in intensity may be caused by the preferred orientation of the powder sample.

Formation and stability of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ in aqueous solution

When the crystal of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ is dissolved in water, the solution is at pH *ca.* 5 (Table 1) and exhibits only one single ³¹P NMR signal at $\delta = -11.00$ ppm (Fig. 1b–1e. The -0.57signal in Fig. 1e is attributed to $Na_2HPO_4-NaH_2PO_4$). The fact that there is only one signal illustrates that there is only one existential state of the {PW₁₁O₃₉} ligand in the solution. Compared with the ³¹P NMR of PW₁₁O₃₉, (Fig. 1a), it is found that the ³¹P NMR signal of the $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ solution shifts negatively. This results from the decrease in the interactions between the P atoms and the central O_a atoms due to the introduction of Ag(I) ions into the lacunary sites of PW₁₁O₃₉⁷⁻. This illustrates that a complex of Ag^+ and PW₁₁O₃₉⁷⁻ is formed.

As shown in Fig. 2, a MS spectrum of K₃[H₃Ag^IP- $W_{11}O_{39}$]·12H₂O solution exhibits several groups of m/z peaks in the range of 920-950. The main peak assignments are listed in Table S2.[†] It is found that there are two complex anions: $[H_{3}Ag^{I}PW_{11}O_{39}]^{3-}$ and $[H_{3}Ag^{I}(H_{2}O)PW_{11}O_{39}]^{3-}$. However, the above-mentioned ³¹P NMR indicates that there may be only one polyoxotungstophosphate complex species in the solution. The question is, which one? The ³¹P NMR chemical shift of K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O in solution is identical with that in the solid state,43 which demonstrates that the distances between the lacunary O atoms and the Ag ion are not changed observably when it is dissolved. Therefore, the valence sum calculation of the solid state is used to determine which is the most probable complex in solution. For $[H_3Ag^{I}PW_{11}O_{39}]^{3-}$, the Ag⁺ is a tetra-coordinated configuration. The valence sum of the Ag^+ is 0.855 (Table S3[†]), which cannot satisfy its valence. Therefore, it can be deduced that the complex should be



Fig. 1 ³¹P NMR spectra for solutions of (a) K_7 [PW₁₁O₃₉]·12H₂O in pure water; (b) K_3 [H₃Ag¹PW₁₁O₃₉]·12H₂O in pure water; (c) K_3 [H₃Ag¹P-W₁₁O₃₉]·12H₂O in HAc-NaAc buffer (pH = 3.5); (d) K_3 [H₃Ag¹P-W₁₁O₃₉]·12H₂O in HAc-NaAc buffer (pH = 5.5); and (e) K_3 [H₃Ag¹PW₁₁O₃₉]·12H₂O in Na₂HPO₄-NaH₂PO₄ buffer (pH = 7.0).



Fig. 2 Mass spectra for K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O solution.

unstable in solution. But, it could be generated in the high temperature and electric field of the MS analysis. For $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, the valence sum of the Ag^+ is 1.1712, which is closer to that in the solid state. This demonstrates that $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is more stable in solution. Combined with the features of substituted Keggin polyoxometalates,⁴⁴ therefore, it is deduced that $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ may be generated when $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ is dissolved in aqueous solution (as expressed in eqn (1)).

$$\begin{split} & K_3[H_3Ag^IPW_{11}O_{39}] \cdot 12H_2O + H_2O \\ & \rightarrow \left[H_3Ag^I(H_2O)PW_{11}O_{39}\right]^{3-} + 3K^+ + 12H_2O \end{split} \tag{1}$$

In order to further confirm the existence of $[H_3Ag^{I}(H_2O)-PW_{11}O_{39}]^{3-}$, the conductivity and the pH values were measured for the aqueous solutions of $K_3[H_3Ag^{I}PW_{11}O_{39}] \cdot 12H_2O$. As shown in Table 1, the degree of H^+ ion dissociation and its estimated K_a are ~0.1% and ~10⁻⁹ for the concentrations of 0.010–0.002 M, respectively. This illustrates that the H^+ ion dissociation in $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ is very slight and its contribution to the conductivity may be negligible. The molar conductivity values are in the range of 400–450 s m² mol⁻¹, indicating that the number of dissociated ions is 4, and that the corresponding compound is the M_3A model.⁴⁵ This confirms that the above conclusion is reasonable.

In order to determine the stability of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ in aqueous solutions at different pH values, the ³¹P NMR of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ solutions were measured in pH = 3.5, 5.5, and 7.0 buffers (Fig. 1c–e). Only one single ³¹P NMR signal is observed and kept at $\delta = -11.00$ ppm. This illustrates that $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is stable in pH 3.5–7.0 solutions.

Oxidation of [H₃Ag^I(H₂O)PW₁₁O₃₉]³⁻

As reported, $S_2O_8^{2-}$ was used to oxidize the coordinated metal ions into a high oxidation state in metal ions (Mn, Am, Tb, and Pr)-substituted polyoxotungstates, where lacunary polyoxometalate anions are used to stabilize the high oxidation states of the coordinated metal ions.⁴⁶⁻⁴⁹ In our work, when an excess of $Na_2S_2O_8$ is added to a colorless $[H_3Ag^I(H_2O)-PW_{11}O_{39}]^{3-}$ solution, a dark green solution is formed. The question is, what is the dark green species?

