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# Remarkable Influence of Structures around Rhenium(V) Centers Constructed in Polyoxotungstates for Methanol Dehydrogenation under Visible Light Irradiation

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## ABSTRACT

The synthesis and characterization of  $\alpha_1$ -Dawson-type mono-rhenium(V)-substituted polyoxotungstate,  $[\alpha_1\text{-P}_2\text{W}_{17}\text{Re}^{\text{V}}\text{O}_{62}]^{7-}$  (**1**), are described. The dimethylammonium salt of **1**,  $[\text{Me}_2\text{NH}_2]_7[\alpha_1\text{-P}_2\text{W}_{17}\text{Re}^{\text{V}}\text{O}_{62}]\cdot 9\text{H}_2\text{O}$  (**Me<sub>2</sub>NH<sub>2</sub>-1**), was obtained as analytically pure homogeneous black-blue crystals by reacting mono-lacunary  $\alpha_1$ -Dawson polyoxotungstate with  $[\text{Re}^{\text{IV}}\text{Cl}_6]^{2-}$  in  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOLi}$  buffer, followed by crystallization via a vapor diffusion from acetonitrile/ethanol. Characterization was also accomplished by X-ray crystallography, elemental analysis, TG/DTA, FTIR, UV-vis, and solution  $^{31}\text{P}$  NMR spectroscopy; these results showed that the polyoxoanion **1** was a monomeric  $\alpha$ -Dawson structure, in which the rhenium(V) ion was coordinated to the monovacant site of  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$ , resulting in an overall  $\text{C}_1$  symmetry. The polyoxoanion **1**,  $[\text{O}\{\text{Re}^{\text{V}}(\text{OH})(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$  (**2**), and  $[\alpha\text{-PW}_{11}\text{Re}^{\text{V}}\text{O}_{40}]^{4-}$  (**3**) showed the hydrogen evolution from methanol under visible light irradiation ( $\geq 400$  nm) in the presence of titanium dioxide. The activities were remarkably depended on the rhenium(V) sites in **1** – **3**; polyoxoanion **2** possessing the dirhenium(V)-oxido-bridged site showed the highest activities among these complexes.

**Keywords:** Rhenium(V); polyoxometalate; crystal structure; photocatalyst; methanol dehydrogenation

## 1. INTRODUCTION

Since the Honda–Fujishima effect, i.e., photoinduced water splitting by titanium dioxide ( $\text{TiO}_2$ ) and platinum electrodes was first reported, various photocatalytic materials have been investigated, because the generated hydrogen ( $\text{H}_2$ ) is a clean and renewable fuel source [1–6]. Although  $\text{TiO}_2$  is one of the most promising photocatalysts owing to its sufficient photostability, commercial availability, easy preparation, and its high activity for a wide range of photocatalytic reactions, it absorbs only ultraviolet (UV) light because of its wide band gap (varying from 3.0 to 3.2 eV, depending on the crystal structure); this limits the use of sunlight as an irradiation source in photocatalytic reactions [7,8]. One of the most powerful

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approaches to developing visible-light-driven TiO<sub>2</sub> materials is surface modification. To date, numerous TiO<sub>2</sub> materials have been prepared by sensitizing transition metals [8–16], organic dyes [4, 7, 17–22], and organic moieties [23–29], and they show high activities in the presence of cocatalysts for various photoreactions. Although these are excellent studies, there is still room for improving TiO<sub>2</sub>-based photocatalytic systems by including a sensitizer and a cocatalyst.

Polyoxometalates have attracted considerable attention because of their high versatility and unique range of properties; these include catalytic and biological activities and/or photochemical, electrochromic, and magnetic properties [30–32]. Photocatalytic systems constructed using TiO<sub>2</sub> and polyoxometalates, e.g., PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>, PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup>, GeW<sub>12</sub>O<sub>40</sub><sup>4-</sup>, SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup>, BW<sub>12</sub>O<sub>40</sub><sup>5-</sup>,  $\alpha$ -P<sub>2</sub>W<sub>18</sub>O<sub>62</sub><sup>6-</sup>, and  $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub><sup>10-</sup>, also exhibit efficient photocatalytic activities under visible light irradiation; however, they required a pretreatment by UV irradiation to form “heteropoly blue” species, and large amounts of cocatalyst [33–38]. Recently, we demonstrated the catalytic activities of  $\alpha_2$ -Dawson and Keggin rhenium(V)-coordinated polyoxotungstates, [O{Re<sup>V</sup>(OH)( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>}<sub>2</sub>]<sup>14-</sup> and [ $\alpha$ -PW<sub>11</sub>Re<sup>V</sup>O<sub>40</sub>]<sup>4-</sup>, in H<sub>2</sub> evolution from water vapor and an aqueous solution of EDTA·2Na (ethylenediamine tetraacetic acid disodium salt) in the presence of TiO<sub>2</sub> under visible light irradiation ( $\geq 400$  and  $\geq 420$  nm) [39, 40]. In this system, the pretreatment by UV irradiation was not necessary, and the rhenium compounds exhibited high photocatalytic activities without cocatalyst. Thus, the rhenium(V)-coordinated polyoxometalates were useful compounds for development of visible-light-driven TiO<sub>2</sub>-based photocatalyst; however, the structure dependence of rhenium(V) sites constructed in polyoxometalate is still open to discussion because significant [ $\alpha$ -PW<sub>11</sub>Re<sup>V</sup>O<sub>40</sub>]<sup>4-</sup> decomposition was observed in an EDTA·2Na aqueous solution during light irradiation.

In this study, we first synthesized  $\alpha_1$ -Dawson-type mono-rhenium(V)-substituted polyoxotungstate [Me<sub>2</sub>NH<sub>2</sub>]<sub>7</sub>[ $\alpha_1$ -P<sub>2</sub>W<sub>17</sub>Re<sup>V</sup>O<sub>62</sub>]·9H<sub>2</sub>O (**Me<sub>2</sub>NH<sub>2</sub>-1**) and characterized it using X-ray crystallography, elemental analysis, thermogravimetric analysis/differential thermal analysis (TG/DTA), and Fourier-transform infrared (FTIR), UV-visible, and solution <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopies. To investigate the structure dependence of rhenium(V) sites for the photocatalytic reactions, we focused on the methanol dehydrogenation catalyzed by **Me<sub>2</sub>NH<sub>2</sub>-1**, K<sub>14</sub>[O{Re<sup>V</sup>(OH)( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>}<sub>2</sub>]·21H<sub>2</sub>O (**K-2**), and [Me<sub>2</sub>NH<sub>2</sub>]<sub>4</sub>[ $\alpha$ -PW<sub>11</sub>Re<sup>V</sup>O<sub>40</sub>] (**Me<sub>2</sub>NH<sub>2</sub>-3**) under visible light irradiation ( $\geq 400$  nm) in the presence of TiO<sub>2</sub>. Here, we report full details of the synthesis and molecular structure of complex **1**, and demonstrate the photocatalytic activities and stabilities of complexes **1** – **3**.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

K<sub>14</sub>[O{Re<sup>V</sup>(OH)( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>}<sub>2</sub>]·21H<sub>2</sub>O (**K-2**) [40], [Me<sub>2</sub>NH<sub>2</sub>]<sub>4</sub>[ $\alpha$ -PW<sub>11</sub>Re<sup>V</sup>O<sub>40</sub>] (**Me<sub>2</sub>NH<sub>2</sub>-3**) [40], K<sub>9</sub>[ $\alpha_1$ -LiP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]·22H<sub>2</sub>O [41], and K<sub>10</sub>[ $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]·27H<sub>2</sub>O [42] were synthesized as described in the literatures. The number of solvated water molecules was determined by TG/DTA analyses. K<sub>2</sub>[Re<sup>IV</sup>Cl<sub>6</sub>] was purified by the reprecipitation from water/ethanol. TiO<sub>2</sub> (anatase/rutile = 80/20; 99.9%; -5  $\mu$ m) was obtained from Wako Pure Chemical Industries, Ltd. Other reagents and solvents were obtained and used as received from commercial sources.

### 2.2 Instrumentation/analytical procedures

The elemental analysis was carried out by using a Mikroanalytisches Labor Pascher instrument (Remagen, Germany). The samples were dried overnight at room temperature under  $10^{-3}$  –  $10^{-4}$  Torr vacuum before analysis. The infrared spectra were recorded on a Parkin Elmer Spectrum100 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) data were obtained using a Rigaku Thermo Plus 2 series TG/DTA TG 8120. The TG/DTA measurements were performed in air with a temperature increase of 4 °C per min between 20 and 500 °C. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  (242.95 MHz) nuclear magnetic resonance (NMR) spectra in solutions were recorded in 5-mm outer diameter tubes on a JEOL ECA-600 NMR spectrometer (Shizuoka University). The  $^{31}\text{P}$  NMR spectra were measured in  $\text{CH}_3\text{COOLi}\cdot\text{D}_2\text{O}$  and  $\text{D}_2\text{O}$  with reference to an external standard of 85%  $\text{H}_3\text{PO}_4$  in a sealed capillary. Chemical shifts were reported as negative on the  $\delta$  scale for resonance upfield of  $\text{H}_3\text{PO}_4$  ( $\delta$  0). Solution UV-vis spectra were recorded on a Perkin-Elmer Spectrum Lambda 650 spectrophotometer. The positions of sharp bands were automatically determined by software of UV-visible spectrometer, and those of broad bands were picked up at the highest values in the ASCII files. Potentiometric titration was carried out with 0.841 mmol/L tetra-*n*-butylammonium hydroxide as a titrant under argon atmosphere [43]. The compound **Me<sub>2</sub>NH<sub>2</sub>-1** (4.12  $\mu\text{mol}$ ) was dissolved in acetonitrile (20 mL) at 25 °C, and the solution was stirred for approximately 5 min. The titration data were obtained with a pH meter (Mettler Toledo). Data points were obtained in millivolt. A solution of tetra-*n*-butylammonium hydroxide (0.841 mmol/L) was syringed into the suspension in 0.20-equivalent intervals.

