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Synthesis, Characterization, and Stability of α -Keggin-type Polyoxotungstate-coordinated Mono-platinum(II) Complex

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Abstract: The first example of mono-platinum(II) complex composed of mono-lacunary α -Keggin-type polyoxotungstate is described. The mono-platinum(II)-containing polyoxotungstate $[(\text{CH}_3)_4\text{N}]_4\text{H}[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{Me}_2\text{ppz})\}]\cdot 5\text{H}_2\text{O}$ ($\text{Me}_2\text{ppz} = N,N'$ -dimethylpiperazine) (**TMA-1**) was synthesized by a 1:1 stoichiometric reaction of mono-lacunary α -Keggin polyoxotungstate, $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$, with *cis*-PtCl₂(Me₂ppz) in an aqueous solution, followed by purification from water. The compound **TMA-1** was characterized by elemental analysis, thermogravimetric/differential thermal analysis (TG/DTA), and Fourier transform infrared (FTIR), ultraviolet-visible (UV-Vis), and solution $\{^1\text{H}, ^{13}\text{C}, ^{31}\text{P}, ^{195}\text{Pt}, \text{ and } ^{183}\text{W}\}$ nuclear magnetic resonance (NMR) spectroscopies. The characterization results indicated that a platinum(II) moiety, $[\text{cis-Pt}(\text{Me}_2\text{ppz})]^{2+}$, was coordinated to two oxygen atoms in a mono-vacant site of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ with asymmetric configuration, resulting in an overall C_1 symmetry. The polyoxoanion $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{Me}_2\text{ppz})\}]^{5-}$ (**1**) was more stable in dimethylsulfoxide and water than the α -Keggin-type polyoxotungstate-coordinated mono-platinum(II) complex, $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}]^{5-}$, which was also obtained by the reaction of $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ with *cis*-diamminedichloroplatinum(II) in an aqueous solution.

Keywords: Polyoxometalate; mono-platinum(II) complex; NMR spectroscopy; stability

Introduction

Polyoxometalates (POMs) are of great interest in the fields of catalysis, surface science, and materials science due to their chemical properties, such as redox potentials, acidities, and solubilities in various media, can be finely tuned by choosing appropriate constituent elements and counteranions. Especially, the introduction of various species, *e.g.*, metal ions and organometallics, into the vacant site(s) of lacunary POMs is one of the most powerful techniques used for the construction and stabilization of efficient and well-defined metal

centers.^[1-4] Among the various metal ions and their derivatives that can be introduced to POM frameworks, platinum and platinum derivatives are of particular interest because of their extreme versatility and efficient properties as catalysts, electronics, and pharmaceutical compounds.^[5]

With regard to platinum-containing POMs, only a few examples of Pt⁴⁺-containing POMs^[6-15] and Pt²⁺-containing POMs^[16-19] have been reported. In particular, examples of Pt²⁺-containing POMs, $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{NH}_3)_2\}_2]^{3-}$,^[17] $[\text{Pt}^{\text{II}}_2(\text{W}_5\text{O}_{18})_2]^{8-}$,^[18] $[\text{anti-Pt}^{\text{II}}_2(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$,^[19] and $[\text{syn-Pt}^{\text{II}}_2(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$,^[19] are rare. In these compounds, the di-platinum(II) sites coordinate each to two terminal oxygen atoms in the vacant sites. Moreover, no synthesis of POM-coordinated mono-platinum(II) complex has been reported.

In this study, we successfully synthesized a tetramethylammonium salt of α -Keggin-type POM-coordinated mono-platinum(II) complex, $[(\text{CH}_3)_4\text{N}]_4\text{H}[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{Me}_2\text{ppz})\}]\cdot 5\text{H}_2\text{O}$ (**TMA-1**), using *cis*-PtCl₂(Me₂ppz) (Me₂ppz = *N,N'*-dimethylpiperazine) as the starting platinum(II) complex. The mono-platinum compound was characterized by elemental analysis, TG/DTA, and FTIR, UV-Vis, and solution $\{^1\text{H}$, ^{31}P , ^{13}C , ^{195}Pt , and $^{183}\text{W}\}$ NMR spectroscopies. Its stability in dimethylsulfoxide (DMSO) and water was also investigated by using NMR spectroscopy.

Results and Discussion

We synthesized a tetramethylammonium salt of α -Keggin-type POM-coordinated mono-platinum compound, $[(\text{CH}_3)_4\text{N}]_4\text{H}[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{Me}_2\text{ppz})\}]\cdot 5\text{H}_2\text{O}$ (Me₂ppz = *N,N'*-dimethylpiperazine) (**TMA-1**), by a 1:1 stoichiometric reaction of *cis*-PtCl₂(Me₂ppz) with $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ in an aqueous solution at approximately 25 °C under air, followed by the addition of tetramethylammonium chloride. The purification was carried out by precipitation from water. **TMA-1** was finally isolated as an analytically pure, yellow powder in a 21% yield. A faster formation of the polyoxoanion **1** was observed when excess of *cis*-PtCl₂(Me₂ppz) was used; however, the di-platinum species was not formed even at the

molar ratio of *cis*-PtCl₂(Me₂ppz):[α-PW₁₁O₃₉]⁷⁻ = 2:1. In contrast, mono-platinum species could not be obtained by using Pt(bpy)Cl₂ (bpy = 2,2'-bipyridine) and PtCl₂(phen) (phen = 1,10-phenanthroline) because of the faster formation of di-platinum compounds.^[20]

The elemental analysis results for C, H, N, Pt, and P are in good agreement with the calculated values for the chemical formula of **TMA-1** with five hydrated water molecules. It should be noted that K analysis shows no contamination (<0.1%). During TG/DTA under atmospheric conditions, a weight loss of 2.90% was observed below 92.5 °C with an endothermic peak at 41.7 °C, corresponding to 5 water molecules (calcd. 2.67%). In addition, a weight loss of 13.03% was observed in the temperature range from 234.6 to 402.8 °C, corresponding to the sum of four tetramethylammonium ions and a Me₂ppz molecule (calcd. 12.17%).