ESR analysis of oxidation of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$. In order to determine the oxidation state of Ag ions after the oxidation of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ by $S_2O_8^{2-}$, we carried out *in situ* ESR spectroscopy of the solutions of $Na_2S_2O_8 + K_3[H_3Ag^I-PW_{11}O_{39}] \cdot 12H_2O$ and $Na_2S_2O_8 + AgNO_3$ at 100 K. As shown in Fig. 3a, markedly anisotropic *g* factors ($g_{\parallel} = 2.345$ and $g_{\perp} =$ 2.058) and the anisotropic doublet hyperfine splittings ($A_{\parallel} =$ 44.1 G and $A_{\perp} = 23.1$ G) obtained from the solution of $Na_2S_2O_8$ + $K_3[H_3Ag^IPW_{11}O_{39}] \cdot 12H_2O$ agree well with those of the divalent silver ions.⁵¹⁻⁵⁵ Compared with the ESR spectrum of the $Na_2S_2O_8 + AgNO_3$ solution (Fig. 3b), the spectra are similar in fashion, but the corresponding parameters are not identical because the Ag(II) ions are located in different coordinated environments. This illustrates that the Ag(I) ions in $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ are oxidized into Ag(II) ions.

Paper



Fig. 3 ESR spectra of solutions of (a) $Na_2S_2O_8$ (0.26 M) + $K_3[H_3Ag^{l}-PW_{11}O_{39}]\cdot12H_2O$ (5.76 × 10^{-3} M), and (b) $Na_2S_2O_8$ (8.8 × 10^{-2} M) + AgNO₃ (1.18 × 10^{-3} M) at 100 K UV-visible spectra of oxidation of $[H_3Ag^{l}(H_2O)PW_{11}O_{39}]^{3-}$.



Fig. 4 UV-Visible spectra of solutions of (a) 7.0×10^{-3} M AgNO₃ and 8.8×10^{-2} M Na₂S₂O₈; (b) 6.0×10^{-3} M K₇[PW₁₁O₃₉]·12H₂O and 8.8×10^{-2} M Na₂S₂O₈; and (c) 6.0×10^{-3} M K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O and 8.8×10^{-2} M Na₂S₂O₈.

UV-Visible spectra of the oxidation of [H₃Ag^I(H₂O)- $PW_{11}O_{39}]^{3-}$. The UV-Visible spectra are recorded for (a) AgNO₃, (b) $K_7[PW_{11}O_{39}]$ ·12H₂O, and (c) $K_3[H_3Ag^IPW_{11}O_{39}]$ ·12H₂O in phosphate buffer solution (pH = 5.5) containing Na₂S₂O₈ (Fig. 4). For the solution of AgNO₃ and Na₂S₂O₈, only one band at 370 nm is observed, which is attributed to $Ag(m)^{50}$ (Fig. 4a). No absorption is observed in the region of 800-400 nm. For the solution of K₇[PW₁₁O₃₉]·12H₂O and Na₂S₂O₈, no absorption is also observed in the region of 800-350 nm (Fig. 4b). However, for solution of Na₂S₂O₈ and K₃[H₃Ag^IP- $W_{11}O_{39}$]·12H₂O, it is noted that two strong absorbance bands appear at 408 nm and 582 nm (Fig. 4c). Based on the position of the bands and the result of the ESR, it is reasonable to deduce that the band at 582 nm corresponds to the electron transition of $^2E_g {\rightarrow}^2T_{2g}$ of Ag(11) in an approximate six-coordinated environment and the band at 408 nm is attributed to the absorbance of Ag(III). Therefore, it is deduced that
$$\begin{split} & [H_{3}Ag^{I}(H_{2}O)PW_{11}O_{39}]^{3-} \text{ may be oxidized by } S_{2}O_{8}{}^{2-}\text{, generating } \\ & [H_{3}Ag^{II}(H_{2}O)PW_{11}O_{39}]^{2-} \text{ and } [H_{3}Ag^{III}OPW_{11}O_{39}]^{3-}\text{.} \end{split}$$



Fig. 5 ³¹P NMR spectra for a solution of $K_3[H_3Ag^{I}PW_{11}O_{39}]\cdot 12H_2O$ and excess of $Na_2S_2O_8$. (a) In pure water; in 0.01 M phosphate buffer solution (pH = 5.5), data were collected three times at one hour intervals, (b) 0 hour; (c) 1 hours; and (d) 2 hours.

³¹P NMR of the oxidation of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$. After an excess of Na2S2O8 is added to the aqueous solution of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, the ³¹P NMR signal of $[H_3Ag^I(H_2O) PW_{11}O_{39}^{3-}$ at -11.00 ppm disappears and a new single 31 P NMR signal at –13.9 ppm appears (Fig. 5a). To the best of our knowledge, the upfield ³¹P NMR chemical shift may result from two possible causes: polymerization of $[PW_{11}O_{39}]^{7-}$ into $[P_2W_{21}O_{71}]^{6-}$ or $[PW_{12}O_{40}]^{3-}$, or oxidation of Ag(I) into Ag(II) or Ag(III). The solution of $[PW_{11}O_{39}]^{7-}$ is stable between pH 2 and pH 6, and even in the presence of $S_2O_8^{2-.45-48}$ The condition in which the former reaction occurs should have acidized the $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ solution. In order to exclude the former cause, a phosphate buffer solution of pH 5.5 is carried out. It is found that the chemical shift of -13.9 ppm is also retained (Fig. 5b-d. The 0.12-0.04 signals in Fig. 5b-d are attributed to Na₂HPO₄-NaH₂PO₄). The buffer solution retains the acidity of the solution unchanged in the oxidation reaction