### 2.3 Synthesis of **[Me<sub>2</sub>NH<sub>2</sub>]<sub>7</sub>[ $\alpha_1$ -P<sub>2</sub>W<sub>17</sub>Re<sup>V</sup>O<sub>62</sub>]-9H<sub>2</sub>O (Me<sub>2</sub>NH<sub>2</sub>-1)**

A solution of  $\text{K}_2[\text{Re}^{\text{IV}}\text{Cl}_6]$  (0.365 g; 0.765 mmol) dissolved in 10 mL of water was added to a solution of  $\text{K}_9[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]\cdot 22\text{H}_2\text{O}$  (1.865 g; 0.379 mmol) dissolved in 25 mL of  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOLi}$  buffer solution (pH = 4.5) at 25 °C. After stirring for 4 h at 25 °C in the dark, a solid  $[\text{Me}_2\text{NH}_2]\text{Cl}$  (3.114 g; 38.3 mmol) was added to the solution, followed by stirring overnight at 25 °C. A deep blue-colored precipitate was collected using a membrane filter (JG 0.2  $\mu\text{m}$ ). At this stage, a crude product was obtained in 1.74 g yield. For crystallization, the crude product (1.74 g) was dissolved in 350 mL of acetonitrile at 25 °C; the resulting solution was filtered through a folded filter paper (Whatman #5). Black block crystals were obtained via vapor diffusion from methanol at 25 °C. The yield was 0.464 g. The percent yield was calculated on the basis of  $[\text{mol of Me}_2\text{NH}_2\text{-1}]/[\text{mol of K}_9\text{Li}[\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61}]\cdot 22\text{H}_2\text{O}] \times 100$  and was 25%. Elemental analysis results showed C, 3.57; H, 1.42; N, 2.05; P, 1.28; Re, 4.00; W, 66.0; K, 0.03; Li, <0.01%. Calculations for  $[(\text{CH}_3)_2\text{NH}_2]_7[\alpha_1\text{-P}_2\text{W}_{17}\text{ReO}_{62}]\cdot x\text{H}_2\text{O}$  ( $x = 2$ ) =  $\text{H}_{60}\text{C}_{14}\text{N}_7\text{O}_{64}\text{P}_2\text{ReW}_{17}$ : C, 3.56; H, 1.28; N, 2.08; P, 1.31; Re, 3.94; W, 66.2%. A weight loss of 2.54% was observed during overnight drying at room temperature under  $10^{-3}$ – $10^{-4}$  torr before analysis, suggesting seven water molecules (2.60%). TG/DTA under atmospheric conditions showed a weight loss of 12.2% below 500 °C with an exothermic point at 381.1 °C. A clear endothermic point was not observed; calculations showed 10.0% for the sum of seven dimethylammonium ions and nine water molecules. IR (KBr disk) results in the 1300 – 400  $\text{cm}^{-1}$  region (polyoxometalate region) showed: 1094m, 1077m, 1014w, 959s, 918m, 823m, 776m, and 733m  $\text{cm}^{-1}$ .  $^{31}\text{P}$  NMR (0.285 M  $\text{CH}_3\text{COOLi}\cdot\text{D}_2\text{O}$  solution, 22.3 °C):  $\delta$  -12.1, -12.4. UV-visible absorption (in  $\text{H}_2\text{O}$ ,  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M) showed:  $\lambda$  263 nm ( $\epsilon$   $4.4 \times 10^4$   $\text{M}^{-1}\text{cm}^{-1}$ ),  $\lambda$  310 nm ( $\epsilon$   $1.8 \times 10^4$   $\text{M}^{-1}\text{cm}^{-1}$ ), and  $\lambda$  468 nm ( $\epsilon$   $3.7 \times 10^3$   $\text{M}^{-1}\text{cm}^{-1}$ ).

### 2.4 X-ray crystallography

A black block crystal of **Me<sub>2</sub>NH<sub>2</sub>-1** ( $0.180 \times 0.050 \times 0.040$   $\text{mm}^3$ ) was mounted in a loop. Data were collected by a Rigaku Mercury70 diffractometer using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å) at 113 K. Data were collected and processed using CrystalClear

software for Windows. The structural analysis was performed using the CrystalStructure software for Windows. All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-97 [44]. Since one rhenium atom was disordering over twelve tungsten sites (W(4) – W (15)) in polyoxoanion **1**, the occupancies for the rhenium and tungsten sites were fixed at 1/12 and 11/12 throughout the refinement. The seven dimethylammonium ions and some acetonitrile and ethanol molecules were observed; however, no acetonitrile and ethanol solvent molecules were observed by elemental analysis and <sup>1</sup>H NMR spectroscopy. Thus, the solvent molecules evaporate gradually when crystals are removed from acetonitrile solution. Accordingly, the residual electron density was removed using the SQUEEZE routine in PLATON [45].

## 2.5 X-ray crystallography

C<sub>14</sub>H<sub>60</sub>N<sub>7</sub>O<sub>64</sub>P<sub>2</sub>ReW<sub>17</sub>; M = 4724.24, *triclinic*, space group *P*-1 (#2), *a* = 13.317(5) Å, *b* = 13.377(4) Å, *c* = 24.248(9) Å,  $\alpha$  = 79.24(2)<sup>o</sup>,  $\beta$  = 79.78(2)<sup>o</sup>,  $\gamma$  = 68.28(2)<sup>o</sup>, *V* = 3914(3) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 4.008 g/cm<sup>3</sup>,  $\mu$ (Mo-K $\alpha$ ) 265.749 cm<sup>-1</sup>. *R*<sub>1</sub> = 0.0678 (*I* > 2 $\sigma$ (*I*)), *wR*<sub>2</sub> = 0.1837 (for all data). GOF = 1.079 (26430 total reflections, 14529 unique reflections where *I* > 2 $\sigma$ (*I*)). CCDC reference number 968914 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## 2.6 Catalytic reaction experiments

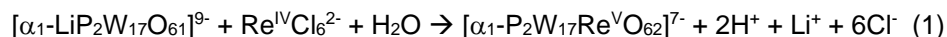
For methanol dehydrogenation, TiO<sub>2</sub> (anatase/rutile = 80/20) (200 mg) and rhenium compounds were suspended in 10 mL of methanol. The mixture was placed into a glass reaction vessel; this was connected to a Pyrex conventional closed gas circulation system (245.5 cm<sup>3</sup>). The compounds **Me<sub>2</sub>NH<sub>2</sub>-1** (2.8 – 9.4 mg; 0.6 – 1.9  $\mu$ mol of Re), **K-2** (2.4 – 10 mg; 0.6 – 2.0  $\mu$ mol of Re), and **Me<sub>2</sub>NH<sub>2</sub>-3** (1.8 – 6.1 mg; 0.6 – 2.0  $\mu$ mol of Re) were used for the photoreactions. The photoreaction was started by light irradiation with a 300 W Xe lamp equipped with a cut-off filter ( $\lambda$   $\geq$  400 nm). H<sub>2</sub>, O<sub>2</sub>, CO, and CH<sub>4</sub> were analyzed by GC (TCD, Molecular Sieve 5A stainless columns): the samples were assigned after they were compared with authentic samples analyzed under the same conditions. Turnover number (TON) was calculated as 2[hydrogen evolved (mol)]/[Re atoms (mol)]. Formaldehyde was observed by the published method [46].

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis and molecular structure of [Me<sub>2</sub>NH<sub>2</sub>]<sub>7</sub>[ $\alpha$ <sub>1</sub>-P<sub>2</sub>W<sub>17</sub>Re<sup>V</sup>O<sub>62</sub>] $\cdot$ 9H<sub>2</sub>O (**Me<sub>2</sub>NH<sub>2</sub>-1**)

The dimethylammonium salt of **1**, [Me<sub>2</sub>NH<sub>2</sub>]<sub>7</sub>[ $\alpha$ <sub>1</sub>-P<sub>2</sub>W<sub>17</sub>Re<sup>V</sup>O<sub>62</sub>] $\cdot$ 9H<sub>2</sub>O (**Me<sub>2</sub>NH<sub>2</sub>-1**), was synthesized by the direct reaction of 2 equiv of K<sub>2</sub>Re<sup>IV</sup>Cl<sub>6</sub> with mono-lacunary  $\alpha$ <sub>1</sub>-Dawson polyoxotungstate, [ $\alpha$ <sub>1</sub>-LiP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>9-</sup>, in a CH<sub>3</sub>COOH/CH<sub>3</sub>COOLi aqueous buffer solution (pH = 4.5) under air, at 25 °C; this was followed by addition of excess Me<sub>2</sub>NH<sub>2</sub>Cl, forming a dark blue precipitate. The formation of polyoxoanion **1** is represented by the ionic balance shown in Eq. 1, in which rhenium(IV) is oxidized to rhenium(V), as observed for compounds **K-2** and **Me<sub>2</sub>NH<sub>2</sub>-3** [39,40]. Notably, polyoxoanion **1** was gradually isomerized to the  $\alpha$ <sub>2</sub>-isomer during the reaction of K<sub>2</sub>Re<sup>IV</sup>Cl<sub>6</sub> with [ $\alpha$ <sub>1</sub>-LiP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>9-</sup> in aqueous solution; the CH<sub>3</sub>COOH/CH<sub>3</sub>COOLi aqueous buffer solution is therefore indispensable in inhibiting isomerization, as observed for [ $\alpha$ <sub>1</sub>-LiP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>9-</sup> [41]. In addition, the reaction temperature

should be kept at ca. 25 °C, even in a buffer solution, because heat treatment accelerated the isomerization. An excess of  $\text{K}_2\text{Re}^{\text{IV}}\text{Cl}_6$  was therefore required to complete (accelerate) the coordination of rhenium ion to the mono-vacant site of  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$ . For purification, the unreacted  $\text{K}_2\text{Re}^{\text{IV}}\text{Cl}_6$  was completely removed by crystallization via vapor diffusion from acetonitrile/ethanol.