The FTIR spectrum, in the polyoxometalate region (1200 – 400 cm⁻¹), of **TMA-1** measured in a KBr disk is shown in Fig. 1a. The spectral pattern of **TMA-1** (1101, 1050, 1043, 949, 891, 857, 813, 795, 776, 723, and 516 cm⁻¹) is different from that of K₇[α-PW₁₁O₃₉]·13H₂O (1086, 1043, 953, 903, 862, 810, and 734 cm⁻¹) (Fig. 1b), suggesting that [Pt(Me₂ppz)]²⁺ coordinated to the vacant site of [α-PW₁₁O₃₉]⁷⁻. The spectral pattern is also different from those of dimeric di-platinum(II) compounds K_{1.5}[(CH₃)₂NH₂]_{8.5}[*anti*-Pt^{II}₂(α-PW₁₁O₃₉)₂]·28H₂O (1103, 1046, 955, 928, 849, 774, 714, and 511 cm⁻¹)^[19] and K_{1.5}[(CH₃)₂NH₂]_{8.5}[*syn*-Pt^{II}₂(α-PW₁₁O₃₉)₂]·18H₂O (1100, 1047, 955, 926, 859, 794, 716, and 511 cm⁻¹).^[19] The band at around 1488 cm⁻¹ is due to the tetramethylammonium ions and Me₂ppz molecule.

The ³¹P NMR spectrum of **TMA-1** in D₂O shows a clear single-line spectrum at -12.03 ppm due to the internal phosphorus atom, confirming the purity and homogeneity of the sample (Fig. 2a). The signal is shifted compared with that of K₇[α-PW₁₁O₃₉]·13H₂O (δ -10.67). A single-line spectrum of **TMA-1** is also observed in DMSO-*d*₆ at -11.75 ppm (Fig. 2b), which is shifted relative to that of K₇[α-PW₁₁O₃₉]·13H₂O (δ -10.12). The ³¹P NMR spectra in H₂O/D₂O at room temperature of [*anti*-Pt^{II}₂(α-PW₁₁O₃₉)₂]¹⁰⁻ and

$[\text{syn-Pt}^{\text{II}}_2(\alpha\text{-PW}_{11}\text{O}_{39})_2]^{10-}$ show signals at -12.65 ppm and -12.43 ppm, respectively,^[19] which are shifted relative to that of **1**.

The ^{183}W NMR spectrum in D_2O of the potassium salt of **1** obtained by the addition of excess KCl instead of tetramethylammonium chloride shows eleven signals at -82.0 , -84.0 , -101.2 , -109.4 , -113.6 , -123.7 , -125.1 , -134.3 , -145.9 , -149.2 , and -213.3 ppm with approximately 1:1:1:1:1:1:1:1:1:1:1 intensities; this indicates that a platinum(II) moiety, $[\text{cis-Pt}(\text{Me}_2\text{ppz})]^{2+}$, is coordinated to two oxygen atoms in a mono-vacant site of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ with asymmetric configuration, resulting in an overall C_1 symmetry (Fig. 3). The ^{195}Pt NMR spectrum of **TMA-1** in $\text{DMSO-}d_6$ is quite noisy; however, a signal is observed at around -1326 ppm, as shown in Fig. 4. This also supported the result that a $[\text{cis-Pt}(\text{Me}_2\text{ppz})]^{2+}$ was coordinated to the mono-vacant site in $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ because α -Keggin-type di-platinum(II)-coordinated polyoxoanion, $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}_2]^{3-}$ (**2**), possessing the two non-equivalent platinum centers showed two broad signals.^[16]

The ^{13}C NMR spectrum of **TMA-1** in $\text{DMSO-}d_6$ shows three signals at 21.7 , 50.9 , and 51.4 ppm, as shown in Fig. 5. The signal at 21.7 ppm can be assigned to the methyl groups of the Me_2ppz molecule, and the two broad signals at 50.9 ppm and 51.4 ppm can be assigned to the two non-equivalent $-\text{CH}_2-\text{CH}_2-$ groups in the Me_2ppz molecule. For $\text{cis-PtCl}_2(\text{Me}_2\text{ppz})$, the elimination of Me_2ppz molecules (δ 48.8 and 57.8) from the platinum center is observed in $\text{DMSO-}d_6$, as shown in Fig. S1, and several signals are observed at 50.9 , 51.8 , 53.1 , 61.0 , 62.9 , and 63.2 ppm, which can be attributed to species such as $[\text{cis-Pt}(\text{Me}_2\text{ppz})\text{Cl}_2]$, $[\text{cis-Pt}(\text{Me}_2\text{ppz})\text{Cl}(\text{DMSO})]^+$, and $[\text{cis-Pt}(\text{Me}_2\text{ppz})_2(\text{DMSO})_2]^{2+}$, formed by the ligand exchange reactions of one or two chloride ions with DMSO molecules.^[21] With regard to **TMA-1**, no signals due to free Me_2ppz molecule were observed, suggesting that the coordination of $[\text{Pt}(\text{Me}_2\text{ppz})]^{2+}$ to the vacant site in $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ inhibits the elimination of Me_2ppz molecules from the platinum center, and the formation of dimeric structures is therefore negligible. The ^1H NMR spectrum of **TMA-1** in $\text{DMSO-}d_6$ was complicated because of the presence of H atoms in the equatorial and axial positions of the Me_2ppz molecule.^[22] The assignments will be reported once the single-crystal X-ray structural

analysis be obtained. The UV-Vis spectrum of **TMA-1** in water shows three absorption bands at around 252, 337, and 405 nm (Fig. 6). The broad bands at 252 and 337 nm can be assigned to the charge transfer (CT) bands of W-O, and the broad absorption band at around 405 nm, which is red-shifted relative to that of PtCl₂(Me₂ppz) ($\lambda = 375$ nm) (Fig. S2), can be attributed to the Pt(II) atoms. The band at 284 nm observed for PtCl₂(Me₂ppz) is hidden by the CT bands of W-O. Therefore, as shown in Fig. 7a, we could estimate the partial structure around the platinum center in **1**.

As a control experiment, we tried to precipitate a mono-platinum(II)-coordinated polyoxoanion, $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}]^{5-}$, which was observed as an intermediate species during the formation of $[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}^{\text{II}}(\text{NH}_3)_2\}_2]^{3-}$ (**2**) in an aqueous solution.^[17] The mono-platinum species (abbreviated as **Intermediate-A**) could be obtained with a relatively high abundance ratio by the method described below. Cisplatin (*cis*-diamminedichloroplatinum(II)) (0.0604 g; 0.201 mmol) and K₇[PW₁₁O₃₉]·13H₂O (0.3172 g; 0.101 mmol) were dissolved in 150 mL of water at 20 ± 2 °C. After stirring for 27 h, solid CsCl (0.7531g; 4.47 mmol) was added to the solution, and the mixture was stirred for 20 min at 20 ± 2 °C. A white-yellow precipitate (0.3547 g) was formed upon the addition of ethanol (540 mL) to the aqueous solution in an ice bath and collected by a membrane filter (JG 0.2 μm). The ³¹P NMR spectrum in D₂O (Fig. 8a) shows a main signal at -11.48 ppm that can be attributed to **Intermediate-A**. The solid still contained both the polyoxoanion **2** (δ -12.81) and $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ (δ -10.67) (the integrated intensity ratio of $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$:**Intermediate-A**:**2** was 0.06:1.00:0.02); however, the elemental analysis results show that the P:Pt ratio is approximately 1:1. Since K was hardly detected by the elemental analysis, **Intermediate-A** was obtained as a cesium salt. The ¹H NMR spectrum in DMSO-*d*₆ shows a signal at 4.15 ppm. In a previous study,^[17] two signals at 4.26 ppm and 4.39 ppm were found in the ¹H NMR spectrum of **2** and attributed to the two sets of NH₃ ligands coordinated to each of the two platinum centers. These results suggest the formation of mono-platinum site in **Intermediate-A** because of the coordination of a $[\text{cis-Pt}(\text{NH}_3)_2]^{2+}$ to the mono-vacant site in $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$. The FTIR spectrum of **Intermediate-A** (measured in