process, so that the polymerization reaction is not possible. If $[PW_{11}O_{39}]^{7-}$ was either degraded or oxidized into polyperoxotungastophosphates, they should have led to downfield and multiple ³¹P NMR chemical shifts. Therefore, considering that only one ³¹P NMR signal at -13.9 ppm appears in the solution of $Na_2S_2O_8$ and $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, it is inferred that the structure of the $[PW_{11}O_{39}]^{7-}$ ligand should remain unchanged during the oxidation reaction. The upfield ³¹P NMR chemical shift in the oxidation of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ should result from the increase in the oxidative state of the Ag atom due to the enhanced interaction between the Ag ions and the central O_a atoms, which was observed in oxidation of $[Ce^{III}(PW_{11}O_{39})_2]^{11-}$ into $[Ce^{IV}(PW_{11}O_{39})]^{3-.56}$ Combined with the ESR and UV-Visible spectra mentioned above, it is reasonable to hypothesize that $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is oxidized by $S_2O_8^{2-}$ into a Ag(II) complex (eqn (3)). In addition, it is found that the oxidation of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ into $[H_3Ag^{II}(H_2O) PW_{11}O_{39}$ ²⁻ is fast and almost complete under the experimental conditions.

In a phosphate buffer solution, as shown in Fig. 5, the chemical shift of $\delta \sim -13.9$ ppm, with a relative intensity of 1.00, is not only retained, but also a new weak signal at δ = $-15.06 \sim -15.08$ ppm, with a relative intensity of 0.10-0.18, emerges. This shows that $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ exists dominantly in the reaction system, and that another intermediate species, with a very low concentration, may be formed. It has even been reported⁴³ that Ag(III) ions may exist as AgO^+ in solution.⁵⁷⁻⁵⁹ Allen et al.⁵⁸ estimated by free energy data that the equilibrium constant K (25 °C) is ca. 2.2 \times 10⁻⁴ for the equation $(2Ag^{2+} + H_2O = AgO^+ + Ag^+ + 2H^+)$. Therefore, it can be deduced that a small amount of $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-1}$ may be oxidized into a Ag(III) complex species, [H₃Ag^{III}(O)- $PW_{11}O_{39}]^{3-}$. The reaction is described in eqn (5). The amount of $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ depends on the pH of the solutions. As the concentration of $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ is increased in pH 5.5 buffer solution, the weak 31 P NMR signal at δ –15.06 ~ -15.08 ppm appears. In pure water solution, the low pH value caused by the oxidation reactions inhibits the formation of $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$, so that the ³¹P NMR signal would not be observed.

UV-Raman spectra of the oxidation of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$. Fig. 6 shows the UV-Raman spectra for the solutions of $K_7[PW_{11}O_{39}]\cdot 12H_2O$, $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$, $K_7[PW_{11}O_{39}]\cdot 12H_2O$ and $Na_2S_2O_8$, and $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ and $Na_2S_2O_8$, and $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ and $Na_2S_2O_8$, as well as $Na_2S_2O_8$. For the solution of $K_7[PW_{11}O_{39}]\cdot 12H_2O$, the peaks at 963(m) cm⁻¹ and 903(w) cm⁻¹ are observed, which are attributed to the W(P)–O bond vibrations of the lacunary $[PW_{11}O_{39}]^{7-}$ anion. When Ag^+ ions are coordinated to the lacunary sites of $[PW_{11}O_{39}]^{7-}$, forming $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, it is found that the peak at 903 cm⁻¹ is clearly enhanced, and that a new shoulder peak at 975 cm⁻¹ appears, which results from improving the symmetry of the polyoxotungstophosphate structure and decreasing its negative charge to some extent when a Ag^+ ion is coordinated to the lacunary site of $[PW_{11}O_{39}]^{7-}$. When an excess of $S_2O_8^{2-}$ is added to the $[PW_{11}O_{39}]^{7-}$ solution, the peaks at 963 cm⁻¹ and 903 cm⁻¹ are



Fig. 6 UV-Raman spectra for 0.01 M solutions of (a) $K_7[PW_{11}O_{39}]\cdot 12H_2O$, (b) $K_3[H_3Ag^{I}PW_{11}O_{39}]\cdot 12H_2O$, (c) $K_7[PW_{11}O_{39}]\cdot 12H_2O$ and $Na_2S_2O_8$, (d) $K_3[H_3Ag^{I}PW_{11}O_{39}]\cdot 12H_2O$ and $Na_2S_2O_8$, (e) $Na_2S_2O_8$. Excited light source: 257 nm.

still retained, but their seemingly enhanced intensity results from the absorption of $S_2O_8^{2-}$. Therefore, it is deduced that the UV-Raman peaks of $[PW_{11}O_{39}]^{7-}$ should be fixed, because the structure of $[PW_{11}O_{39}]^{7-}$ is kept unchanged in the solution containing $S_2O_8^{2-}$.⁴⁵⁻⁴⁸ However, when an excess of $S_2O_8^{2-}$ is added to the $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ solution, the peaks at 963, 903, and 975 cm⁻¹ are enhanced obviously. This shows that the $[PW_{11}O_{39}]^{7-}$ ligand is stable and the central Ag^+ ion in the complex is oxidized into $Ag(\pi)$ or Ag(m). This is consistent with the result of the ${}^{31}P$ NMR for the oxidation of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ solution.