The sample was dried overnight at room temperature under a vacuum of  $10^{-3} - 10^{-4}$  Torr for elemental analysis. The elemental results for C, H, N, Re, P, and W were in good agreement with the calculated values for the chemical formula of **Me<sub>2</sub>NH<sub>2</sub>-1** with two hydrated water molecules. The presence of seven dimethylammonium ions suggested that the oxidation state of the rhenium site was 5+; this was also supported by the fact that no protonation was observed in potentiometric titration with tetra-*n*-butylammonium hydroxide in acetonitrile. The weight loss observed during drying before analysis was 2.54% for **Me<sub>2</sub>NH<sub>2</sub>-1**, corresponding to seven weakly solvated or adsorbed water molecules. However, during TG/DTA under atmospheric conditions, a weight loss of 12.2% was observed below 500 °C, corresponding to seven dimethylammonium ions and nine water molecules.

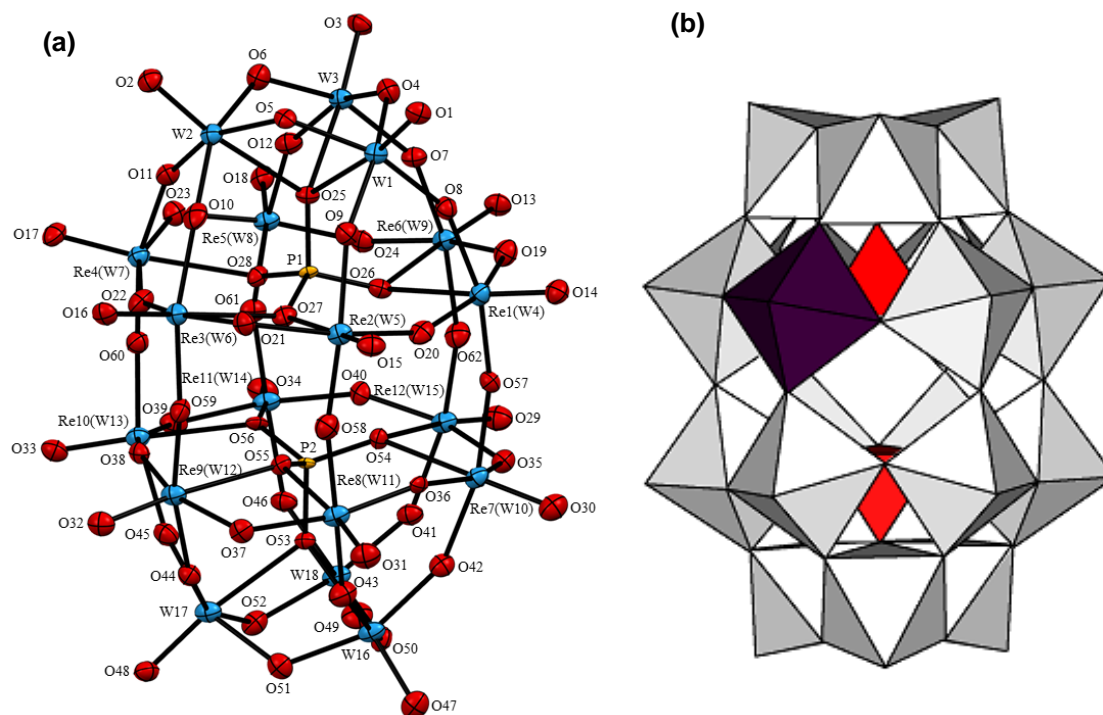
The X-ray structural analysis of crystalline  $[\text{Me}_2\text{NH}_2]_7[\alpha_1\text{-P}_2\text{W}_{17}\text{Re}^{\text{V}}\text{O}_{62}] \cdot 2\text{H}_2\text{O}$  revealed that the molecular structure of **1** was identical to that of a monomeric  $\alpha$ -Dawson polyoxotungstate,  $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ , as shown in Figure 1. The bond lengths and bond angles are shown in Appendix. As a result of the high-symmetry space group, 12 tungsten sites [W(4) – W(15)] were disordered and a mono-rhenium-substituted site was not identified, as observed for  $[\text{W}_9\text{ReO}_{32}]^{5-}$  [47] and  $[\alpha\text{-PW}_{11}\text{Re}^{\text{V}}\text{O}_{40}]^{5-}$  [48]. Some ethanol and acetonitrile molecules were observed in a single crystal of **Me<sub>2</sub>NH<sub>2</sub>-1**; however, no acetonitrile and ethanol solvent molecules were observed by elemental analysis and  $^1\text{H}$  NMR spectroscopy. The solvent molecules therefore evaporate gradually when the crystals are removed from acetonitrile solution.

The FTIR spectrum of compound **Me<sub>2</sub>NH<sub>2</sub>-1**, which was obtained using a KBr disk, is shown in Figure 2. The positions of all the bands (1094, 1077, 1014, 959, 918, 823, 776, and 733  $\text{cm}^{-1}$ ) in the polyoxoanion region of this compound are characteristic of polyoxoanions; however, they were different from those for  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$  (1122, 1092, 1011, 944, 908, 828, 783, and 744  $\text{cm}^{-1}$ ), **K-2** (1091, 1018, 955, 910, and 788  $\text{cm}^{-1}$ ), and  $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (1091, 1020, 958, 912, 777, and 528  $\text{cm}^{-1}$ ). This suggests coordination of a rhenium(V) ion in the monovacant site of  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$ .

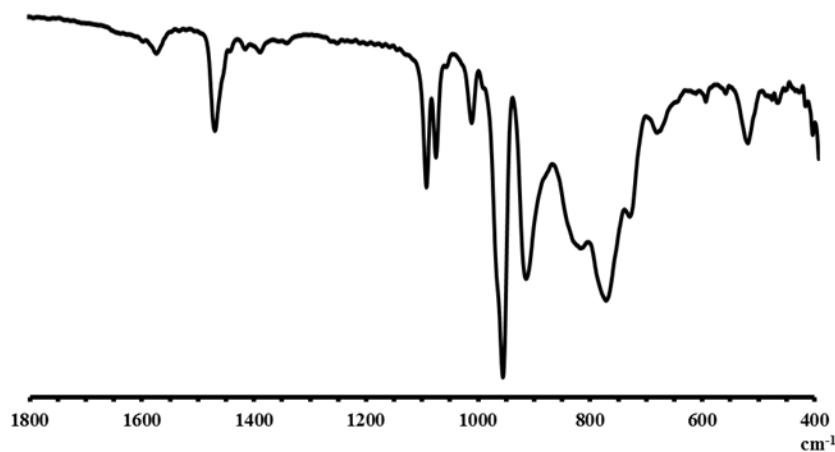
The  $^{31}\text{P}$  NMR spectrum in  $\text{CH}_3\text{COOLi}\text{-D}_2\text{O}$  solution of **Me<sub>2</sub>NH<sub>2</sub>-1** showed a clear two-line spectrum, with signals at -12.1 ppm and -12.4 ppm, as shown in Figure 3(a). The signals were shifted compared with those of  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$  (-8.7 ppm and -13.0 ppm) and  $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  (-12.8 ppm), indicating complete coordination of rhenium atom to monovacant site of  $[\alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}$ , as shown in Figure 1. No contamination of the sample by polyoxoanion **2** (-11.9 ppm and -12.9 ppm in  $\text{D}_2\text{O}$ ) was observed; however, polyoxoanion **1** gradually isomerized to polyoxoanion **2** in aqueous solution. The  $^{183}\text{W}$  NMR spectrum of **Me<sub>2</sub>NH<sub>2</sub>-1** was failed to obtain because of its low solubility in water and acetonitrile.

The UV-visible spectrum of **Me<sub>2</sub>NH<sub>2</sub>-1** in water showed four absorption bands, at 263 ( $\epsilon 4.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ), 310 ( $\epsilon 1.8 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ), 468 ( $\epsilon 3.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), and 613 nm ( $\epsilon 5.2 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ), as shown in Figure 4. The bands at 263 nm and 310 nm were assigned to the charge transfer (CT) band of W-O bonds. The two bands at 468 and 613 nm were assigned to the  $\text{Re}^{\text{V}} \rightarrow \text{W}^{\text{VI}}$  intervalence charge transfer (IVCT) band and the *d-d* band of the

243 rhenium(V) atom, respectively [39,40]. It was noted that the bands at 468 nm and 613 nm  
 244 for **Me<sub>2</sub>NH<sub>2</sub>-1** were significantly broader rather than those for **K-2** and **Me<sub>2</sub>NH<sub>2</sub>-3**, and the  
 245 positions were blue-shifted compared with those for **K-2** (496 nm and 737 nm) and **Me<sub>2</sub>NH<sub>2</sub>-**  
 246 **3** (513 nm and 698 nm); this also suggested coordination of the rhenium(V) ion to the  
 247 monovacant site in [ $\alpha_1$ -LiP<sub>2</sub>W<sub>17</sub>O<sub>61</sub>]<sup>9-</sup>.  
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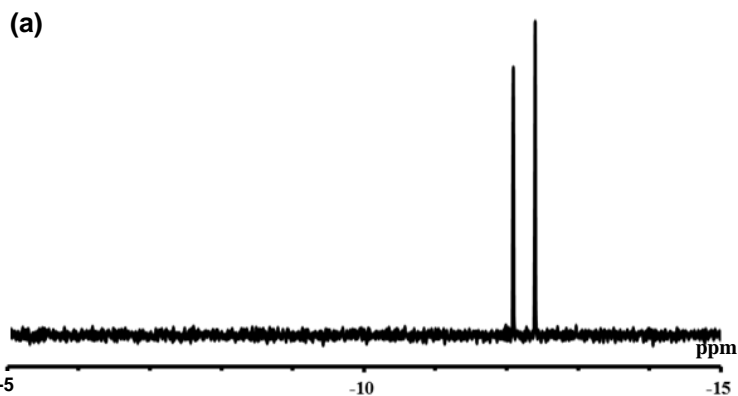


