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# Short communication

# Synthesis and catalytic activities of two new extended Preyssler–type tungstophosphates with different cavity centers



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#### A R T I C L E I N F O

## ABSTRACT

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Keywords: Preyssler-type polyoxometalate Tungstophosphate Iron (III)-complex Hydrothermal synthesis Acid catalysis Two new extended Preyssler-type polyoxometalates (POMs) constructed by Fe(III), 2,2'-biimidazole and Preyssler-type tungstophosphate anions with Na and Ag cavity centers respectively, namely  $\{(H_4biim)_5H[Fe(H_2biim)(H_2O)_2(ZP_5W_{30}O_{110})]\cdot 17H_2O\}_n$  (Z = Na, compound **1**; Z = Ag, compound **2**;  $H_2biim = 2,2'$ -biimidazole), were designed and synthesized under hydrothermal conditions, and were systematically characterized by physico-chemical and spectroscopic methods. The two compounds are isostructural coordination polymers. In compound **1** or **2**, there exists interesting infinite 1D chains composed of Preyssler-type  $[ZP_5W_{30}O_{110}]^{14-}$  (abbreviated as  $\{ZP_5W_{30}\}$ ) polyanions bridged by Fe(III)-complex fragments, and these chains further formed 3D supramolecular frameworks *via* extensive hydrogen-bonding interactions. Especially for compound **2**, two types of transition metals, *i.e.* one  $Ag^+$  ion as a center in the inner cavity and two Fe<sup>3+</sup> ions as modified cations on the outer surface of one  $\{ZP_5W_{30}\}$  unit, existed in the same compound. Additionally, the electrochemical behaviors and acid catalytic activities of compounds **1** and **2** have been investigated.

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As a kind of well-known metal-oxo-cluster compounds, polyoxometalates (POMs) have aroused wide concern due to their controllable molecular size, inimitable structural features and promising applications in catalysis, electrochemistry and material science [1]. The oxygen-rich surface of POM can be modified by transition metalorganic complexes [2]. The Preyssler-type polyanion cluster  $[ZP_5W_{30}O_{110}]^{14-}$  ({ $ZP_5W_{30}$ }) with an inner cavity and 30 terminal O atoms, as one of largest phosphotungstate clusters, possesses unusual doughnut-shaped structure and exhibits remarkable physico-chemical stability [3]. The {ZP<sub>5</sub>W<sub>30</sub>} polyanions can capture different cations with appropriate size, such as various alkali, alkaline-earth, transition metal, lanthanide and actinide cations on the inner surface of the polyanion [4], and provide opportunities to bind metal ions or metal-complexes forming extended hybrid materials [5]. That is to say, Preyssler-type polyanion can be modified both on its surface and in its inner cavity. Therefore, {ZP<sub>5</sub>W<sub>30</sub>} polyanions can be regarded as promising building blocks to construct novel POM-based inorganic-organic hybrid materials with distinct properties. For example, a series of Preyssler-type polyanion-based inorganic-organic hybrid materials containing different first-row transition-metal ions (e.g., Cu(II), Ni(II), or Co(II) ions) and N-donor polydentate ligands have been reported by Wang's and Sun's groups, respectively [6]. However, in the above Preyssler-type polyanion-based hybrid materials, the introduced transition metal ions located on their exteriors only. In 2014, a 3D Preyssler-type POM-based coordination polymer decorated with transition metal Ag(I) complex has been harvested. In this work,  $Ag^+$  ions exist both in the inner cavity and the exterior of the Preyssler-type polyanion [7]. Nevertheless, a Preyssler-type polyanion modified by different kinds of transition metal ions both on its surface and in its cavity has not been reported. The main reason is that it is difficult to isolate and purify the {ZP<sub>5</sub>W<sub>30</sub>} polyanion encapsulated with metal ions and to find suitable synthesis method to obtain highquality single crystals. 2,2'-biimidazole (H<sub>2</sub>biim), a kind of N donor ligand, possessing effective and multiple coordination ability as well as intricate hydrogen-bond interaction [8], can be introduced into the skeleton of the Prevssler-type polyanion to form high quality inorganic-organic hybrid crystalline materials. Herein, two new extended Preyssler-type polyoxometalates with the same structure and different inner cavities modified by Fe(III) and 2,2'-H<sub>2</sub>biim/  $H_2O_1 \{(H_4 \text{biim})_5 H[Fe(H_2 \text{biim})(H_2O)_2(ZP_5W_{30}O_{110})] \cdot 17H_2O\}_n (Z =$ Na, compound 1; Z = Ag, compound 2) were successfully harvested by hydrothermal method from a system inclusion of  $\{NaP_5W_{30}\}/$  $\{AgP_5W_{30}\}$  polyanion, FeCl<sub>3</sub>·6H<sub>2</sub>O, H<sub>2</sub>biim and H<sub>2</sub>O (Scheme 1) [9]. The acid catalysis activities of the as-prepared compounds were explored. In addition, the optimal catalytic conditions and reusability of the catalysts were researched in detail.