Homogenous catalytic water oxidation into O_2 for $[H_3Ag^I\!(H_2O)\!\!-\!PW_{11}O_{39}]^{3-}$

As known, the pure $S_2O_8^{2-}$ solution is stable dynamically and almost no O₂ evolution is observed at room temperature. In recent years, the S₂O₈²⁻ ion has been used as a two-electron oxidizing agent to evaluate the activity of WOCs.^{15,19,22,27,29-32} To ensure that $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ is not decomposed, the catalytic water oxidation is carried out in a phosphate buffer solution (1 M, pH = 5.5) at 25 °C to keep the pH values at 3.5-7.0. Isotope-labelling water oxidation experiments using ¹⁸O enriched water (8.3%) instead of H₂¹⁶O were carried out with the catalyst to determine if the water is the source of the evolved oxygen. The EI mass spectra of the gas sample evolved from the catalytic oxidation in normal water and in $H_2^{18}O$ enriched water (8.3% H₂¹⁸O) are shown in Fig. S7 and Fig. S8.† The relative abundances of the oxygen isotopes, determined from the intensities of the three molecular ion peaks, are shown in Fig. 7. The ratio of ¹⁶O¹⁶O: ¹⁶O¹⁸O: ¹⁸O¹⁸O is determined to be 118:20:1, which is in good agreement with the simulated ratio of 121:22:1 for oxygen coming exclusively from water. The above data clearly demonstrate that the evolved O₂ originates exclusively from the water, which is consistent with the results reported in the references.³²

Firstly, the catalytic activity of $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$, $[Ag^I(2,2'-bpy)NO_3]^{42}$ and AgNO₃ are compared. As shown in

Dalton Transactions



Fig. 7 Observed and theoretical relative abundances of ¹⁸O-labeled and unlabeled oxygen evolved during the photocatalytic oxidation of a buffer solution (12 ml) prepared with H₂¹⁸O-enriched water (8.3% H₂¹⁸O) containing K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O (2.0 × 10⁻³ M) and Na₂S₂O₈ (8.8 × 10⁻² M). (green, observed mass intensity; red, calculated values assuming that the evolved O₂ results exclusively from water).



Fig. 8 Time course of O₂ evolution from 100 ml of 8.8 × 10⁻² M Na₂S₂O₈ solution containing 1.0 × 10⁻³ M of (a) [Ag^I(2,2'-bpy)NO₃]; (b) AgNO₃, and (c) K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O in 1 M phosphate buffer solution (pH = 5.5) at 25 °C.

Fig. 8, no O_2 evolution is observed for $[Ag^I(2,2'-bpy)NO_3]$. For both AgNO₃ and $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$, however, obvious O_2 evolution has been detected, and the amount of O_2 comes to 196 and 328 µmol in 6 hours, respectively. For the $K_3[H_3Ag^IPW_{11}O_{39}]\cdot 12H_2O$ catalyst, the obviously increasing of O_2 evolution illustrates that $[PW_{11}O_{39}]^{7-}$ ligand plays a significant role in both the transmission of electrons and protons and the improvement of the redox performance of the active Ag centers.

As shown in Fig. 9, the rates of O_2 evolution increase with the increasing concentrations of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$. For 1.0, 2.0, 3.0 and 5.0 mM $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, the amount of O_2 evolution comes to 328, 622, 935, 1575 µmol in 6 hours, respectively. It is also found in Fig. 9 that the amount of O_2 evolution in the first hour is lower relatively, especially for 3.0



Fig. 9 Time course of O₂ evolution from 100 ml of 8.8 × 10⁻² M Na₂S₂O₈ solution containing different concentrations of [H₃Ag¹(H₂O)-PW₁₁O₃₉]³⁻ in 1 M phosphate buffer solution (pH = 5.5) at 25 °C. a: 1.0 × 10⁻³ M; b: 2.0 × 10⁻³ M; c: 3.0 × 10⁻³ M and d: 5.0 × 10⁻³ M.

and 5.0 mM concentrations, which may be an induced period of the oxidation process of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ into $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$. This process is also observed by UV spectra (Fig. S4†). Therefore, the kinetics of O₂ evolution is investigated in the time range of the second to the sixth hour. Within this time range the amount of O₂ evolution *vs.* the time exhibits an excellent linear relationship (Fig. 9). The rates of O₂ evolution from systems with different concentrations of $S_2O_8^{2-}$ and $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ in 1 M phosphate buffer solution (pH = 5.5) at 25 °C are listed in Table 2.

It is obvious that the rate of O_2 evolution is a first-order law with respect to the concentrations of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ and $S_2O_8^{-2-}$, respectively. The rate equation can be described as follows:

$$dc(O_2)/dt = kc([H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}) \cdot c(S_2O_8^{2-})$$
(2)

The average rate constant at 25 $^{\rm o}{\rm C}$ is 63.1 \times 10^{6} L mol $^{-1}$ $h^{-1}.$

For the solutions of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ containing an excess of $S_2O_8^{2-}$, it is noteworthy to mention the experimental evidence of the catalytic mechanism. First, the ³¹P NMR indi- $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ that there are cates $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$, but no $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ in the solutions. This demonstrates that the oxidation reaction of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ into $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ and $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ is a fast reaction, not a rate-determining step for water oxidation leading to O2 evolution. Second, the organic substances (CH₃COO⁻, 2,2-bipy, etc.) quench the O₂ evolution, owing to their competition for the free radicals with the oxidation of [H₃Ag^{II}(H₂O)PW₁₁O₃₉]²⁻. This also demonstrates that the free radicals participate in the water oxidation into O₂. Third, the rate of O₂ evolution is a first-order law with respect to the concentrations of [H₃Ag^I(H₂O)PW₁₁O₃₉]³⁻ and $S_2O_8^{2-}$, respectively. Finally, our recent results about the catalytic water oxidation of $AgNO_3$ indicate that the reaction (AgO^+ + $H_2O \rightarrow Ag^+ + H_2O_2$) may be the rate-determining step.⁶⁰ Based on the aforementioned evidence, a possible mechanism for