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 250  
 251 **Fig. 1. (a) The molecular structure (ORTEP drawing) of**  
 252 **polyoxoanion 1 with all atom numberings and (b) polyhedral**  
 253 **representation of polyoxoanion 1. In (b), WO<sub>6</sub> and ReO<sub>6</sub> units are**  
 254 **represented by the white and purple octahedra, respectively. The**  
 255 **internal PO<sub>4</sub> units are represented by the red tetrahedra.**  
 256

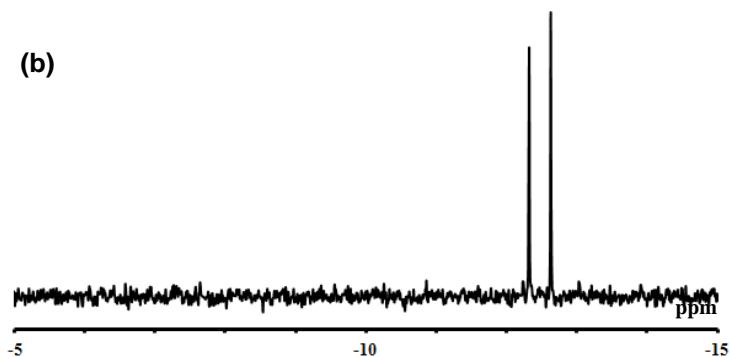


257  
 258 **Fig. 2. FTIR spectrum as a KBr disk of Me<sub>2</sub>NH<sub>2</sub>-1.**

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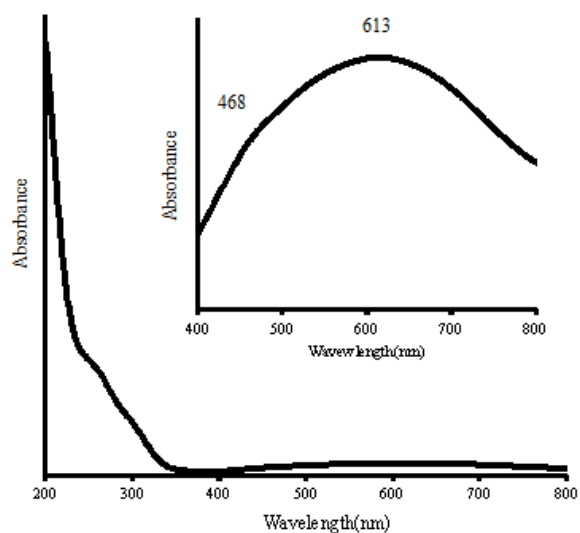
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**Fig. 3.**  $^{31}\text{P}$  NMR spectra in 0.285 M  $\text{CH}_3\text{COOLi-D}_2\text{O}$  of (a)  $\text{Me}_2\text{NH}_2\text{-1}$  and (b) after photoreaction. The spectrum was referenced to an external standard of 85%  $\text{H}_3\text{PO}_4$  in a sealed capillary. In (b),  $\text{Me}_2\text{NH}_2\text{-1}$  (50 mg) and  $\text{TiO}_2$  (500 mg) were suspended in methanol (25 mL), and they were irradiated under the visible light ( $\geq 400$  nm) for 6 h.



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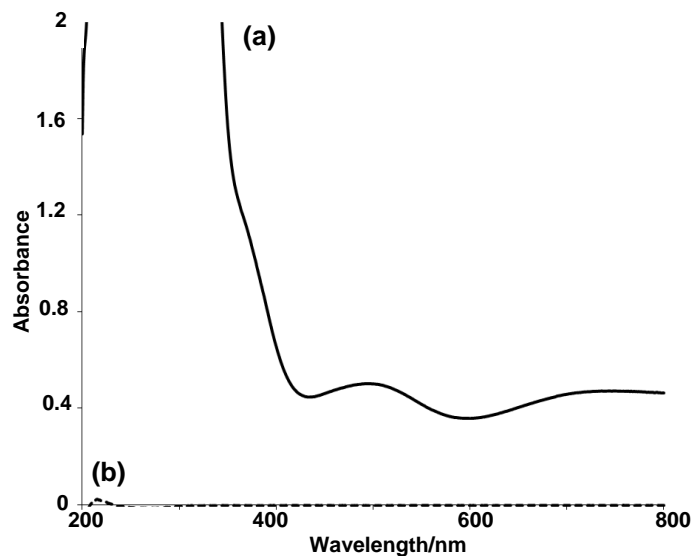
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**Fig. 4.** UV-visible spectra in  $\text{H}_2\text{O}$  of  $\text{Me}_2\text{NH}_2\text{-1}$  ( $1.0 \times 10^{-5}$  M) at 200 – 800 nm. Inset: 400 – 800 nm ( $1.0 \times 10^{-4}$  M).



### 3.2 Catalytic activities in methanol dehydrogenation catalyzed by rhenium(V)-coordinated polyoxotungstates in the presence of TiO<sub>2</sub> under visible-light irradiation ( $\geq 400$ nm)

Methanol dehydrogenation catalyzed by rhenium(V)-coordinated polyoxotungstates at 25 °C in the presence of TiO<sub>2</sub> under light irradiation ( $\geq 400$  nm) was investigated; the results are summarized in Table 1. Hydrogen was evolved from methanol catalyzed by **Me<sub>2</sub>NH<sub>2</sub>-1**, **K-2**, and **Me<sub>2</sub>NH<sub>2</sub>-3**. Formaldehyde was also observed; while, O<sub>2</sub>, CO, and CH<sub>4</sub> were not observed. The three rhenium(V) compounds were hardly soluble in methanol. When a suspension of **K-2** (50 mg) and TiO<sub>2</sub> (200 mg) in methanol (25 mL) was irradiated under visible light ( $\geq 400$  nm) for 6 h, followed by filtration through a membrane filter (JG 0.2  $\mu$ m), UV-vis spectrum of the filtrate showed a small band at around 220 nm due to a charge transfer band of W<sup>VI</sup>-O; however, this was significantly smaller than that in 30 mM EDTA·2Na aqueous solution (25 mL) under the same reaction conditions, as shown in Figure 5. Even when the cesium salts of **1** – **3** were used as catalysts, a slight leaching into methanol was observed. These results suggested that the rhenium(V) compounds were predominantly active in the solid state under the present reaction conditions. The initial dehydrogenation rates with **Me<sub>2</sub>NH<sub>2</sub>-1** and **Me<sub>2</sub>NH<sub>2</sub>-3** were slow; while, no induction period was observed for **K-2**, as shown in Figure 6. The colors of these materials changed from white-purple to blue during the reactions; however, the blue color disappeared and the photoreactions stopped when visible light irradiation stopped.



**Fig. 5. UV-visible spectra of K-2 at 200 – 800 nm.**  
**K-2 (50 mg) and TiO<sub>2</sub> (500 mg) were suspended in (a) 30 mM EDTA·2Na aqueous solution (25 mL) and (b) methanol (25 mL), and they were irradiated under the visible light ( $\geq 400$  nm) for 6 h at 25 °C. After a filtration through a membrane filter (JG 0.2  $\mu$ m), UV-vis spectra of the filtrates were observed, respectively.**

In control experiments, hydrogen was not detected when the reaction was catalyzed by TiO<sub>2</sub>. The rhenium(V)-coordinated polyoxotungstates showed no reaction in the absence of TiO<sub>2</sub>. K<sub>10</sub>[ $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>] $\cdot$ 27H<sub>2</sub>O also showed no reaction even in the presence of TiO<sub>2</sub>. A combination of rhenium(V)-coordinated sites in the polyoxotungstates and TiO<sub>2</sub> was therefore necessary, as reported for photoreactions using an EDTA·2Na aqueous solution in

the presence of TiO<sub>2</sub> under light irradiation ( $\geq 400$  nm) [39,40]. For the three rhenium compounds (1.0  $\mu\text{mol}$  of Re), the evolved amounts of H<sub>2</sub> after 6 h were 17.7, 206, and 72.4  $\mu\text{mol}$  [the turnover numbers (TONs) were 35, 412, and 145, respectively]; these results showed that **K-2** had the highest activity among these samples under the present reaction conditions. Even for 0.6 and 2.0  $\mu\text{mol}$  of Re, **K-2** exhibited the highest activities; however, the TONs decreased with increasing concentration of rhenium(V) atoms. When the cesium salts of **2** and **3**, Cs<sub>14</sub>[O{Re(OH)( $\alpha_2$ -P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)<sub>2</sub>}] (**Cs-2**) [40] and Cs<sub>3.5</sub>H<sub>0.5</sub>[PW<sub>11</sub>ReO<sub>40</sub>] (**Cs-3**) [40], were used as catalysts, the activities decreased compared with those of **K-2** and **Me<sub>2</sub>NH<sub>2</sub>-3**; however, the activities of **Cs-2** were higher than those of **Cs-3**. These results suggested that the structure dependence was not influenced by the counter ion.