Single crystal X-ray structural analysis [10] reveals that compounds **1** and **2** are isomorphic compounds, their asymmetric unit contains three types of subunits, *i.e.* a {NaP<sub>5</sub>W<sub>30</sub>}/{AgP<sub>5</sub>W<sub>30</sub>} polyanion, one  $[Fe(H_2biim)(H_2O)_2]^{3+}$  and five  $[H_4biim]^{2+}$  cations (Figs. S1 and S2). The structures of the {ZP<sub>5</sub>W<sub>30</sub>} polyanions in the two compounds are essentially the same as the {NaP<sub>5</sub>W<sub>30</sub>} derivative previously reported in

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Scheme 1. Designation and synthetic process of compound 1/2.

1985 [11]. Compared with compound **1**, there are two types of transition metals in the structure of compound **2**, one transition metal Ag<sup>+</sup> cation as a center is trapped in the inner cavity of a {AgP<sub>5</sub>W<sub>30</sub>} unit, and two Fe<sup>3+</sup> ions combined with H<sub>2</sub>biim/H<sub>2</sub>O as a complex fragments are hung on the outer surface of a {AgP<sub>5</sub>W<sub>30</sub>} polyanion. Crystal data and structural refinement parameters of compounds **1** and **2** were listed in Table S1. As shown in Fig. 1a, the {ZP<sub>5</sub>W<sub>30</sub>} cluster acts as a bidentate ligand and coordinates with two [Fe(H<sub>2</sub>biim)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> subunits through the terminal oxygen atoms of two equivalent WO<sub>6</sub> octahedra. All Fe centers exhibit the same six–coordination environments, coordinating with two oxygen atoms (O1W, O2W) from two coordinated water molecules, two oxygen atoms (O38, O40) from two symmetrical {ZP<sub>5</sub>W<sub>30</sub>} clusters, and two nitrogen atoms (N1, N2) from a H<sub>2</sub>biim molecule (Fig. 1c). The bond lengths of Fe1—N are in the range of 2.097(15)–2.105(15) and 2.106(15)–2.110(15) Å for compounds **1** 



**Fig. 1.** The polyhedral and ball–and–stick view of the coordination pattern of  $\{ZP_5W_{30}\}$  (a), the 1D chain (b) and the coordination pattern of Fe(III) (c) in compound **1**/2.

and **2**, respectively. And the bond lengths of Fe1—O are 1.918(12)-2.116(13) and 1.894(13)–2.102(15) Å for compounds 1 and 2, respectively (see Tables S2 and S3). Bond valence sum (BVS) calculations [12] show all W, P, Ag, Fe atoms are in +6, +5, +1 and +3 oxidation states in compounds 1 and 2, respectively, which are consistent with the results of X-ray photoelectron spectroscopy (XPS) analysis (see below). In addition, no protonated O atom was noted on the polyanions, and H protons were added due to charge-balance considerations. As shown in Fig. 1b, each pair of adjacent {ZP<sub>5</sub>W<sub>30</sub>} polyanions are bridged by one  $[Fe(H_2biim)(H_2O)_2]^{3+}$  subunit, forming into infinite 1D linear chains, and further packed into a 3D supramolecular structure through hydrogen bonding interactions (N-H···O/OW 2.43(3)-3.27(4) and 2.51(3)-3.26(3) Å for compounds 1 and 2, see Tables S4 and S5) and electrostatic attractions (Fig. 2). The discrete protonated H<sub>2</sub>biim molecules ( $[H_4 \text{biim}]^{2+}$  cations) (Fig. 2c) fill in the spaces as compensating cations, and the results indicate that the positive charges of [H<sub>4</sub>biim]<sup>2+</sup> cations are important for the formation of the final supramolecular network (Fig. 2a, Figs. S3-S5).