Table 2 Kinetics analysis of the rates of O_2 evolution from systems with different concentrations of $S_2O_8^{2-}$ and $[H_3AgPW_{11}O_{39}]^{3-}$ in 1 M phosphate buffer solution (pH = 5.5) at 25 °C

No.	$c([H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-})/mol L^{-1}$	$c([S_2O_8]^{2-})^a/mol L^{-1}$	$\nu_{m}\left(O_{2}\right)^{b}\!/\mu mol~h^{-1}$	$\nu \big(O_2\big)^c/mol \ L^{-1} \ h^{-1}$	$k/L \operatorname{mol}^{-1} h^{-1}$	$k/L \text{ mol}^{-1} \text{ h}^{-1}$
1 2 3 4 5	$\begin{array}{c} 1.0 \times 10^{-3} \\ 1.0 \times 10^{-3} \\ 2.0 \times 10^{-3} \\ 2.0 \times 10^{-3} \\ 3.0 \times 10^{-3} \end{array}$	$8.8 \times 10^{-2} \\ 17.6 \times 10^{-2} \\ 4.4 \times 10^{-2} \\ 8.8 \times 10^{-2} \\ 8.8 \times 10^{-2} \\ 8.8 \times 10^{-2} \\ \end{array}$	55.2 109.2 54.4 115.8 174.3	$\begin{array}{c} 5.5\times10^{-4}\\ 1.1\times10^{-3}\\ 5.4\times10^{-4}\\ 1.2\times10^{-3}\\ 1.7\times10^{-3} \end{array}$	62.7 62.1 61.8 65.8 65.9	63.1
6	$5.0 imes 10^{-3}$	8.8×10^{-2}	267.0	2.7×10^{-3}	60.7	

 ${}^{a}c([S_2O_8]^{2-})$ is approximately equal to the initial concentration of $S_2O_8^{2-}$. ${}^{b}\nu_m(O_2)$ represents the average rate of O_2 evolution during the second to the sixth hour in the 100 ml solution and the values are a slope of a curve of the amount of O_2 evolution νs . time. ${}^{c}\nu(O_2)$ represents the rate of O_2 evolution per volume of the solution, and the values are $\nu_m(O_2)/0.1$ L.

the catalytic water oxidation leading to O_2 evolution for $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is proposed:

$$\begin{split} & \left[H_{3}Ag^{I}(H_{2}O)PW_{11}O_{39} \right]^{3-} + S_{2}O_{8}^{\ 2-} \\ & \rightarrow \left[H_{3}Ag^{II}(H_{2}O)PW_{11}O_{39} \right]^{2-} + SO_{4}^{\ -\bullet} + SO_{4}^{\ 2-} \end{split} \tag{3}$$

$$\mathrm{SO_4}^{-\bullet} + \mathrm{H_2O} \to \mathrm{OH}^{\bullet} + \mathrm{H}^+ + \mathrm{SO_4}^{2-}$$
 (4)

$$\begin{split} & \left[H_{3}Ag^{II}(H_{2}O)PW_{11}O_{39} \right]^{2-} + OH^{\bullet} \\ & \rightarrow \left[H_{3}Ag^{III}OPW_{11}O_{39} \right]^{3-} + H^{+} + H_{2}O \end{split} \tag{5}$$

$$\begin{split} & [H_{3}Ag^{III}OPW_{11}O_{39}]^{3-} + 2H_{2}O \\ & \rightarrow [H_{3}Ag^{I}(H_{2}O)PW_{11}O_{39}]^{3-} + H_{2}O_{2} \end{split} \tag{6}$$

$$\begin{split} \left[H_{3}Ag^{III}OPW_{11}O_{39} \right]^{3-} + H_{2}O_{2} &\rightarrow \left[H_{3}Ag^{I}(H_{2}O)PW_{11}O_{39} \right]^{3-} \\ &+ O_{2} \end{split} \tag{7}$$

Among these, eqn (6), the formation of the O_2 evolution, is the rate-determining step. The result is different from the catalytic mechanism of simple Ag(i) ions proposed by Kimura *et al.*, in which the step $(Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{-*} + SO_4^{2-})$ was considered as the rate-determining reaction for the O_2 evolution.⁴¹

Applying the steady-state approximation to the aforementioned mechanism, a theoretical rate equation can be deduced as follows:

$$dc(O_2)/dt = kc([H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}) \cdot c(S_2O_8^{2-})$$
(8)

This is consistent with the effects of the concentrations of $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ and $S_2O_8^{2-}$ on the rate of O_2 evolution in the kinetic experiment.

In order to test the stability of the catalyst, we performed the catalytic reaction for 5.0×10^{-5} M of K₃[H₃AgP-W₁₁O₃₉]·12H₂O and AgNO₃. As shown in Fig. S9,† it is found that the TON values are 95.0 and 66.0 in 96 hours, respectively. The catalytic oxidation reaction is still undergoing even with the high rate of O₂ evolution.