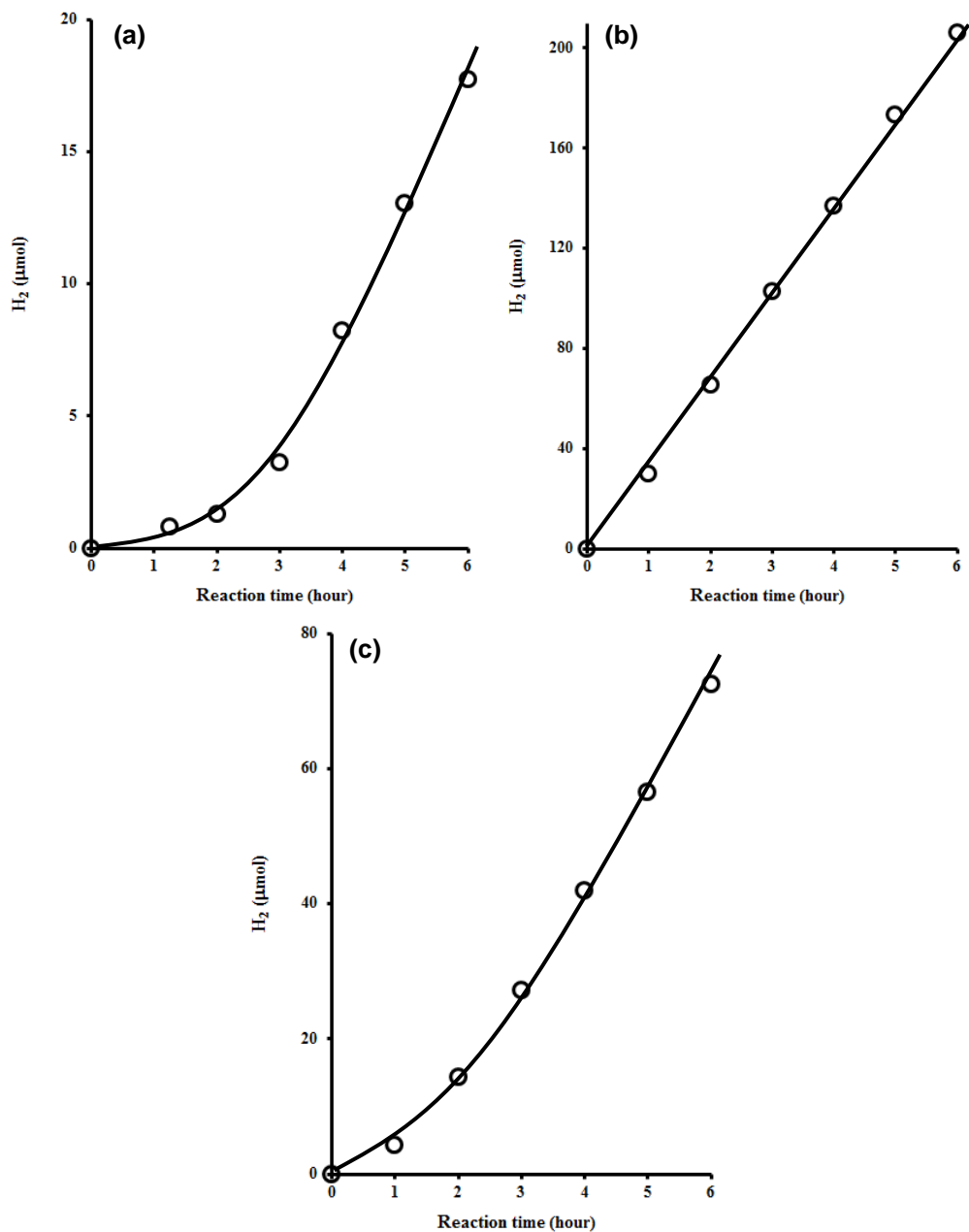
**Table 1. Hydrogen evolution from methanol catalyzed by rhenium(V)-coordinated polyoxometalates under visible light irradiation<sup>a</sup>**

Catalyst ( $\mu\text{mol}$ of rhenium atom)	H <sub>2</sub> [ $\mu\text{mol}$ ]	TON <sup>b</sup>
<b>Me<sub>2</sub>NH<sub>2</sub>-1</b> /TiO <sub>2</sub> (0.6)	10.8	36
<b>Me<sub>2</sub>NH<sub>2</sub>-1</b> /TiO <sub>2</sub> (1.0)	17.7	35
<b>Me<sub>2</sub>NH<sub>2</sub>-1</b> /TiO <sub>2</sub> (1.9)	29.9	31
<b>K-2</b> /TiO <sub>2</sub> (0.6)	103	345
<b>K-2</b> /TiO <sub>2</sub> (1.0)	206	412
<b>K-2</b> /TiO <sub>2</sub> (2.0)	116	116
<b>Me<sub>2</sub>NH<sub>2</sub>-3</b> /TiO <sub>2</sub> (0.6)	42.4	141
<b>Me<sub>2</sub>NH<sub>2</sub>-3</b> /TiO <sub>2</sub> (1.0)	72.4	145
<b>Me<sub>2</sub>NH<sub>2</sub>-3</b> /TiO <sub>2</sub> (2.0)	34.0	34

<sup>a</sup> = Reaction conditions are as follows: methanol (10 mL), **Me<sub>2</sub>NH<sub>2</sub>-1** (0.6 – 1.9  $\mu\text{mol}$  of Re), **K-2** (0.6 – 2.0  $\mu\text{mol}$  of Re), and **Me<sub>2</sub>NH<sub>2</sub>-3** (0.6 – 2.0  $\mu\text{mol}$  of Re), titanium dioxide (anatase/rutile = 80/20) (200 mg), reaction time 6 h, light ( $\geq 400$  nm), 25 °C

<sup>b</sup> = Turnover number (TON) was calculated as 2[H<sub>2</sub> evolved (mol)] per [Re atoms (mol)]

The stabilities of polyoxoanions **1** – **3** during methanol dehydrogenation were determined by <sup>31</sup>P NMR spectroscopy, as follows: TiO<sub>2</sub> (500 mg) and the rhenium compounds (50 mg) were suspended in 25 mL of methanol. After light irradiation for 6 h, the solids were collected using a membrane filter (JG 0.2  $\mu\text{m}$ ). The solids were suspended in 10 mL of water, and the filtrates, containing dissolved polyoxoanions **1** – **3**, were evaporated to dryness at 40 °C. As shown in Figures 3(b) and 7, the <sup>31</sup>P NMR spectra in CH<sub>3</sub>COOLi-D<sub>2</sub>O of **1**, and in D<sub>2</sub>O of **2** and **3**, were the same as those of the as-prepared samples. This showed that these compounds did not decompose or isomerize during methanol dehydrogenation under light irradiation. It was clear that the rhenium(V) sites in polyoxometalates significantly affected the photocatalytic activities, and the dirhenium(V)-oxido-bridged site in **2** exhibited the highest activity among these three samples under the present reaction conditions.



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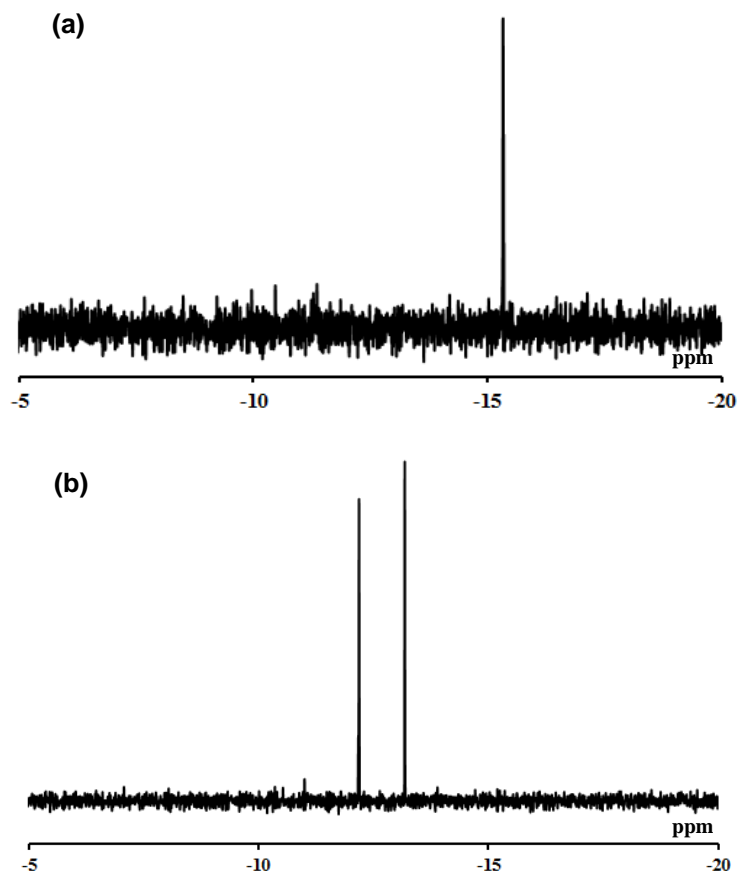
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**Fig. 6. Time course for methanol dehydrogenation catalyzed by (a) Me<sub>2</sub>NH<sub>2</sub>-1 (1.0 μmol of Re), (b) K-2 (1.0 μmol of Re), and (c) Me<sub>2</sub>NH<sub>2</sub>-3 (1.0 μmol of Re). In this system, the three polyoxotungstates and TiO<sub>2</sub> were suspended in methanol, and the visible light (≥400 nm) was irradiated for 6 h at 25 °C. Reaction conditions are shown in Table 1.**



**Fig. 7.**  $^{31}\text{P}$  NMR spectra in  $\text{D}_2\text{O}$  of (a) K-2 and (b)  $\text{Me}_2\text{NH}_2\text{-3}$  after photoreactions. The rhenium compounds (50 mg) and  $\text{TiO}_2$  (500 mg) were suspended in methanol (25 mL), and they were irradiated under the visible light ( $\geq 400$  nm) for 6 h.