a KBr disk) contains several bands at 1091, 1045, 952, 894, 862, 807, 760, and 730 cm^{-1} , as shown in Fig. S3a. Its spectral pattern is different from those of $\text{Cs}_3[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{cis-Pt}(\text{NH}_3)_2\}_2]\cdot 8\text{H}_2\text{O}$ (**Cs-2**) (1099, 1047, 955, 915, 859, 801, 757, and 721 cm^{-1}) (Fig. S3b) and $\text{K}_7[\alpha\text{-PW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ (Fig. 1b). A band arising from the NH_3 groups is observed at around 1346 cm^{-1} , as found for **Cs-2**.^[17] The UV-Vis spectrum of **Intermediate-A** in water also shows a broad absorption band at around 405 nm due to Pt^{2+} , as shown in Fig. S4. Therefore, the estimated partial structure around the platinum center in **Intermediate-A** is shown in Fig. 7b.

As illustrated in Fig. S5, the ^{31}P NMR spectra in D_2O (600 μL) shows that **Intermediate-A** (10.5 mg) gradually decomposed into the polyoxoanion **2** and $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ with time at 50 ± 2 $^\circ\text{C}$ in the absence of any additives. After 24-h heating at 50 ± 2 $^\circ\text{C}$, the relative integrated intensity ratio of $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$:**Intermediate-A**:**2** was 0.36 : 1.00 : 0.71, as shown in Fig. 8b. At 30 ± 2 $^\circ\text{C}$, the rates were significantly slower, and no clear increase of **2** and $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ was observed during the first few hours. In $\text{DMSO-}d_6$, a rapid decomposition of **Intermediate-A** was observed even at approximately 25 $^\circ\text{C}$. In contrast, the ^{31}P NMR spectrum of **TMA-1** (4.4 μmol) in D_2O (600 μL) did not change even after 7 days at 50 ± 2 $^\circ\text{C}$ (Fig. S6), showing that **1** was significantly more stable than **Intermediate-A**. The ^{31}P NMR spectrum of **TMA-1** in $\text{DMSO-}d_6$ also showed the high stability of **1**, and no signal due to $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ was observed, at least for a few days, at approximately 25 $^\circ\text{C}$.

When cisplatin (0.9 mg) was added to **Intermediate-A** (11 mg) dissolved in D_2O (600 μL) at 30 ± 2 $^\circ\text{C}$, the polyoxoanion **2** gradually formed with time (Fig. S7). The formation of $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ was hardly observed by ^{31}P NMR spectroscopy during 24 h. These results suggest that a di-platinum(II) site was formed by the coordination of one of the $[\text{cis-Pt}(\text{NH}_3)_2]^{2+}$ moieties to the two terminal oxygen atoms adjacent to the mono-platinum site in **Intermediate-A**. With regard to **TMA-1**, the second coordination of $[\text{cis-Pt}(\text{NH}_3)_2]^{2+}$ was not observed upon reaction of **TMA-1** (19 μmol) with cisplatin (34 μmol) at 50 ± 2 $^\circ\text{C}$ for 8 h. Therefore, a stable and single mono-platinum(II) compound can be synthesized by using $\text{cis-PtCl}_2(\text{Me}_2\text{ppz})$ as the platinum source; however, the introduction of a second

platinum center is inhibited by the presence of Me₂ppz ligand under the present conditions. Attempts to obtain a single crystal of **1** and introduce a second platinum center coordinated to the terminal atoms that are adjacent to the mono-platinum site are in progress. The results will be reported elsewhere.

Conclusion

The tetramethylammonium salt of α -Keggin-type polyoxometalate-coordinated mono-platinum(II) complex, [(CH₃)₄N]₄H[α -PW₁₁O₃₉{*cis*-Pt^{II}(Me₂ppz)}]·5H₂O (**TMA-1**), was successfully synthesized by a 1:1 stoichiometric reaction of *cis*-PtCl₂(Me₂ppz) with [α -PW₁₁O₃₉]⁷⁻ in an aqueous solution at approximately 25 °C under air, followed by the addition of tetramethylammonium chloride. The purification was carried out by precipitation from water. The characterization was accomplished by elemental analysis, TG/DTA, and FTIR, UV-Vis, and solution {¹H, ¹³C, ³¹P, ¹⁹⁵Pt, and ¹⁸³W} NMR spectroscopies. The polyoxoanion **1** was stable in DMSO and water compared with an α -Keggin-type polyoxometalate-coordinated mono-platinum(II) complex, [α -PW₁₁O₃₉{*cis*-Pt(NH₃)₂}]⁵⁻ (**Intermediate-A**), and obtained as a cesium salt with a relatively high abundance ratio by controlling the reaction conditions. The coordination of [*cis*-Pt(NH₃)₂]²⁺ to the terminal oxygen atoms adjacent to the mono-platinum site in **Intermediate-A** was observed using ³¹P NMR spectroscopy, while **1** did not react with cisplatin under the present conditions. **TMA-1** is the first example of a mono-platinum(II) complex containing a POM framework, and a high stability of the mono-platinum(II) center was observed by using *cis*-PtCl₂(Me₂ppz) as the platinum source.