Experimental section

Materials and methods

All chemicals were commercially purchased and used as supplied. $Na_9[A-PW_9O_{34}]\cdot 7H_2O_{,61}^{61}$ $K_7[\alpha-PW_{11}O_{39}]\cdot 12H_2O_{,62}^{62}$ and [Ag(2,2'-bpy)NO₃]⁶³ were synthesized according to the corresponding references and identified by IR spectroscopy. The contents of K, P, Ag, and W elements were determined by ICP-PRODIGY XP analysis. IR spectra were recorded in the range of 400-4000 cm⁻¹ on a TENSOR27 Bruker AXS spectrometer with a pressed KBr pellet. TG-DTA analyses were carried out on a Pyris Diamond TG/DTA instrument in an immobile airflow from 30 °C to 900 °C, with a heating rate of 10 °C min⁻¹. H₂O molecules in the crystal were determined according to the TG analysis result. Powder X-ray diffraction measurements were collected on a D8 Advance instrument in the angular range of $2\theta = 5-60^{\circ}$ at 293 K with Cu K α radiation. MS analysis was performed on a LTQ Orbitrap XL, equipped with an ESI[†] source. The following mass spectrometric conditions were used for the analysis in the negative ion electrospray mode: ispray voltage, 4.00 kV; sheath gas flow rate, 30 arb; aux gas flow rate, 10 arb; capillary temperature, 275.00 °C. The conductivity was measured by a DDS-11A conductometer, using redistilled water. pH values were measured by a Cyberscan 510 pH meter, using redistilled water. The ³¹P NMR spectra were recorded on a Bruker AVANCE500 spectrometer at 11.75 T using the D₂O locking field. The ³¹P chemical shifts were referenced to 85% H₃PO₄. The ESR signals at 100 K were recorded on a Brucker ESR A 200 spectrometer. The settings for the ESR spectrometer were as follows: center field, 3275.00 G; sweep width, 2000 G; microwave frequency, 9.43 GHz; modulation frequency, 100 kHz; power, 20.32 mW. UV-Visible spectra were obtained by a UV-240 UV-Vis spectrophotometer with the conditions: scan rate, 100 nm min⁻¹; wavenumber, 800-200 nm.

Synthesis and characteristic of K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O

5.0 ml of silver nitrate solution (0.26 g, 1.5 mmol) was added to 30 ml of $Na_9[A-PW_9O_{34}]$ -7H₂O solution (2.56 g, 1.0 mmol). The resulting solution was adjusted to pH = 5.0 using 6 M HNO₃. After 3 hours, the resulting small amount of white

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precipitate was filtered off and 2.0 g KNO₃ was added to the filtered mother-liquor. After one day, white acicular crystals of $K_3[H_3Ag^IPW_{11}O_{39}]$ ·12H₂O were obtained in a yield of 70% (based on Na₉[A-PW₉O₃₄]·7H₂O). Found: K, 3.89%; P, 1.00%; W, 64.56%; Ag, 3.51%. Calc. for $K_3H_{27}AgO_{51}PW_{11}$: K, 3.76%; P, 0.99%; W, 64.78%; Ag, 3.45%. Characteristic bands in the FT-IR spectrum of 955 cm⁻¹; 904, 859, 808 and 730 cm⁻¹; 1046 and 1090 cm⁻¹ are assigned to $\nu_{as}(W=O)$, $\nu_{as}(W=O-W)$ and $\nu_{as}(P-O)$, respectively (Fig. S5†), confirming its presence as a lacunary α -Keggin polyxotungstophosphate. The TG/DTA analysis is shown in Fig. S6.† From 30 °C to 480 °C, the total weight loss is 7.60%, which is attributed to the loss of absorption water, coordinated water, and constitution water.

Single-crystal X-ray diffraction

The crystal data of K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O were collected on a SMART APEX II-CCD X-ray single crystal diffractometer at 293 K with graphite-monochromatic Mo K α radiation (λ = 0.71073 Å). The structure was solved by a direct method and refined by a full-matrix least squares method on F^2 using the SHELXS-97 software.⁶⁴ The H⁺ ions in polyoxometalates were determined according to the research results in the aqueous solution, and required charge balance. A summary of the crystallographic data is shown in Table S1.† The selected bond lengths and angles of K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O are listed in Table S4.† The CSD number: 427568. Further details of the crystal structure investigation may 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).

Catalytic water oxidation into O_2

The catalytic activity was examined in a self-made closed 500 ml Quartz reaction cell with 100 ml of 1 M phosphate buffer (pH = 5.5) solution. The reaction was carried out in an Ar atmosphere. The amount of the produced O_2 was analyzed using gas chromatography (with a thermal conductivity detector and an Ar carrier).

¹⁸O isotope-labeled experiment

12.0 ml of Na₂HPO₄–NaH₂PO₄ buffer (1 M pH = 5.5) containing 8.3 atom% H₂¹⁸O, K₃[H₃Ag^IPW₁₁O₃₉]·12H₂O (2.0×10^{-3} M), and Na₂S₂O₈ (8.8×10^{-2} M) was deaerated with N₂ in a 100 ml flask that was sealed with a rubber septum. After 6 h, 20 µL of the gas sample was withdrawn using a gas-tight syringe for gas analysis. A HP Series 6890 model chromatograph interfaced with a HP Series 5973 model mass spectrometer operating in the electron impact ionization mode was used to collect the mass spectrometry data. The MS detector was tuned for maximum sensitivity (quadrupole temperature, 150 °C; ion source temperature, 230 °C, and He carrier). The single ion mode was used to scan for the ions m/z = 29, 32, 34, 36. Ions in the m/z range of 29 to 50 were also scanned in order to observe the abundance change of ¹⁶O¹⁸O and ¹⁸O¹⁸O, which evolved from H₂¹⁶O and H₂¹⁸O, respectively. The total flow rate into the spectrometer was limited to 1 ml min⁻¹. The GC was equipped with a molecular sieve column (30 m \times 0.25 mm \times 0.25 μ m), and the vaporizing chamber temperature and column temperature were set at 200 °C and 35 °C, respectively.