The IR spectra of  $\{NaP_5W_{30}\}, \{AgP_5W_{30}\}, compounds 1 and 2 are pre$ sented in Figs. S6 and S7. They all exhibit the characteristic vibrations of the {ZP<sub>5</sub>W<sub>30</sub>} polyanion:  $v_{as}$ (P–O<sub>a</sub>) (1168–1076 cm<sup>-1</sup>),  $v_{as}$ (W–O<sub>t</sub>) (925–918 cm<sup>-1</sup>), and  $\nu_{as}$ (W–O<sub>b/c</sub>) vibrations (801–762 cm<sup>-1</sup>) (O<sub>a</sub>: central oxygen;  $O_t$ : terminal oxygen;  $O_{b/c}$ : bridging oxygen) [6,8]. The wide frequency ranges of 3479–3450 cm<sup>-1</sup> are associated to  $\nu$ (O–H) of water molecules. The weak bonds in the range of 3147–2931 cm<sup>-1</sup> can be assigned to v(C-H) of H<sub>2</sub>biim molecules. The absorption in the range of 1604-1596 cm<sup>-1</sup> can be regarded as the stretching vibrations of the imidazole ring [8]. To investigate the thermal stability, thermogravimetric analysis (TG/DTA) was applied, and the result curves of compounds 1 and 2 were shown in Fig. S8. The first weight loss step at 35 to 200 °C is 3.8% (calcd. 3.5%) for compound 1 and 3.6% (calcd. 3.5%) for compound 2, which are ascribed to the loss of all lattice water molecules. From 200 to 1000 °C, a main weight loss of 13.3% for compound 1 (11.9% for compound 2) corresponds to the loss of all organic composites, coordinated water molecules and sublimable phosphorus oxide species originating from partly collapse of the {ZP<sub>5</sub>W<sub>30</sub>} polyoxoanion skeleton. The two exothermal peaks in DTA curves observed at 460 and 605 °C for compound 1 and 472 and 620 °C for compound **2** respectively are assigned to the combustion of the  $H_2$  biim molecules and the sublimation of phosphorus oxide species [13]. In addition, there are apparent weight additions appear at 600 °C in TG curves, which could be due to the decomposition of complex  $[Fe(H_2biim)(H_2O)_2]^{3+}$  and the formation of iron oxides [14]. In order to further verify the oxidation states of elements in the compounds, XPS analysis was carried out. As shown in Figs. S9 and S10, the XPS spectra exhibit the characteristic peaks of C 1s, N 1s, O 1s, P 2p, W 4f, Fe 2p and Na 1s for compound 1, and the characteristic peaks of C 1s, N 1s, O 1s, P 2p, W 4f, Fe 2p and Ag 3d for compound 2, respectively. These results are consistent with the BVS calculation and elemental analysis, which further confirm that all W, P, Ag and Fe atoms are in +6, +5, +1 and +3 oxidation states, respectively [15]. The above results indicate that the {NaP<sub>5</sub>W<sub>30</sub>}/{AgP<sub>5</sub>W<sub>30</sub>} polyanion skeleton in compound 1/2 are thermally stable at lower than 400 °C. The experimental and simulated results in powder X-ray diffraction (PXRD) patterns of compounds 1 and 2 are presented in Fig. S11, the main diffraction peaks positions are accordant, indicating the products are in a pure phase. The different intensities of peaks may be caused by the diverse preferred orientations of the powder samples.