Experimental

Materials and methods: K₇[α -PW₁₁O₃₉]₇·13H₂O^[23] and *cis*-PtCl₂(Me₂ppz) (Me₂ppz = *N,N'*-dimethylpiperazine)^[22] were prepared according to the published methods. The number of solvated water molecules was determined using thermogravimetric/differential thermal

analysis (TG/DTA). All the reagents and solvents were obtained from commercial sources and used as received. The elemental analysis results for C, H, and N were obtained using Flash EA (Thermo Electron Corporation) at Shizuoka University (Japan). The elemental analysis results for P, Pt, and K were obtained by Optima 2100DV (PerkinElmer Inc.) at Shizuoka University (Japan). The infrared spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer in KBr disks at ambient temperature. The TG/DTA data were obtained using Rigaku Thermo Plus EVO2 TG/DTA 81205Z instruments in air while increasing the temperature from 20 to 500°C at a rate of 4°C/min. Solution ^1H (600.17 MHz), ^{13}C (150.92 MHz), and ^{31}P (242.95 MHz) NMR spectra were recorded in 5 mm outer diameter tubes on a JEOL ECA-600 NMR spectrometer. The ^1H and ^{13}C NMR spectra were measured in DMSO- d_6 with reference to an internal 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS). Chemical shifts are reported as positive for resonances downfield of DSS (δ 0). The ^{31}P NMR spectra were measured in D $_2$ O and DMSO- d_6 with reference to an external standard of 85% H $_3$ PO $_4$ in a sealed capillary. Chemical shifts are reported as negative on the δ scale for resonances upfield of H $_3$ PO $_4$ (δ 0). The ^{195}Pt NMR (129.02 MHz) spectrum was recorded on a JEOL ECA-600 NMR spectrometer (Kyusyu University, Japan). The ^{195}Pt NMR spectrum was measured in DMSO- d_6 with reference to an external standard of K $_2$ PtCl $_4$ dissolved in D $_2$ O (1 M HCl) solution (substitution method). Chemical shifts are reported as negative for resonances upfield of K $_2$ PtCl $_4$ (δ 0). The ^{183}W NMR (25.00 MHz) spectrum was recorded in a tube (outer diameter: 10 mm) on a JEOL ECA-600 NMR spectrometer (Kyusyu University, Japan). The ^{183}W NMR spectrum measured in D $_2$ O was referenced to an external standard of saturated Na $_2$ WO $_4$ -D $_2$ O solution (substitution method). Chemical shifts were reported as negative for the resonance upfield of Na $_2$ WO $_4$ (δ 0). Solution ultraviolet-visible (UV-Vis) spectra were recorded using a Perkin-Elmer Spectrum Lambda 650 spectrophotometer.

Synthesis of [(CH $_3$) $_4$ N] $_4$ H[α -PW $_{11}$ O $_{39}$ {Pt(Me $_2$ ppz)}]·5H $_2$ O (TMA-1): A solution of *cis*-PtCl $_2$ (Me $_2$ ppz) (0.0758 g; 0.2 mmol) dissolved in 35 mL of water at 50 °C was added to a

solution of $\text{K}_7[\alpha\text{-PW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}$ (0.643 g; 0.2 mmol) dissolved in 5 mL of water. After stirring for 24 h at 25 °C, solid $(\text{CH}_3)_4\text{NBr}$ (1.035 g; 9.4 mmol) was added, and the mixture was stirred for 24 h. Then, a yellow precipitate was collected by a membrane filter (JG 0.2 μm) and washed with a small amount of ethanol. At this stage, a crude product (0.4387 g) was obtained. For purification, it was dissolved in 20 mL of water at 50 °C, and stood in a refrigerator overnight. A yellow precipitate was collected by a membrane filter (JG 0.2 μm) and washed with a small amount of ethanol to yield 0.1447 g of product (The yield was calculated on the basis of $[\text{mol of TMA-1}]/[\text{mol of K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}] \times 100$ and was 21%). This product was soluble in water and DMSO and insoluble in methanol, ethanol, acetone, and diethylether. Elemental analysis results showed: C, 7.78; H, 1.89; N, 2.48; P, 0.98; Pt, 5.76; K, <0.1%. Calculations for $[(\text{CH}_3)_4\text{N}]_4\text{H}[\alpha\text{-PW}_{11}\text{O}_{39}\{\text{Pt}(\text{Me}_2\text{ppz})\}] \cdot x\text{H}_2\text{O}$ ($x = 5$) = $\text{H}_{73}\text{C}_{22}\text{N}_6\text{Pt}_1\text{O}_{44}\text{P}_1\text{W}_{11}$ (MW: 3374.129): C, 7.83; H, 2.18; N, 2.49; P, 0.92; Pt, 5.78%; K, 0%. TG/DTA under atmospheric conditions showed a weight loss of 2.90% with an endothermic point at 41.7 °C observed below 92.5 °C (based on calculations, 2.67% corresponds to five water molecules). Additionally, a weight loss of 13.03% with two exothermic peaks at 273.8 and 374.9 °C was observed in the temperature range from 234.6 to 402.8 °C corresponding to four $[(\text{CH}_3)_4\text{N}]^+$ and a Me_2ppz molecule (calculated 12.17%). FTIR (KBr disk) results in the 1300 – 400 cm^{-1} region (polyoxometalate region) showed: 1101, 1050, 1043, 949, 891, 857, 813, 795, 776, 723, and 516 cm^{-1} . The NMR results gave ^{13}C NMR (DMSO- d_6 , 23.4 °C) δ 57.7 ($[(\text{CH}_3)_4\text{N}]^+$), 50.9 and 51.4 ($-\text{CH}_2\text{CH}_2-$ groups in Me_2ppz), 21.7 ($(\text{CH}_3)_2\text{ppz}$); ^{31}P NMR: (D_2O , 21.3 °C): δ -12.03; ^{31}P NMR (DMSO- d_6 , 22.6 °C): δ -11.75; ^{195}Pt NMR (DMSO- d_6 , 20.7 °C): δ -1326. UV-Vis absorption (in H_2O , 7.11×10^{-5} M and 5.00×10^{-4} M) showed: λ 252 nm (ϵ 39135 $\text{M}^{-1}\text{cm}^{-1}$), λ 337 nm (ϵ 3406 $\text{M}^{-1}\text{cm}^{-1}$), and 405 nm (ϵ 882 $\text{M}^{-1}\text{cm}^{-1}$).

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Figure captions

Figure 1. FT-IR spectra (as KBr disks) of (a) **TMA-1** and (b) $\text{K}_7[\alpha\text{-PW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$.

Figure 2. ^{31}P NMR spectra of **TMA-1** (a) in D_2O and (b) in $\text{DMSO-}d_6$.

Figure 3. ^{183}W NMR spectrum in D_2O of the potassium salt of **1**. The spectrum was obtained at $24.0\text{ }^\circ\text{C}$. The eleven signals are indicated with an asterisk. The high purity of the potassium salt of **1** is confirmed by ^{31}P NMR spectroscopy.

Figure 4. ^{195}Pt NMR spectrum in $\text{DMSO-}d_6$ of **TMA-1**.