#### 4. CONCLUSION

A rhenium(V) complex composed of mono-lacunary  $\alpha_1$ -Dawson polyoxotungstate was presented. We successfully obtained single crystals of dimethylammonium salt  $[\text{Me}_2\text{NH}_2]_7[\alpha_1\text{-P}_2\text{W}_{17}\text{Re}^{\text{VO}}_{62}]\cdot 9\text{H}_2\text{O}$  (**Me<sub>2</sub>NH<sub>2</sub>-1**) by reacting hexachlororhenate with a mono-lacunary  $\alpha_1$ -Dawson polyoxoanion in  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COOLi}$  buffer, followed by crystallization via vapor diffusion from acetonitrile/ethanol. The characterization of compound **Me<sub>2</sub>NH<sub>2</sub>-1** was accomplished by X-ray structure analysis, elemental analysis, TG/DTA, FTIR, UV-visible, and solution  $^{31}\text{P}$  NMR spectroscopy. For methanol dehydrogenation under visible light irradiation ( $\geq 400$  nm) in the presence of  $\text{TiO}_2$ , the molecular structures of three rhenium(V) compounds were stable during the photoreactions, and the dirhenium(V)-oxido-bridged site in **2** exhibited the most effective activities compared with those of the mono-rhenium(V)-substituted sites in **1** and **3**.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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## APPENDIX

Bond lengths (Å) of **Me<sub>2</sub>NH<sub>2</sub>-1**: Re(1)(W(4))-O(8) 1.915(14); Re(1)(W(4))-O(14) 1.702(14); Re(1)(W(4))-O(19) 1.912(16); Re(1)(W(4))-O(20) 1.870(17); Re(1)(W(4))-O(26) 2.374(12); Re(1)(W(4))-O(57) 1.896(12); Re(2)(W(5))-O(9) 1.968(13); Re(2)(W(5))-O(15) 1.733(13); Re(2)(W(5))-O(20) 1.900(18); Re(2)(W(5))-O(21) 1.928(17); Re(2)(W(5))-O(27) 2.353(12); Re(2)(W(5))-O(58) 1.889(13); Re(3)(W(6))-O(10) 1.951(14); Re(3)(W(6))-O(16) 1.696(18); Re(3)(W(6))-O(21) 1.896(12); Re(3)(W(6))-O(22) 1.909(13); Re(3)(W(6))-O(27) 2.376(18); Re(3)(W(6))-O(59) 1.924(13); Re(4)(W(7))-O(11) 1.968(12); Re(4)(W(7))-O(17) 1.714(16); Re(4)(W(7))-O(22) 1.877(14); Re(4)(W(7))-O(23) 1.929(16); Re(4)(W(7))-O(28) 2.353(15);

525 Re(4)(W(7))-O(60) 1.893(13); Re(5)(W(8))-O(12) 1.951(13); Re(5)(W(8))-O(18) 1.689(14);  
 526 Re(5)(W(8))-O(23) 1.891(17); Re(5)(W(8))-O(24) 1.906(15); Re(5)(W(8))-O(28) 2.360(13);  
 527 Re(5)(W(8))-O(61) 1.881(12); Re(6)(W(9))-O(7) 1.905(14); Re(6)(W(9))-O(13) 1.691(17);  
 528 Re(6)(W(9))-O(19) 1.899(13); Re(6)(W(9))-O(24) 1.866(13); Re(6)(W(9))-O(26) 2.379(16);  
 529 Re(6)(W(9))-O(62) 1.924(14); Re(7)(W(10))-O(30) 1.708(16); Re(7)(W(10))-O(35) 1.916(16);  
 530 Re(7)(W(10))-O(36) 1.863(16); Re(7)(W(10))-O(42) 1.943(12); Re(7)(W(10))-O(54)  
 531 2.360(12); Re(7)(W(10))-O(57) 1.919(12); Re(8)(W(11))-O(31) 1.734(14); Re(8)(W(11))-  
 532 O(36) 1.911(15); Re(8)(W(11))-O(37) 1.884(16); Re(8)(W(11))-O(43) 1.960(15);  
 533 Re(8)(W(11))-O(55) 2.385(11); Re(8)(W(11))-O(58) 1.881(14); Re(9)(W(12))-O(32)  
 534 1.689(18); Re(9)(W(12))-O(37) 1.941(12); Re(9)(W(12))-O(38) 1.879(12); Re(9)(W(12))-  
 535 O(44) 1.968(14); Re(9)(W(12))-O(55) 2.345(16); Re(9)(W(12))-O(59) 1.861(13);  
 536 Re(10)(W(13))-O(33) 1.694(15); Re(10)(W(13))-O(38) 1.892(13); Re(10)(W(13))-O(39)  
 537 1.902(16); Re(10)(W(13))-O(45) 1.981(14); Re(10)(W(13))-O(56) 2.351(14); Re(10)(W(13))-  
 538 O(60) 1.890(13); Re(11)(W(14))-O(34) 1.701(15); Re(11)(W(14))-O(39) 1.897(17);  
 539 Re(11)(W(14))-O(40) 1.872(14); Re(11)(W(14))-O(46) 1.980(13); Re(11)(W(14))-O(56)  
 540 2.374(13); Re(12)(W(15))-O(61) 1.891(13); Re(12)(W(15))-O(29) 1.679(19); Re(12)(W(15))-  
 541 O(35) 1.907(12); Re(12)(W(15))-O(40) 1.899(13); Re(12)(W(15))-O(41) 1.958(13);  
 542 Re(12)(W(15))-O(54) 2.384(16); Re(12)(W(15))-O(62) 1.867(13); W(1)-O(1) 1.690(11); W(1)-  
 543 O(4) 1.921(15); W(1)-O(5) 1.910(15); W(1)-O(8) 1.912(16); W(1)-O(9) 1.870(14); W(1)-O(25)  
 544 2.402(11); W(2)-O(2) 1.705(16); W(2)-O(5) 1.902(11); W(2)-O(6) 1.920(17); W(2)-O(10)  
 545 1.880(15); W(2)-O(11) 1.882(12); W(2)-O(25) 2.364(15); W(3)-O(3) 1.692(14); W(3)-O(4)  
 546 1.915(12); W(3)-O(6) 1.887(18); W(3)-O(7) 1.918(16); W(3)-O(12) 1.874(12); W(3)-O(25)  
 547 2.386(13); W(16)-O(42) 1.892(15); W(16)-O(43) 1.874(17); W(16)-O(47) 1.730(14); W(16)-  
 548 O(50) 1.908(15); W(16)-O(51) 1.932(15); W(16)-O(53) 2.415(12); W(17)-O(44) 1.865(15);  
 549 W(17)-O(45) 1.865(13); W(17)-O(48) 1.680(14); W(17)-O(51) 1.898(14); W(17)-O(52)  
 550 1.932(17); W(17)-O(53) 2.352(13); W(18)-O(41) 1.886(14); W(18)-O(46) 1.877(13); W(18)-  
 551 O(49) 1.705(16); W(18)-O(50) 1.966(12); W(18)-O(52) 1.900(17); W(18)-O(53) 2.354(14);  
 552 P(1)-O(25) 1.593(12); P(1)-O(26) 1.494(17); P(1)-O(27) 1.517(16); P(1)-O(28) 1.543(12);  
 553 P(2)-O(53) 1.600(12); P(2)-O(54) 1.500(15); P(2)-O(55) 1.514(16); P(2)-O(56) 1.531(12).  
 554

555 Bond angles (°) of **Me<sub>2</sub>NH<sub>2</sub>-1**: O(8)-Re(1)(W(4))-O(14) 97.6(6); O(8)-Re(1)(W(4))-O(19)  
 556 89.9(7); O(8)-Re(1)(W(4))-O(20) 85.3(7); O(8)-Re(1)(W(4))-O(26) 81.4(5); O(8)-Re(1)(W(4))-  
 557 O(57) 164.6(6); O(14)-Re(1)(W(4))-O(19) 99.4(7); O(14)-Re(1)(W(4))-O(20) 103.4(7); O(14)-  
 558 Re(1)(W(4))-O(26) 172.2(7); O(14)-Re(1)(W(4))-O(57) 97.7(6); O(19)-Re(1)(W(4))-O(20)  
 559 157.1(6); O(19)-Re(1)(W(4))-O(26) 72.9(6); O(19)-Re(1)(W(4))-O(57) 89.4(6); O(20)-  
 560 Re(1)(W(4))-O(26) 84.3(6); O(20)-Re(1)(W(4))-O(57) 89.5(6); O(26)-Re(1)(W(4))-O(57)  
 561 83.7(5); O(9)-Re(2)(W(5))-O(15) 97.4(6); O(9)-Re(2)(W(5))-O(20) 84.8(7); O(9)-Re(2)(W(5))-  
 562 O(21) 88.1(6); O(9)-Re(2)(W(5))-O(27) 81.8(5); O(9)-Re(2)(W(5))-O(58) 163.3(6); O(15)-  
 563 Re(2)(W(5))-O(20) 102.0(7); O(15)-Re(2)(W(5))-O(21) 99.5(7); O(15)-Re(2)(W(5))-O(27)  
 564 173.0(8); O(15)-Re(2)(W(5))-O(58) 99.1(6); O(20)-Re(2)(W(5))-O(21) 158.1(6); O(20)-  
 565 Re(2)(W(5))-O(27) 84.9(6); O(20)-Re(2)(W(5))-O(58) 89.5(7); O(21)-Re(2)(W(5))-O(27)  
 566 73.5(6); O(21)-Re(2)(W(5))-O(58) 91.4(7); O(27)-Re(2)(W(5))-O(58) 82.1(5); O(10)-  
 567 Re(3)(W(6))-O(16) 98.5(7); O(10)-Re(3)(W(6))-O(21) 88.0(6); O(10)-Re(3)(W(6))-O(22)  
 568 86.8(6); O(10)-Re(3)(W(6))-O(27) 81.4(7); O(10)-Re(3)(W(6))-O(59) 163.6(8); O(16)-  
 569 Re(3)(W(6))-O(21) 100.1(7); O(16)-Re(3)(W(6))-O(22) 102.0(7); O(16)-Re(3)(W(6))-O(27)  
 570 173.7(5); O(16)-Re(3)(W(6))-O(59) 97.8(7); O(21)-Re(3)(W(6))-O(22) 157.7(8); O(21)-  
 571 Re(3)(W(6))-O(27) 73.5(6); O(21)-Re(3)(W(6))-O(59) 90.8(6); O(22)-Re(3)(W(6))-O(27)  
 572 84.3(7); O(22)-Re(3)(W(6))-O(59) 88.1(6); O(27)-Re(3)(W(6))-O(59) 82.6(6); O(11)-  
 573 Re(4)(W(7))-O(17) 96.9(6); O(11)-Re(4)(W(7))-O(22) 86.0(6); O(11)-Re(4)(W(7))-O(23)  
 574 87.8(6); O(11)-Re(4)(W(7))-O(28) 81.7(6); O(11)-Re(4)(W(7))-O(60) 163.4(6); O(17)-  
 575 Re(4)(W(7))-O(22) 102.7(8); O(17)-Re(4)(W(7))-O(23) 99.3(7); O(17)-Re(4)(W(7))-O(28)  
 576 172.2(6); O(17)-Re(4)(W(7))-O(60) 99.6(6); O(22)-Re(4)(W(7))-O(23) 157.7(7); O(22)-  
 577 Re(4)(W(7))-O(28) 84.9(6); O(22)-Re(4)(W(7))-O(60) 89.1(6); O(23)-Re(4)(W(7))-O(28)