The UV–Vis diffuse reflectance spectra of {NaP<sub>5</sub>W<sub>30</sub>}, {AgP<sub>5</sub>W<sub>30</sub>}, compounds **1** and **2** were performed at 200–800 nm at room temperature (Fig. S12). Comparing with the spectra of parents {NaP<sub>5</sub>W<sub>30</sub>} and {AgP<sub>5</sub>W<sub>30</sub>}, the strong absorption bands at 265 and 350 nm of compounds **1** and **2** respectively are assigned to the  $p\pi \rightarrow d\pi$  charge–transfer transitions of the O<sub>b/c</sub>  $\rightarrow$  W bonds (LMCT). The wide absorption bands at 560 nm for compound **1** and 570 nm for compound **2** respectively are attributed to the d–d transitions of Fe(III) [5b], indicating



**Fig. 2.** The polyhedral and ball-and-stick view of the 3D packing arrangement (a), the 1D chain packing arrangements (b) and the  $[H_4 \text{biim}]^{2+}$  fragments (c) fill in the spaces of compound 1/2 along *a* direction.

that the transition metal Fe(III) is successfully introduced into compound 1/2. The fluorescent properties of {NaP<sub>5</sub>W<sub>30</sub>}, {AgP<sub>5</sub>W<sub>30</sub>}, compounds 1 and 2 were characterized in the solid state at room temperature, and the results were shown in Fig. S13. The parent  ${\rm ZP}_5W_{30}$ , compounds **1** and **2** all exist three emission peaks at 422, 452–453 and 470 nm with  $\lambda_{ex} = 265$  nm due to LMCT (O  $\rightarrow$  W) [5b]. This result indicates the structures of the parent  $\{ZP_5W_{30}\}$  polyanions have been kept in compounds 1 and 2. The POMs can proceeded multi-electron oxidation-reduction process, the electrochemical behaviors of compounds 1 and 2 were carried by cyclic voltammograms (CV) in the potential range of +0.25 to -0.70 V at the scan rate of 100 mV s<sup>-1</sup> under the carbon paste electrodes (**1**–CPE and **2**–CPE). As shown in Fig. S14, there are two reversible redox peaks at -0.367 (I), -0.489 (I') and -0.210 (II), -0.203 (II') V for compound 1 and -0.391 (I), -0.474 (I') and -0.195 (II), -0.194 (II') V for compound 2. Redox peaks I–I' and II–II' for compounds 1 and 2 correspond to two consecutive redox processes of W centers [8].

The acid catalytic synthesis of ketal is more important for the protection of the carbonyl group in multi-steps organic synthesis. To evaluate the catalytic activity of as-prepared compounds, ketalization of cyclohexanone with glycol was selected as a model reaction (Scheme S1) [16]. It is well known that the high chemical stability in catalysis is critical to the applications of catalysts. To evaluate the stability of the catalysts in different solvents, compounds 1 and 2 were soaked in glycol, cyclohexanone and water respectively at the temperature required for the catalytic reaction, and in cyclohexane at the reflux temperature, and then the XRD and IR spectra of these solid samples were tested before and after being soaked in the solvents (Figs. S15 and S16). As seen from Figs. S15 and S16, it is found that compounds 1 and 2 are still stable in glycol, cyclohexane, cyclohexanone and H<sub>2</sub>O, respectively. Subsequently, taking compound 1 as an example, the optimal catalytic conditions of the above model reaction, such as the reaction time, molar ratio of starting materials and the amount of catalyst were tested and selected systemically (Figs. S17-S19). It is found that the optimum conditions for the synthesis of cyclohexanone ethylene ketal are: the reaction time is 2.5 h, the molar ratio of the catalyst (based on W) to cyclohexanone is 1:200, the cyclohexanone (0.05 mol)/glycol molar ratio is 1:1.4, reaction temperature is 95–100 °C. Furthermore, compounds 1 and 2 can be recovered by simple filtration without any treatment, and reused for three cycles without distinct decrease of the cyclohexanone conversion under the optimum reaction conditions (Fig. 3). In addition, the acid catalytic activities of FeCl<sub>3</sub>, {NaP<sub>5</sub>W<sub>30</sub>}, {AgP<sub>5</sub>W<sub>30</sub>} and compound **2** were also tested in the optimum conditions for comparison. From the results listed in Table 1, it is found that the conversion of the cyclohexanone is 70, 72, 99.9, 91 and 93% for {NaP<sub>5</sub>W<sub>30</sub>}, {AgP<sub>5</sub>W<sub>30</sub>}, FeCl<sub>3</sub>, compound 1 and compound 2, respectively. Though FeCl<sub>3</sub> provided a higher cyclohexanone conversion than compound 1/2, the former was completely dissolved in the reaction mixture for bringing the trouble of catalyst reuse. Compound 1/2 exhibits higher catalytic activity than {NaP<sub>5</sub>W<sub>30</sub>} and  $\{AgP_5W_{30}\}$ , which means that the acid catalytic activity of the {ZP<sub>5</sub>W<sub>30</sub>} catalyst was effectively improved after introducing the transition metal-H<sub>2</sub>biim complexes. It can be conjectured that the Fe<sup>3+</sup> moieties, as Lewis acids, are the catalytically active centers, which play the most important roles in the catalytic reaction. Besides, the protons in the molecule  $\{(H_4 \text{biim})_5 H[Fe(H_2 \text{biim})(H_2 O)_2 (ZP_5 W_{30} O_{110})] \cdot 17H_2 O\}_n$ provide Brönsted acid centers [16b]. In a word, the acid catalysis test results suggest that these kind of POM-based inorganic-organic hybrid compounds containing  $\{ZP_5W_{30}\}$  with different center are excellent acid catalysts. In addition, to confirm the stability of these compounds after catalytic processes, the PXRD patterns and IR spectra of samples after four runs were tested and shown in Figs. S20 and S21. As seen from Fig. S20, the main diffraction peaks positions are consistent with the simulated values of compounds 1 and 2, the different intensity of peaks may be caused by the diverse preferred orientation of the powder samples. As shown in Fig. S21, the IR characteristic peaks of the powder samples after catalysis are consistent with those of crystalline compounds 1 and 2 before catalysis. These results indicate that the