Figure 5. ^{13}C NMR spectrum in $\text{DMSO-}d_6$ of **TMA-1**.

Figure 6. UV-Vis spectra of (a) **TMA-1** ($7.11 \times 10^{-5}\text{ M}$) in water. Inset: **TMA-1** ($5.00 \times 10^{-4}\text{ M}$) in the range 350 – 650 nm.

Figure 7. The proposed partial structures around the platinum center in (a) **TMA-1** and (b) **Intermediate-A**.

Figure 8. ^{31}P NMR spectra in D_2O of (a) as-prepared **Intermediate-A** and (b) the sample after 1-day heating at $50 \pm 2\text{ }^\circ\text{C}$.

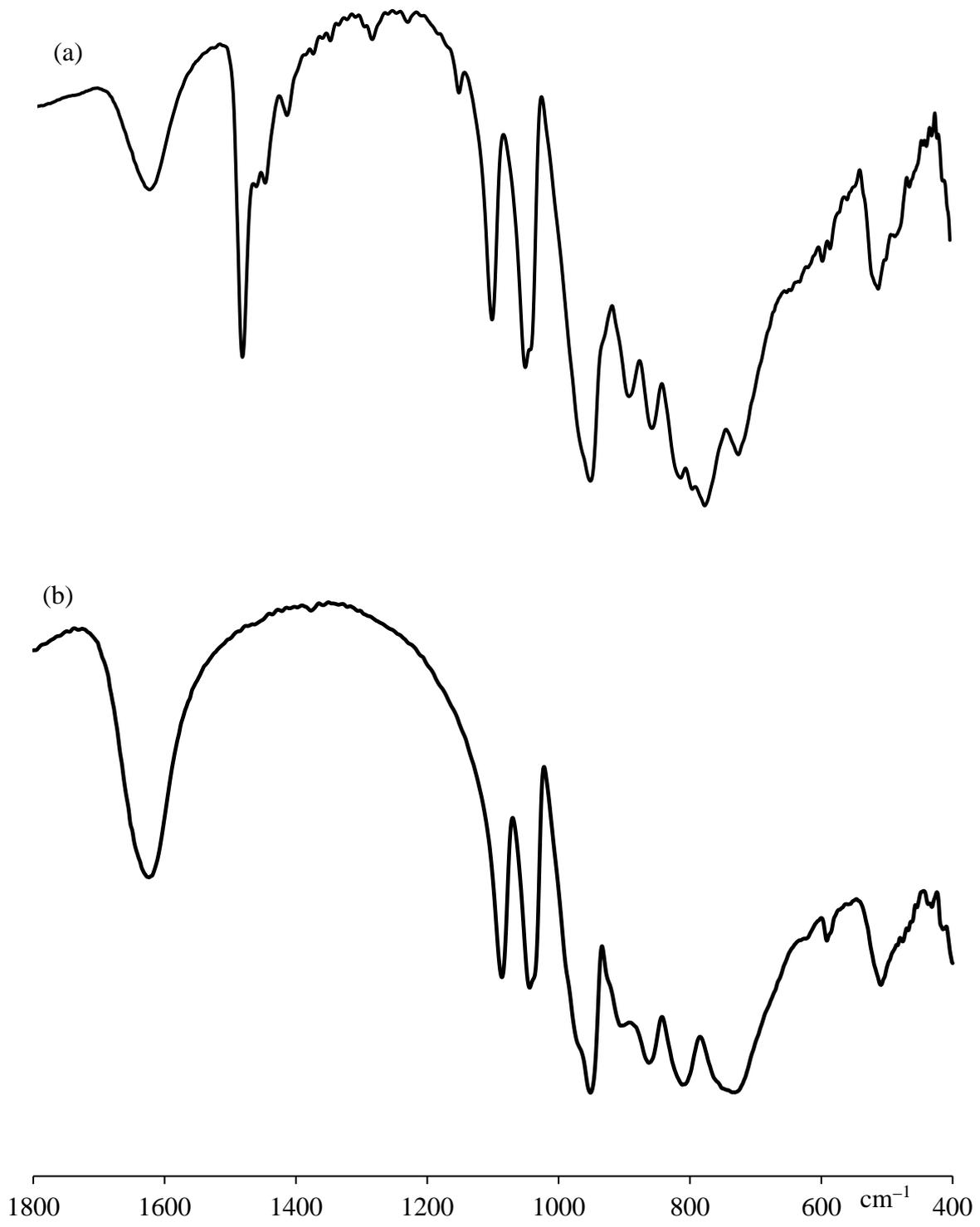


Fig. 1

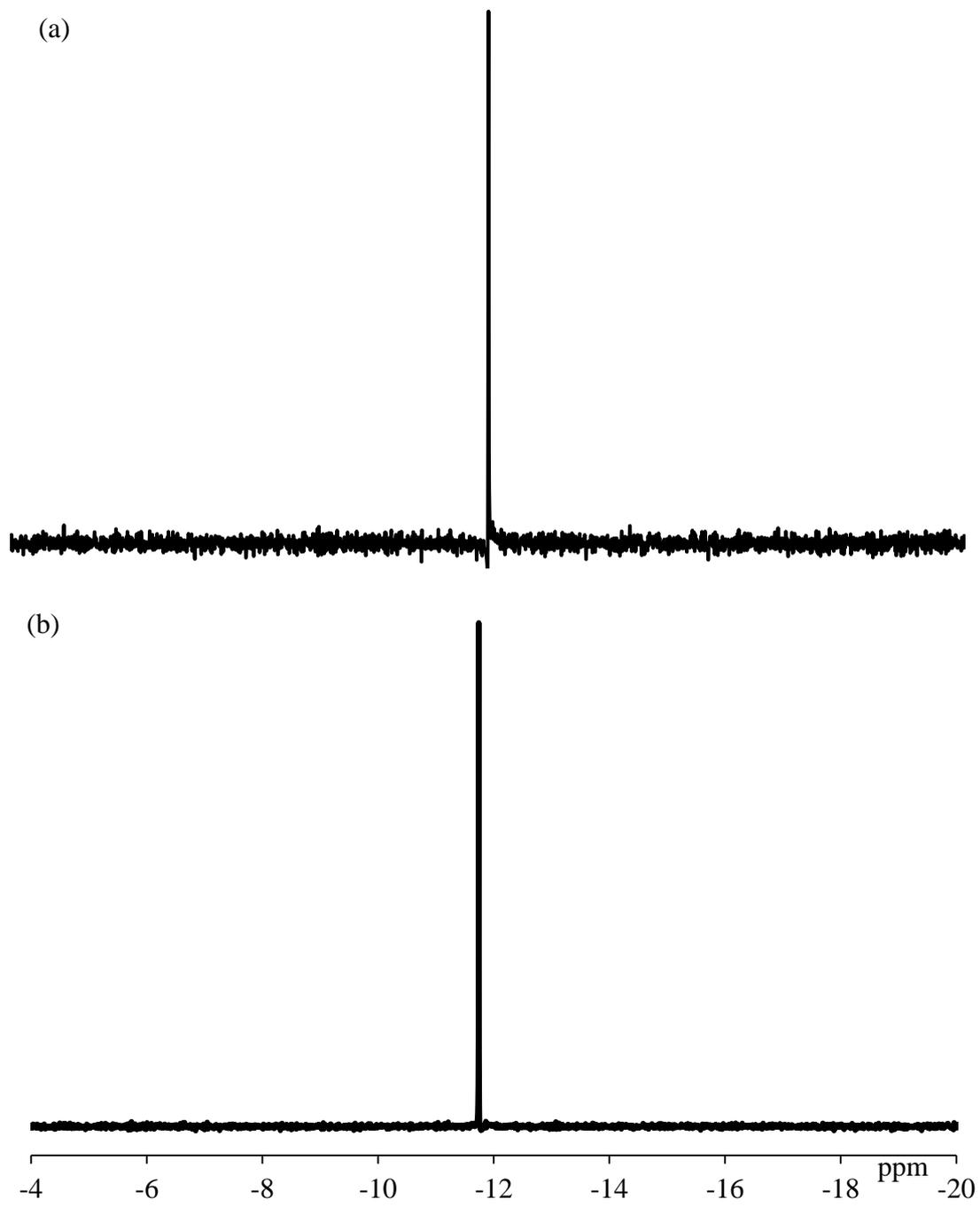


Fig. 2

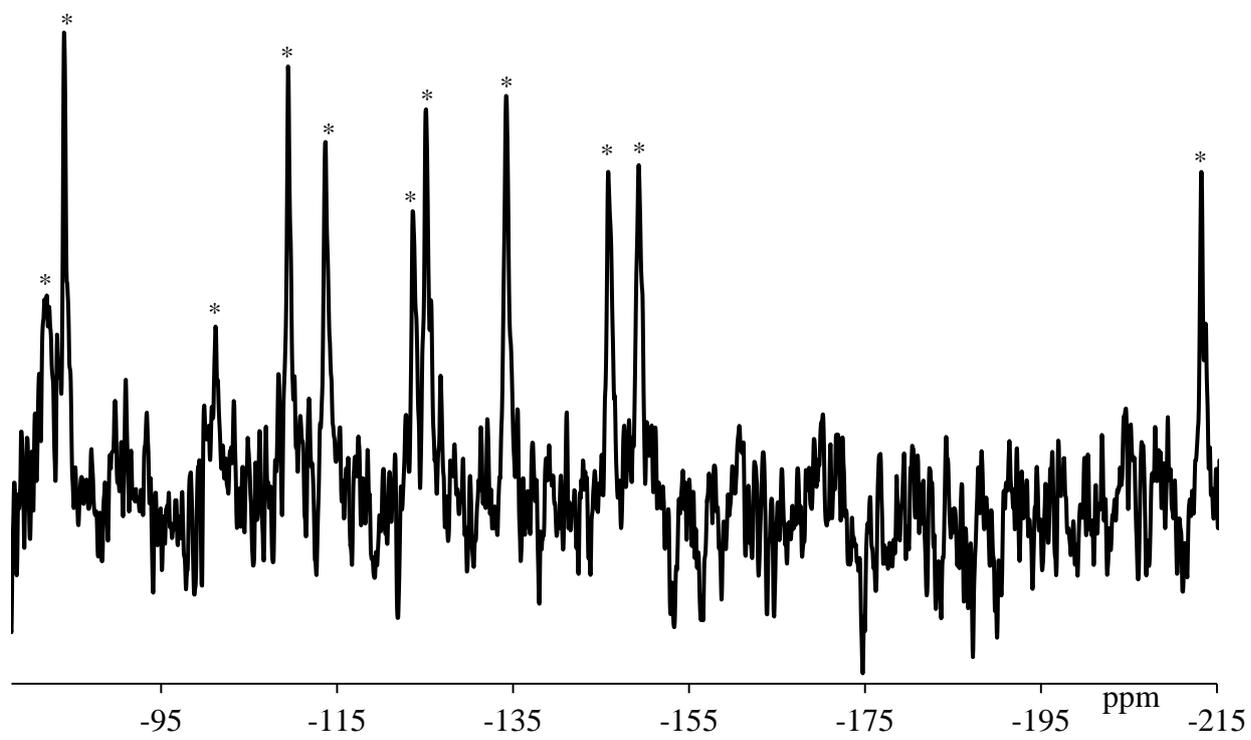


Fig. 3

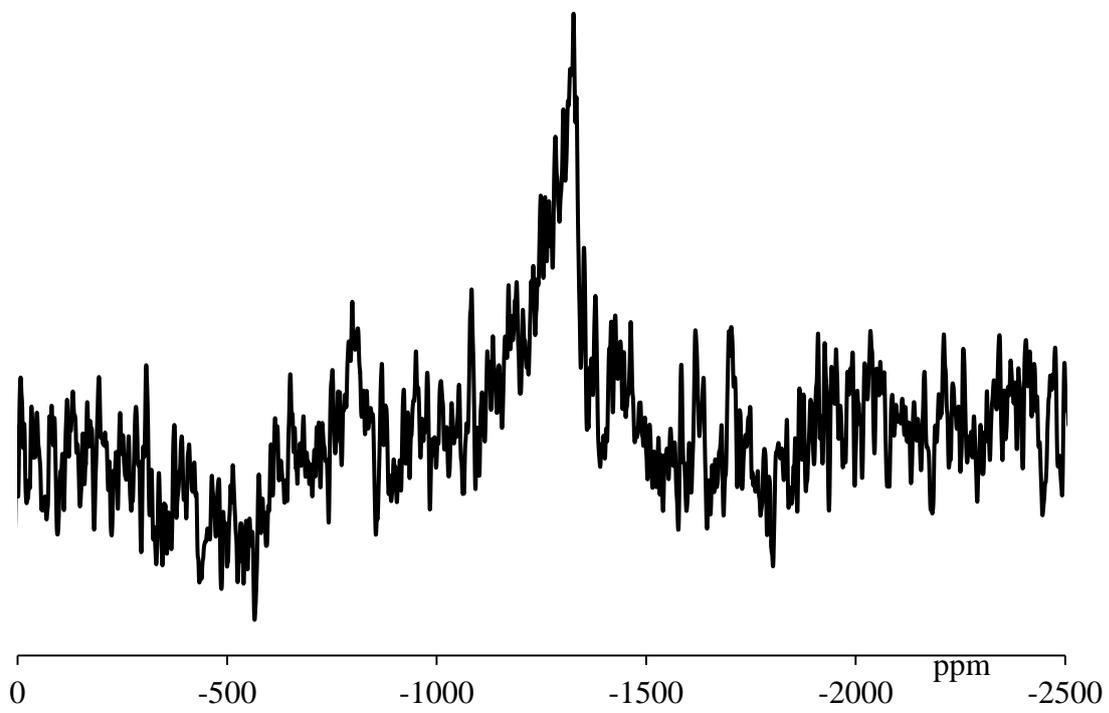


Fig. 4