Conclusions

1. When the crystal of $K_3[H_3Ag^IPW_{11}O_{39}]$ -12H₂O is dissolved in water, the $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ anion is formed and stays stable in the pH range of 3.5–7.0. This illustrates that the lacunary polyoxometalates are excellent inorganic ligands, and which can be coordinated with Ag^+ ions to generate stable complexes.

2. It was determined that $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ is oxidized by $S_2O_8^{2-}$ into $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ dominantly and a small amount of $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$. This illustrates that lacunary polyoxomelates play an important role in stabilizing the high-oxidation states of silver ions.

3. $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$ is a better catalyst for $S_2O_8^{2-}$ oxidizing water into O_2 . This illustrates that the $[PW_{11}O_{39}]^{7-}$ ligand plays important roles in both the transmission of electrons and protons, and in the improvement of the redox performance of silver ions.

4. A possible catalytic mechanism is proposed. In the oxidation reaction, the $[H_3Ag^{II}(H_2O)PW_{11}O_{39}]^{2-}$ and $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ intermediates are determined and the rate-determining step is $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ oxidizing water into H_2O_2 . The rate law is a first order one with the concentrations of $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ and $S_2O_8^{2-}$, respectively.

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Notes and references

- M. G. Walter, E. L. Warren, J. R. Mckone, S. W. Boettcher, Q. X. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, 110, 6446.
- 2 X. Sala, I. Romero, M. Rodriguez, L. Escriche and A. Llobet, *Angew. Chem., Int. Ed.*, 2009, **48**, 2842.
- 3 H. Yamazaki, A. Shouji, M. Kajita and M. Yagi, *Coord. Chem. Rev.*, 2010, 254, 2483.
- 4 R. Brimblecombe, G. C. Dismukes, G. F. Swiegers and L. Spiccia, *Dalton Trans.*, 2009, 9374.
- 5 S. W. Gersten, G. J. Samuels and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4029.
- 6 J. J. Concepcion, M. K. Tsai, J. T. Muckerman and T. J. Meyer, *J. Am. Chem. Soc.*, 2010, **132**, 1545.

- 7 J. Nyhlén, L. L. Duan, B. Akermark, L. C. Sun and T. Privalov, *Angew. Chem., Int. Ed.*, 2010, **49**, 1773.
- 8 X. Sala, I. Romero, M. Rodríguez, L. Escriche and A. Llobet, Angew. Chem., Int. Ed., 2009, 48, 2842.
- 9 R. Zong and R. P. Thummel, J. Am. Chem. Soc., 2005, 127, 12802.
- 10 S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron and D. Milstein, *Science*, 2009, **324**, 74.
- N. D. McDaniel, F. J. Coughlin, L. L. Tinker and S. Bernhard, *J. Am. Chem. Soc.*, 2008, **130**, 210.
- 12 H. Kunkely and A. Vogler, Angew. Chem., Int. Ed., 2009, 48, 1685.
- J. Limburg, J. S. Vrettos, J. M. LiableSands, A. L. Rheingold, R. H. Crabtree and G. W. Brudvig, *Science*, 1999, 283, 1524.
- 14 W. C. Ellis, N. D. McDaniel, S. Bernhard and T. J. Collins, J. Am. Chem. Soc., 2010, 132, 10990.
- 15 Y. H. Xu, L. L. Duan, L. P. Tong, B. Akermarkb and L. C. Sun, *Chem. Commun.*, 2010, **46**, 6506.
- 16 M. Yagi and K. Narita, J. Am. Chem. Soc., 2004, 126, 8084.
- 17 L. L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet and L. C. Sun, *Nat. Chem.*, 2012, 4, 418.
- 18 H. Lv, Y. V. Geletii, C. Zhao, J. W. Vickers, G. Zhu, Z. Luo, J. Song, T. Lian, D. G. Musaev and C. L. Hill, *Chem. Soc. Rev.*, 2012, 41, 7572.
- 19 Y. V. Geletii, B. Botar, P. Kogerler, D. A. Hillesheim, D. G. Musaev and C. L. Hill, Angew. Chem., Int. Ed., 2008, 47, 3896.
- 20 A. Sartorel, M. Carraro, G. Scorrano, R. D. Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard and M. Bonchio, *J. Am. Chem. Soc.*, 2008, 130, 5006.
- 21 M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and F. Scandola, *Chem. Commun.*, 2010, 46, 3152.
- 22 Y. V. Geletii, Z. Q. Huang, Y. Hou, D. G. Musaev, T. Q. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 7522.
- 23 Y. V. Geletii, C. Besson, Y. Hou, Q. S. Yin, D. G. Musaev,
 D. Quiñonero, R. Cao, K. I. Hardcastle, A. Proust,
 P. Kögerler and C. L. Hill, *J. Am. Chem. Soc.*, 2009, 131, 17360.
- 24 A. Sartorel, P. Miró, E. Salvadori, S. Romain, M. Carraro, G. Scorrano, M. D. Valentin, A. Llobet, C. Bo and M. Bonchio, *J. Am. Chem. Soc.*, 2009, 131, 16051.
- 25 F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse,
 C. Maccato, S. Rapino, B. R. Gonzalez, H. Amenitsch,
 T. D. Ros, L. Casalis, A. Goldoni, M. Marcaccio,
 G. Scorrano, G. Scoles, F. Paolucci, M. Pratol and
 M. Bonchio, *Nat. Chem.*, 2010, 2, 826.
- 26 M. Murakami, D. Hong, T. Suenobu, S. Yamaguchi, T. Ogura and S. Fukuzumi, *J. Am. Chem. Soc.*, 2011, 133, 11605.
- 27 P. Car, M. Guttentag, K. K. Baldridge, R. Alberto and G. R. Patzk, *Green Chem.*, 2012, **14**, 1680.
- 28 Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, *Science*, 2010, **328**, 342.