Fig. 3. The catalytic activity of compounds 1 and 2 used after four runs.

#### Table 1

The catalytic performances of compounds **1** and **2** compared with the reference catalysts for the synthesis of cyclohexanone ethylene ketal.

Entry	Catalyst <sup>a</sup>	Solubility	Time (h)	Conversion (%)
1	-	-	2.5	9
2	FeCl <sub>3</sub>	Soluble	2.5	99.9
3	{NaP5W30}	Partially soluble	2.5	70
4	${AgP_5W_{30}}$	Partially soluble	2.5	72
5	Compound 1	Insoluble	2.5	91
6	Compound 2	Insoluble	2.5	93

<sup>a</sup> Reaction conditions: the reaction time is 2.5 h, the molar ratio of the catalyst to cyclohexanone is 1:200; the cyclohexanone/glycol molar ratio is 1:1.4; the reaction temperature 95–100  $^{\circ}$ C.

structures of compounds **1** and **2** are intact after catalytic process. Based on the above results, compounds **1** and **2** are stable and efficient heterogeneous acid catalysts for the synthesis of cyclohexanone ethylene ketal.

In conclusion, two new extended Preyssler–type POMs with different cavity centers containing  $\{NaP_5W_{30}\}/\{AgP_5W_{30}\}$  clusters and Fe(III)/H<sub>2</sub>O/2,2'–H<sub>2</sub>biim fragments have been successfully synthesized under hydrothermal conditions. Compound **2** represents the first extended Preyssler–type POMs which the inner center and the outer of the Preyssler–type anion have two types of transition metals (Ag and Fe). The two compounds displayed higher catalytic performance toward the synthesis of cyclohexanone ethylene ketal. They also can be reused for three cycles without significant deactivation, which may have promising properties in catalysis and material science. Further study is in progress to construct new interesting structures with other transition metal ions under hydrothermal conditions.

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#### Appendix A. Supplementary material

CCDC No. 1491919 for compound **1** and 1491920 for compound **2** can be obtained free of charge from the Cambridge Crystallographic Data. Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2016.10.018.