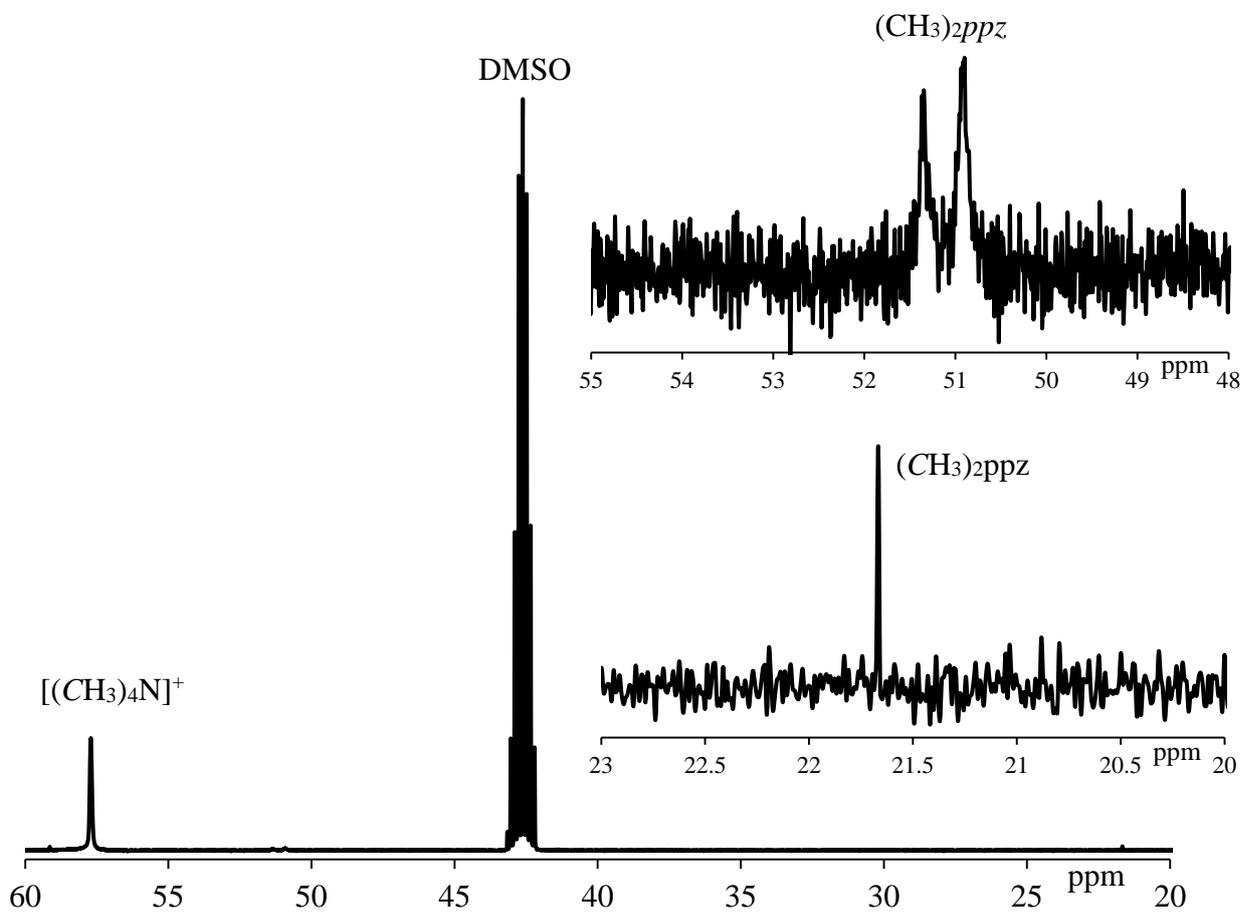


Fig. 5

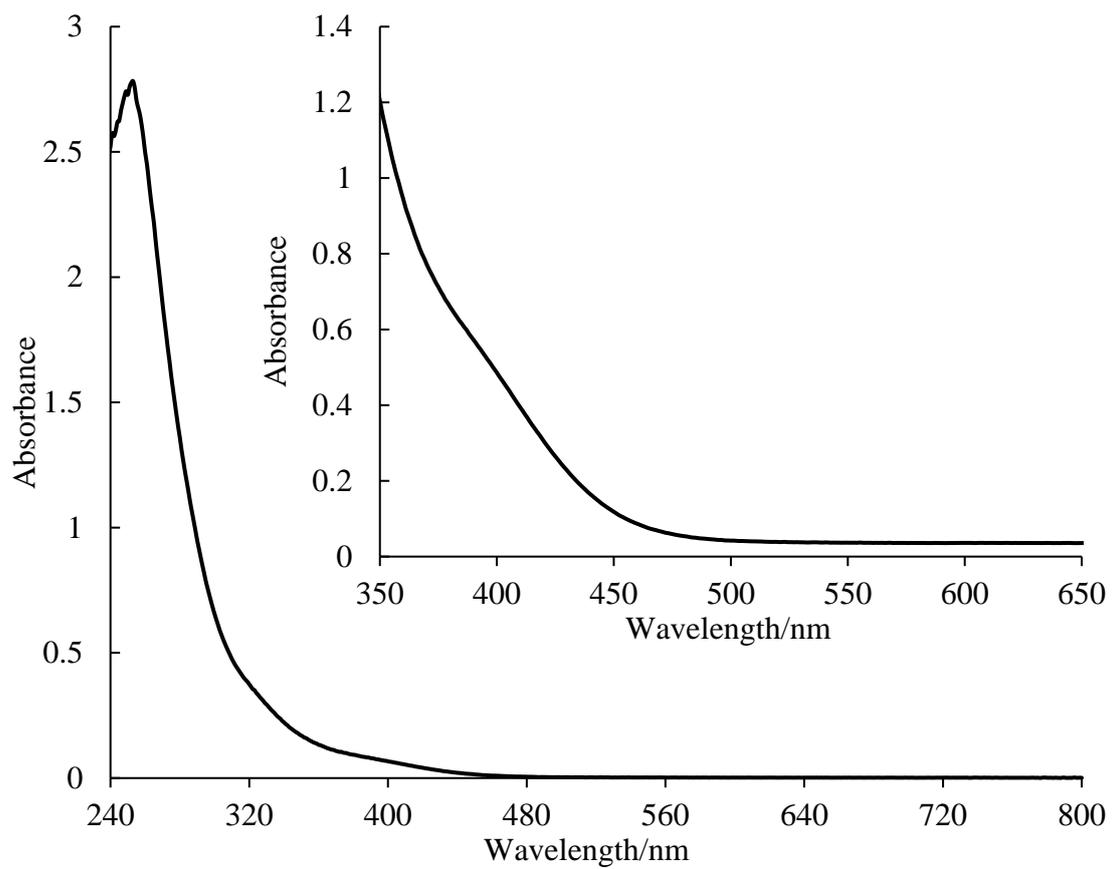
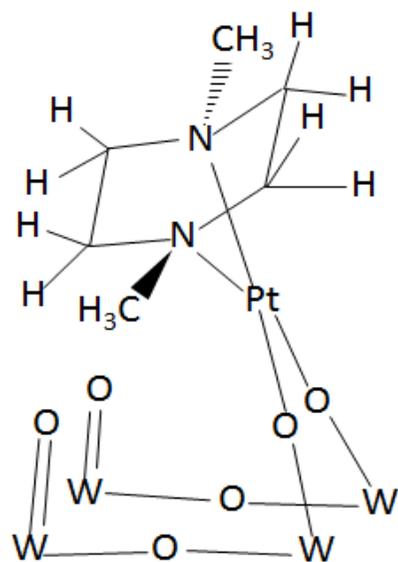


Fig. 6

(a)



(b)

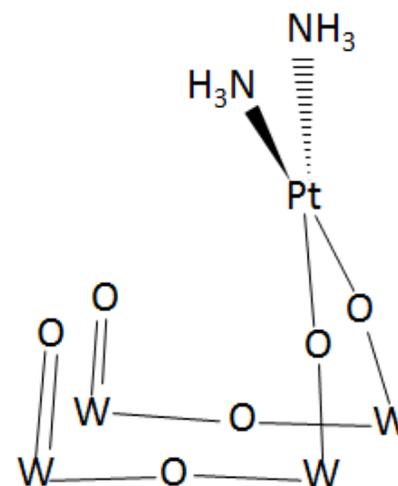


Fig. 7

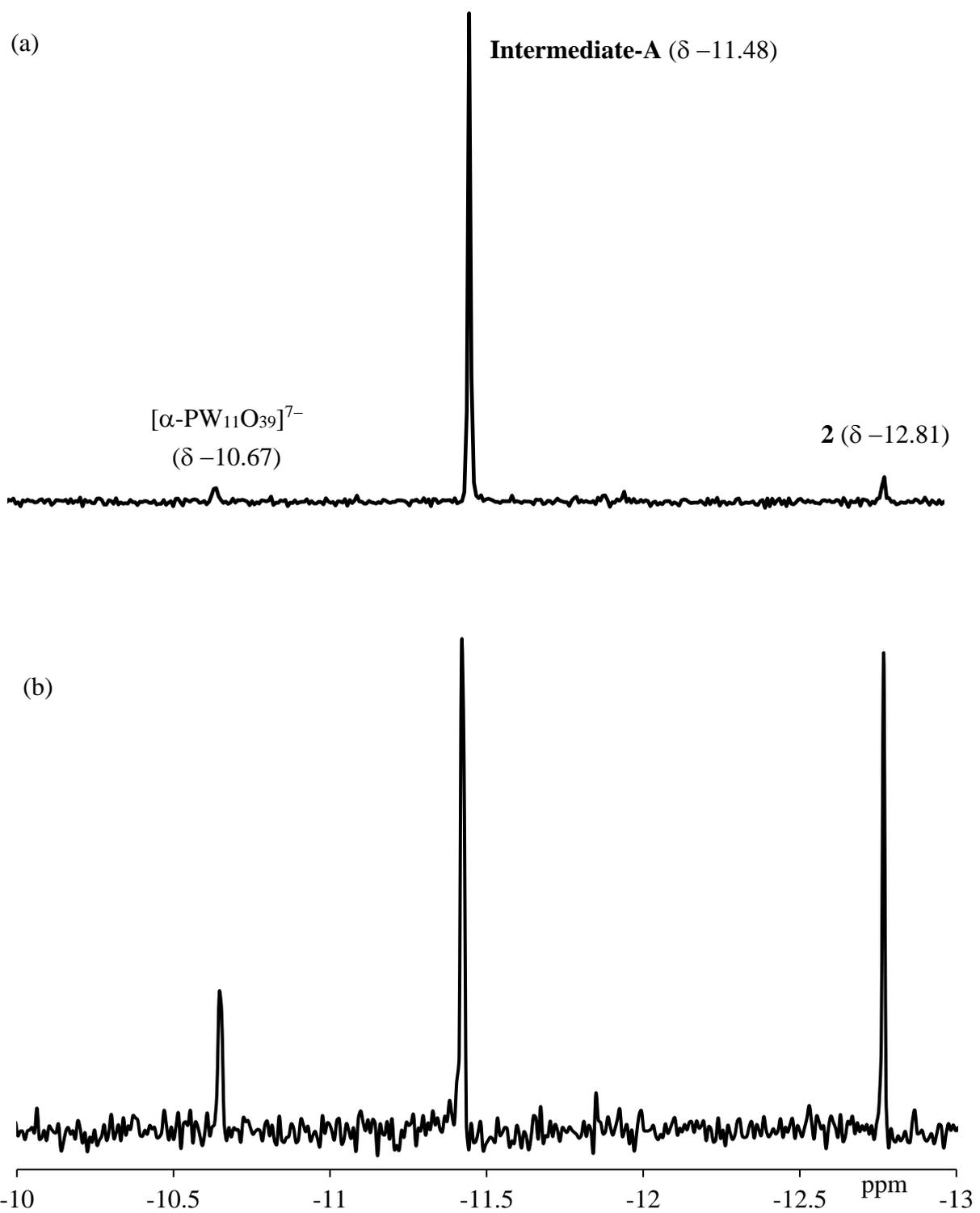


Fig. 8