- 29 Z. Q. Huang, Z. Luo, Y. V. Geletii, J. W. Vickers, Q. S. Yin, D. Wu, Y. Hou, Y. Ding, J. Song, D. G. Musaev, C. L. Hill and T. Q. Lian, *J. Am. Chem. Soc.*, 2011, 133, 2068.
- 30 M. Natali, S. Berardi, A. Sartorel, M. Bonchio, S. Campagnac and F. Scandola, *Chem. Commun.*, 2012, 48, 8808.
- 31 S. Tanaka, M. Annaka and K. Sakai, *Chem. Commun.*, 2012, 48, 1653.
- 32 F. Y. Song, Y. Ding, B. C. Ma, C. M. Wang, Q. Wang, X. Q. Du, S. Fu and J. Song, *Energy Environ. Sci.*, 2013, 6, 1170.
- 33 J. Soriano-López, S. Goberna-Ferrón, L. Vigara, J. J. Carbó and J. M. Poblet, *Inorg. Chem.*, 2013, 52, 4753.
- 34 M. K. Kanan and D. G. Nocera, Science, 2008, 321, 1072.
- 35 M. J. Mas-Marza, E. Sala, X. Romero, I. Rodríguez, M. Viñas, C. Parella and T. Llobet, *Angew. Chem., Int. Ed.*, 2008, 47, 5830.
- 36 J. W. Vickers, H. Lv, J. M. Sumliner, G. Zhu, Z. Luo, D. G. Musaev, Y. V. Geletii and C. L. Hill, *J. Am. Chem. Soc.*, 2013, **135**, 14110.
- 37 J. J. Stracke and R. G. Finke, *J. Am. Chem. Soc.*, 2011, **133**, 14872.
- 38 J. J. Stracke and R. G. Finke, *Catalysis*, 2013, 3, 1209.
- 39 Z. L. Lang, G. C. Yang, N. N. Ma, S. Z. Wen, L. K. Yan, W. Guan and Z. M. Su, *Dalton Trans.*, 2013, **42**, 10617.
- 40 D. A. House, Chem. Rev., 1962, 62, 185.
- 41 M. Kimura and T. Kawajiri, J. Chem. Soc., Dalton Trans., 1980, 726.
- 42 W. Wang, Q. Zhao, X. J. Deng and J. P. Li, *J. Hydrogen* Energy, 2011, **36**, 7374.
- 43 H. I. S. Nogueira, F. A. A. Paz, P. A. F. Teixeira and J. Klinowsk, *Chem. Commun.*, 2006, 2953.
- 44 M. T. Pope, *Heteropoly and isopoly oximetalates*, Springger-Verlag, Berlin, 1983.
- 45 Z. Ma, *Experimental methods of applied inorganic chemistry*, Higher Education Press, 1991.
- 46 I. A. Weinstock, Chem. Rev., 1998, 98, 113.
- 47 X. Y. Zhang, M. T. Pope, M. R. Chance and G. B. Jameson, *Polyhedron*, 1995, **14**, 1381.
- 48 W. You and Y. Gu, Chin. Chem. Lett., 1993, 4, 369-370.
- 49 G. A. Ayoko, J. F. Iyun and I. F. EI-Idris, *Transition Met. Chem.*, 1992, **17**, 46.
- 50 J. D. Miller, J. Chem. Soc. A, 1968, 1778.
- 51 M. Mazloum-Ardakani, H. Beitollahi, M. K. Amini, F. Mirkhalaf and B. F. Mirjalili, *Biosens. Bioelectron.*, 2011, 26, 2102.
- 52 J. A. Harrison and Z. A. Khan, J. Electroanal. Chem. Interfacial Electrochem., 1970, 28, 131.
- 53 T. Buch, J. Chem. Phys., 1965, 43, 761.
- 54 J. A. McMlllan and B. Smaller, *J. Chem. Phys.*, 1961, 35, 1698.
- 55 N. Kanrakl and I. Yasumorl, J. Phys. Chem., 1978, 82, 2351.
- 56 N. M. Gresley, W. P. Griffith, A. C. Laemmel and H. I. S. Nogueira, *J. Mol. Catal. A: Chem.*, 1997, 117, 185–198.
- 57 A. A. Noyes, J. L. Hoard and K. S. Pitzer, *J. Am. Chem. Soc.*, 1935, 57, 1221.

Paper

- 58 H. N. Po, J. H. Swinehart and T. L. Allen, *Inorg. Chem.*, 1968, 7, 244.
- 59 D. M. Yos, J. Am. Chem. Soc., 1926, 47, 152.
- 60 L. Yu, J. Wang, D. Guo, W. You, M. Liu, L. Zhang and C. Li, *Dalton Trans.*, submitted. DT-COM-07-2014-002308.
- 61 A. P. Ginsberg, *Inorganic syntheses*, John Wiley & Sons, 1990, 27, 100.
- 62 N. Haraguchi, Y. Okaue, T. Isobe and Y. Matsuda, *Inorg. Chem.*, 1994, **33**, 1015.
- 63 G. T. Morgan and F. H. Burstal, *Chemical Research Laboratory*, Teddington, Middlesex, 1930, p. 2594.
- 64 G. M. Sheldrick, *SHELXS97, program for crystal structure solution*, University of Gottingen, Germany, 1997.