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- [9] Syntheses of K14[AgP5W30O110] · 18H2O({AgP5W30}): In the synthetic experiment, {NaP<sub>5</sub>W<sub>30</sub>} (1.000 g, 0.12 mmol) was dissolved in 15 mL of redistilled water, and AgNO<sub>3</sub> (0.040 g, 0.24 mmol) was added to this solution under stirring. The resulting mixture was transferred into a Teflon-lined autoclave (30 mL) and kept at 160 °C for 3 days. After slow cooling to room temperature, the precipitated product was isolated by the addition of 1.000 g of solid KNO3. After filtration, the precipitate was dissolved in hot water (10 mL), and then the solution was gradually cooled, colourless block crystals formed. Finally, the crystals were filtered and dried in air. The amount of product was 0.75 g. Elemental analysis (%), found: H 0.46, K 6.64, Ag 1.20, P1.88, W 65.80. Calcd. for K14H36O128AgP5W30: H 0.43, K 6.51, Ag 1.28, P1.84, W 65.58. FT IR: 3460 (s), 2931 (w), 1620 (s), 1168 (m), 1.087 (w), 933 (m), 767 (s) cm<sup>-1.31</sup>P NMR: -10.29 ppm. Synthesis of compound **1**: A mixture of {NaP<sub>5</sub>W<sub>30</sub>} (0.200 g, 0.024 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.150 g, 0.56 mmol), H<sub>2</sub>biim (0.035 g, 0.26 mmol) and distilled water (10 mL) was stirred for 1.0 h. The resulting suspension was sealed in a Teflon-lined autoclave (25 mL) and kept at 140 °C for 3 days. After slow cooling to room temperature, dark-purple crystals were obtained and filtered off, and washed with distilled water and dried at room temperature to give a yield of 52% based on W. Elemental analysis (%), found: C 5.15, H 0.97, N 3.68, P1.83, Na 0.25, Fe 0.61, W 63.74. Calcd. for C36H85FeN24NaO129P5W30: C 5.00, H 1.00, N 3.88, P1.79, Na 0.27, Fe 0.64, W 63.63. FT IR: 3542 (m), 3456 (w), 3147 (w), 2931 (w), 1604 (m), 1164 (m), 1087 (w), 918 (m), 763 (s) cm<sup>-1</sup>. Synthesis of compound **2**: The synthetic method of compound **1** was applied except replacing  $\{NaP_5W_{30}\}$ with {AgP5W30} under the same conditions, and dark-purple crystals can also be obtained. Yield: 47% based on W. Elemental analysis (%), found: C 5.02, H 0.94, N 3.79, P1.74, Fe 0.63, Ag 1.28, W 63.18. Calcd. for C<sub>36</sub>H<sub>85</sub>ÁgFeN<sub>24</sub>O<sub>129</sub>P<sub>5</sub>W<sub>30</sub>: C4.94, H 0.98, N 3.84, P1.77, Fe 0.64, Ag 1.23, W 63.02. FT IR: 3479 (m), 3148 (w), 2954 (w), 1596 (m), 1164 (m), 1080 (w), 925 (s), 762 (s) cm<sup>-1</sup>
- [10] The structures were solved by direct methods and refined by the full-matrix least-squares fitting on F<sup>2</sup> using SHELXTL-97 package [G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997)]. Cell parameters were obtained by the global refinement of the positions of all collected reflections. All the non-hydrogen atoms were refined anisotropically. H atoms on C or N atoms were added in calculated positions. Crystal data and structure refinement parameters of compounds 1 and 2 are listed in Table S1. All H

atoms on water molecules were directly included in the final molecular formula. Selected bond lengths and angles are listed in Tables S1 and S2. Hydrogen bonds are listed in Tables S3 and S4. The CCDC reference numbers are 1491919 and 1491920. Crystal data for compound **1**:  $C_{36}H_{85}FeN_{24}NaO_{129}P_5W_{30}$ , M = 8667.47, Monoclinic, space group  $P_{21}/n$ , a = 20.073(2) Å, b = 23.917(3) Å, c = 29.783(3) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 91.576(2)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 14293(3) Å<sup>3</sup>, Z = 4,  $F_{0000} = 15332$ ,  $R_1(wR_2) = 0.0459$  (0.0997) and S = 1.006 for 25167 independent reflections with  $I > 2\sigma(I)$ . Crystal data for compound **2**:  $C_{36}H_{85}AgFeN_{24}O_{129}P_5W_{30}$ , M = 8752.35, Monoclinic, space group  $P_{21}/n$ , a = 20.0755 Å, b = 23.9151(18) Å, c = 29.746(2) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 91.533(2)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 14276.3(18) Å<sup>3</sup>, Z = 4,  $F_{000} = 15476$ ,  $R_1(wR_2) = 0.0483$  (0.1007) and S = 1.007 for 25140 independent reflections with  $I > 2\sigma(I)$ .

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