578 73.0(6); O(23)-Re(4)(W(7))-O(60) 90.8(6); O(28)-Re(4)(W(7))-O(60) 82.1(6); O(12)-  
579 Re(5)(W(8))-O(18) 97.7(6); O(12)-Re(5)(W(8))-O(23) 89.1(7); O(12)-Re(5)(W(8))-O(24)  
580 84.5(6); O(12)-Re(5)(W(8))-O(28) 81.5(5); O(12)-Re(5)(W(8))-O(61) 162.6(5); O(18)-  
581 Re(5)(W(8))-O(23) 99.0(7); O(18)-Re(5)(W(8))-O(24) 102.5(7); O(18)-Re(5)(W(8))-O(28)  
582 172.4(7); O(18)-Re(5)(W(8))-O(61) 99.3(6); O(23)-Re(5)(W(8))-O(24) 158.3(6); O(23)-  
583 Re(5)(W(8))-O(28) 73.5(6); O(23)-Re(5)(W(8))-O(61) 91.9(7); O(24)-Re(5)(W(8))-O(28)  
584 85.1(6); O(24)-Re(5)(W(8))-O(61) 88.3(6); O(28)-Re(5)(W(8))-O(61) 82.1(5); O(7)-  
585 Re(6)(W(9))-O(13) 97.4(7); O(7)-Re(6)(W(9))-O(19) 89.2(6); O(7)-Re(6)(W(9))-O(24)  
586 87.0(6); O(7)-Re(6)(W(9))-O(26) 81.7(6); O(7)-Re(6)(W(9))-O(62) 163.7(7); O(13)-  
587 Re(6)(W(9))-O(19) 100.8(7); O(13)-Re(6)(W(9))-O(24) 101.6(7); O(13)-Re(6)(W(9))-O(26)  
588 173.7(5); O(13)-Re(6)(W(9))-O(62) 98.9(7); O(19)-Re(6)(W(9))-O(24) 157.6(8); O(19)-  
589 Re(6)(W(9))-O(26) 73.0(6); O(19)-Re(6)(W(9))-O(62) 88.2(6); O(24)-Re(6)(W(9))-O(26)  
590 84.6(6); O(24)-Re(6)(W(9))-O(62) 89.2(6); O(26)-Re(6)(W(9))-O(62) 82.1(6); O(30)-  
591 Re(7)(W(10))-O(35) 99.4(8); O(30)-Re(7)(W(10))-O(36) 103.2(7); O(30)-Re(7)(W(10))-O(42)  
592 96.7(6); O(30)-Re(7)(W(10))-O(54) 172.0(7); O(30)-Re(7)(W(10))-O(57) 99.0(6); O(35)-  
593 Re(7)(W(10))-O(36) 157.2(6); O(35)-Re(7)(W(10))-O(42) 87.2(6); O(35)-Re(7)(W(10))-O(54)  
594 72.8(6); O(35)-Re(7)(W(10))-O(57) 88.4(6); O(36)-Re(7)(W(10))-O(42) 87.4(6); O(36)-  
595 Re(7)(W(10))-O(54) 84.5(5); O(36)-Re(7)(W(10))-O(57) 90.8(6); O(42)-Re(7)(W(10))-O(54)  
596 81.2(5); O(42)-Re(7)(W(10))-O(57) 164.2(6); O(54)-Re(7)(W(10))-O(57) 82.9(5); O(31)-  
597 Re(8)(W(11))-O(36) 102.7(7); O(31)-Re(8)(W(11))-O(37) 99.2(7); O(31)-Re(8)(W(11))-O(43)  
598 98.5(7); O(31)-Re(8)(W(11))-O(55) 172.6(8); O(31)-Re(8)(W(11))-O(58) 98.3(6); O(36)-  
599 Re(8)(W(11))-O(37) 158.1(5); O(36)-Re(8)(W(11))-O(43) 85.7(7); O(36)-Re(8)(W(11))-O(55)  
600 84.8(5); O(36)-Re(8)(W(11))-O(58) 86.6(7); O(37)-Re(8)(W(11))-O(43) 90.8(7); O(37)-  
601 Re(8)(W(11))-O(55) 73.4(6); O(37)-Re(8)(W(11))-O(58) 90.6(7); O(43)-Re(8)(W(11))-O(55)  
602 82.3(5); O(43)-Re(8)(W(11))-O(58) 162.8(6); O(55)-Re(8)(W(11))-O(58) 81.7(5); O(32)-  
603 Re(9)(W(12))-O(37) 100.3(7); O(32)-Re(9)(W(12))-O(38) 101.6(7); O(32)-Re(9)(W(12))-  
604 O(44) 96.9(7); O(32)-Re(9)(W(12))-O(55) 173.4(5); O(32)-Re(9)(W(12))-O(59) 98.5(7);  
605 O(37)-Re(9)(W(12))-O(38) 157.8(7); O(37)-Re(9)(W(12))-O(44) 88.8(6); O(37)-Re(9)(W(12))-  
606 O(55) 73.4(6); O(37)-Re(9)(W(12))-O(59) 88.9(6); O(38)-Re(9)(W(12))-O(44) 85.4(6); O(38)-  
607 Re(9)(W(12))-O(55) 84.6(6); O(38)-Re(9)(W(12))-O(59) 91.1(6); O(44)-Re(9)(W(12))-O(55)  
608 81.2(6); O(44)-Re(9)(W(12))-O(59) 164.6(7); O(55)-Re(9)(W(12))-O(59) 83.6(6); O(33)-  
609 Re(10)(W(13))-O(38) 101.9(7); O(33)-Re(10)(W(13))-O(39) 100.0(7); O(33)-Re(10)(W(13))-  
610 O(45) 96.1(6); O(33)-Re(10)(W(13))-O(56) 172.5(6); O(33)-Re(10)(W(13))-O(60) 100.7(7);  
611 O(38)-Re(10)(W(13))-O(39) 157.6(7); O(38)-Re(10)(W(13))-O(45) 84.7(6); O(38)-  
612 Re(10)(W(13))-O(56) 84.7(6); O(38)-Re(10)(W(13))-O(60) 88.5(6); O(39)-Re(10)(W(13))-  
613 O(45) 88.6(6); O(39)-Re(10)(W(13))-O(56) 73.1(6); O(39)-Re(10)(W(13))-O(60) 91.8(6);  
614 O(45)-Re(10)(W(13))-O(56) 80.9(5); O(45)-Re(10)(W(13))-O(60) 162.8(6); O(56)-  
615 Re(10)(W(13))-O(60) 82.7(6); O(34)-Re(11)(W(14))-O(39) 100.0(7); O(34)-Re(11)(W(14))-  
616 O(40) 102.2(8); O(34)-Re(11)(W(14))-O(46) 96.5(7); O(34)-Re(11)(W(14))-O(56) 172.5(7);  
617 O(34)-Re(11)(W(14))-O(61) 99.5(6); O(39)-Re(11)(W(14))-O(40) 157.3(6); O(39)-  
618 Re(11)(W(14))-O(46) 87.3(7); O(39)-Re(11)(W(14))-O(56) 72.7(5); O(39)-Re(11)(W(14))-  
619 O(61) 91.2(7); O(40)-Re(11)(W(14))-O(46) 85.6(6); O(40)-Re(11)(W(14))-O(56) 85.0(6);  
620 O(40)-Re(11)(W(14))-O(61) 89.8(6); O(46)-Re(11)(W(14))-O(56) 82.1(5); O(46)-  
621 Re(11)(W(14))-O(61) 163.9(6); O(56)-Re(11)(W(14))-O(61) 82.2(5); O(29)-Re(12)(W(15))-  
622 O(35) 100.3(7); O(29)-Re(12)(W(15))-O(40) 101.8(7); O(29)-Re(12)(W(15))-O(41) 96.3(7);  
623 O(29)-Re(12)(W(15))-O(54) 172.4(6); O(29)-Re(12)(W(15))-O(62) 99.3(7); O(35)-  
624 Re(12)(W(15))-O(40) 157.3(7); O(35)-Re(12)(W(15))-O(41) 88.0(5); O(35)-Re(12)(W(15))-  
625 O(54) 72.4(6); O(35)-Re(12)(W(15))-O(62) 91.2(6); O(40)-Re(12)(W(15))-O(41) 84.6(6);  
626 O(40)-Re(12)(W(15))-O(54) 85.3(6); O(40)-Re(12)(W(15))-O(62) 90.1(6); O(41)-  
627 Re(12)(W(15))-O(54) 81.4(6); O(41)-Re(12)(W(15))-O(62) 164.2(8); O(54)-Re(12)(W(15))-  
628 O(62) 83.4(6); O(1)-W(1)-O(4) 102.0(6); O(1)-W(1)-O(5) 101.9(7); O(1)-W(1)-O(8) 102.5(7);  
629 O(1)-W(1)-O(9) 102.1(6); O(1)-W(1)-O(25) 171.7(6); O(4)-W(1)-O(5) 88.7(7); O(4)-W(1)-O(8)  
630 87.0(7); O(4)-W(1)-O(9) 155.9(6); O(4)-W(1)-O(25) 72.9(5); O(5)-W(1)-O(8) 155.5(5); O(5)-

631 W(1)-O(9) 88.2(7); O(5)-W(1)-O(25) 71.8(5); O(8)-W(1)-O(9) 86.1(7); O(8)-W(1)-O(25)  
632 83.9(5); O(9)-W(1)-O(25) 83.5(5); O(2)-W(2)-O(5) 102.4(6); O(2)-W(2)-O(6) 101.5(7); O(2)-  
633 W(2)-O(10) 103.6(8); O(2)-W(2)-O(11) 101.8(7); O(2)-W(2)-O(25) 171.7(6); O(5)-W(2)-O(6)  
634 87.7(6); O(5)-W(2)-O(10) 87.2(6); O(5)-W(2)-O(11) 155.8(7); O(5)-W(2)-O(25) 72.9(6); O(6)-  
635 W(2)-O(10) 154.9(7); O(6)-W(2)-O(11) 87.1(6); O(6)-W(2)-O(25) 71.8(6); O(10)-W(2)-O(11)  
636 87.6(6); O(10)-W(2)-O(25) 83.3(7); O(11)-W(2)-O(25) 83.0(6); O(3)-W(3)-O(4) 103.2(6);  
637 O(3)-W(3)-O(6) 101.7(7); O(3)-W(3)-O(7) 102.2(7); O(3)-W(3)-O(12) 101.3(6); O(3)-W(3)-  
638 O(25) 172.4(7); O(4)-W(3)-O(6) 89.2(7); O(4)-W(3)-O(7) 87.4(6); O(4)-W(3)-O(12) 155.4(6);  
639 O(4)-W(3)-O(25) 73.4(5); O(6)-W(3)-O(7) 156.0(6); O(6)-W(3)-O(12) 88.0(7); O(6)-W(3)-  
640 O(25) 71.7(6); O(7)-W(3)-O(12) 85.4(6); O(7)-W(3)-O(25) 84.5(6); O(12)-W(3)-O(25) 82.6(5);  
641 O(42)-W(16)-O(43) 87.8(7); O(42)-W(16)-O(47) 102.4(7); O(42)-W(16)-O(50) 87.8(6); O(42)-  
642 W(16)-O(51) 155.2(6); O(42)-W(16)-O(53) 82.9(5); O(43)-W(16)-O(47) 103.3(7); O(43)-  
643 W(16)-O(50) 157.1(6); O(43)-W(16)-O(51) 89.2(7); O(43)-W(16)-O(53) 84.0(6); O(47)-  
644 W(16)-O(50) 99.6(7); O(47)-W(16)-O(51) 102.2(7); O(47)-W(16)-O(53) 171.0(5); O(50)-  
645 W(16)-O(51) 85.4(7); O(50)-W(16)-O(53) 73.1(6); O(51)-W(16)-O(53) 72.3(5); O(44)-W(17)-  
646 O(45) 86.8(6); O(44)-W(17)-O(48) 101.3(7); O(44)-W(17)-O(51) 91.4(6); O(44)-W(17)-O(52)  
647 157.7(6); O(44)-W(17)-O(53) 85.4(6); O(45)-W(17)-O(48) 102.4(6); O(45)-W(17)-O(51)  
648 157.3(7); O(45)-W(17)-O(52) 87.9(7); O(45)-W(17)-O(53) 82.9(6); O(48)-W(17)-O(51)  
649 100.1(6); O(48)-W(17)-O(52) 100.9(7); O(48)-W(17)-O(53) 171.5(7); O(51)-W(17)-O(52)  
650 85.3(7); O(51)-W(17)-O(53) 74.4(5); O(52)-W(17)-O(53) 72.4(6); O(41)-W(18)-O(46) 87.6(6);  
651 O(41)-W(18)-O(49) 101.8(8); O(41)-W(18)-O(50) 89.3(6); O(41)-W(18)-O(52) 157.7(7);  
652 O(41)-W(18)-O(53) 84.8(6); O(46)-W(18)-O(49) 102.1(7); O(46)-W(18)-O(50) 158.9(7);  
653 O(46)-W(18)-O(52) 89.4(7); O(46)-W(18)-O(53) 85.3(6); O(49)-W(18)-O(50) 98.9(7); O(49)-  
654 W(18)-O(52) 100.5(7); O(49)-W(18)-O(53) 170.2(6); O(50)-W(18)-O(52) 85.7(6); O(50)-  
655 W(18)-O(53) 73.6(6); O(52)-W(18)-O(53) 72.9(6); O(25)-P(1)-O(26) 107.4(8); O(25)-P(1)-  
656 O(27) 106.8(8); O(25)-P(1)-O(28) 106.4(7); O(26)-P(1)-O(27) 112.6(8); O(26)-P(1)-O(28)  
657 112.2(8); O(27)-P(1)-O(28) 111.0(8); O(53)-P(2)-O(54) 107.0(8); O(53)-P(2)-O(55) 106.4(7);  
658 O(53)-P(2)-O(56) 106.3(6); O(54)-P(2)-O(55) 112.9(7); O(54)-P(2)-O(56) 113.0(8); O(55)-  
659 P(2)-O(56) 110.8(8); W(1)-O(4)-W(3) 123.7(7); W(1)-O(5)-W(2) 124.9(7); W(2)-O(6)-W(3)  
660 125.5(7); Re(6)(W(9))-O(7)-W(3) 150.1(8); Re(1)(W(4))-O(8)-W(1) 151.3(9); Re(2)(W(5))-  
661 O(9)-W(1) 150.7(10); Re(3)(W(6))-O(10)-W(2) 150.0(9); Re(4)(W(7))-O(11)-W(2) 150.4(7);  
662 Re(5)(W(8))-O(12)-W(3) 153.0(8); Re(1)(W(4))-O(19)-Re(6)(W(9)) 124.0(9); Re(1)(W(4))-  
663 O(20)-Re(2)(W(5)) 152.9(8); Re(2)(W(5))-O(21)-Re(3)(W(6)) 122.4(8); Re(3)(W(6))-O(22)-  
664 Re(4)(W(7)) 151.7(9); Re(4)(W(7))-O(23)-Re(5)(W(8)) 122.6(7); Re(5)(W(8))-O(24)-  
665 Re(6)(W(9)) 151.7(9); W(1)-O(25)-W(2) 90.3(5); W(1)-O(25)-W(3) 89.9(4); W(1)-O(25)-P(1)  
666 123.8(6); W(2)-O(25)-W(3) 90.9(4); W(2)-O(25)-P(1) 126.4(8); W(3)-O(25)-P(1) 124.7(8);  
667 Re(1)(W(4))-O(26)-Re(6)(W(9)) 90.1(6); Re(1)(W(4))-O(26)-P(1) 128.6(8); Re(6)(W(9))-  
668 O(26)-P(1) 128.6(7); Re(2)(W(5))-O(27)-Re(3)(W(6)) 90.3(6); Re(2)(W(5))-O(27)-P(1)  
669 127.8(8); Re(3)(W(6))-O(27)-P(1) 128.3(8); Re(4)(W(7))-O(28)-Re(5)(W(8)) 90.6(4);  
670 Re(4)(W(7))-O(28)-P(1) 128.2(9); Re(5)(W(8))-O(28)-P(1) 127.2(8); Re(7)(W(10))-O(35)-  
671 Re(12)(W(15)) 123.9(9); Re(7)(W(10))-O(36)-Re(8)(W(11)) 151.8(6); Re(8)(W(11))-O(37)-  
672 Re(9)(W(12)) 122.7(8); Re(9)(W(12))-O(38)-Re(10)(W(13)) 152.9(9); Re(10)(W(13))-O(39)-  
673 Re(11)(W(14)) 123.6(7); Re(11)(W(14))-O(40)-Re(12)(W(15)) 153.3(8); Re(12)(W(15))-  
674 O(41)-W(18) 150.1(9); Re(7)(W(10))-O(42)-W(16) 149.4(10); Re(8)(W(11))-O(43)-W(16)  
675 150.4(10); Re(9)(W(12))-O(44)-W(17) 150.1(8); Re(10)(W(13))-O(45)-W(17) 151.1(7);  
676 Re(11)(W(14))-O(46)-W(18) 148.4(7); W(16)-O(50)-W(18) 122.5(8); W(16)-O(51)-W(17)  
677 123.3(7); W(17)-O(52)-W(18) 123.2(7); W(16)-O(53)-W(17) 90.0(4); W(16)-O(53)-W(18)  
678 90.8(5); W(16)-O(53)-P(2) 124.1(6); W(17)-O(53)-W(18) 91.5(4); W(17)-O(53)-P(2) 125.3(9);  
679 W(18)-O(53)-P(2) 124.9(8); Re(7)(W(10))-O(54)-Re(12)(W(15)) 90.6(6); Re(7)(W(10))-  
680 O(54)-P(2) 129.0(7); Re(12)(W(15))-O(54)-P(2) 127.8(7); Re(8)(W(11))-O(55)-Re(9)(W(12))  
681 90.4(5); Re(8)(W(11))-O(55)-P(2) 127.2(8); Re(9)(W(12))-O(55)-P(2) 130.2(7);  
682 Re(10)(W(13))-O(56)-Re(11)(W(14)) 90.3(4); Re(10)(W(13))-O(56)-P(2) 128.6(8);  
683 Re(11)(W(14))-O(56)-P(2) 127.8(9); Re(1)(W(4))-O(57)-Re(7)(W(10)) 160.2(10);

684 Re(2)(W(5))-O(58)-Re(8)(W(11)) 165.3(11); Re(3)(W(6))-O(59)-Re(9)(W(12)) 162.0(8);  
685 Re(4)(W(7))-O(60)-Re(10)(W(13)) 163.4(8); Re(5)(W(8))-O(61)-Re(11)(W(14)) 163.7(9);  
686 Re(6)(W(9))-O(62)-Re(12)(W(15)) 162.0(9).  
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