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# A Keggin-type polyoxotungstate-coordinated diplatinum(II) complex: Synthesis, characterization, and stability of the *cis*-platinum(II) moieties in dimethylsulfoxide and water

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#### Introduction

Platinum and its derivatives, *e.g.*, alloys, oxides, organometallics, and inorganic compounds, have attracted considerable attention due to their efficient physical and chemical properties [1]. Since platinum is an imperative metal for catalysts, electronics, and pharmaceutical compounds, numerous studies on the syntheses, properties, and activities of various platinum compounds have been reported; however, there is still a need for improved properties and activities.

Polyoxometalates (POMs) are of particular interest in the fields of catalysis, surface science, and materials science because their chemical properties, such as redox potentials, acidities, and solubility in various media, can be finely tuned by choosing appropriate constituent elements and countercations [2]. In particular, the coordination of various species, *e.g.*, metal ions and organometallics, into the vacant site(s) of lacunary polyoxometalates is one of the most powerful techniques used for construction and stabilization of efficient and well-defined metal centers. However, only a few examples regarding platinum species-coordinated POMs, *e.g.*,  $K_{12}$  [[WZnPt<sup>II</sup><sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ZnW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>)·36H<sub>2</sub>O [3],  $K_7$ Na<sub>9</sub>[O = Pt<sup>IV</sup>(H<sub>2</sub>O) (PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]·21.5H<sub>2</sub>O [4], Na<sub>5</sub>[H<sub>2</sub>Pt<sup>IV</sup>V<sub>9</sub>O<sub>28</sub>]·21H<sub>2</sub>O [5], and (NBu<sub>4</sub>)<sub>7</sub> [{Pt(cod)}(P<sub>2</sub>W<sub>15</sub>V<sub>3</sub>O<sub>62</sub>)]·2NBu<sub>4</sub>BF<sub>4</sub> (cod = 1,5-cyclooctadiene) [6], have been reported, and some of the results are still debated [7].

In this paper, we report the full details of the synthesis and characterization of the tetramethylammonium salt of a diplatinum(II)-coordinated polyoxoanion,  $[(CH_3)_4N]_3[PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2] \cdot 10H_2O$ 

#### ABSTRACT

The synthesis of a Keggin-type polyoxotungstate-coordinated diplatinum(II) complex,  $[(CH_3)_4N]_3[\alpha-PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2]$ , obtained by reaction of Keggin-type mono-lacunary polyoxotungstate,  $[\alpha-PW_{11}O_{39}]^{7-}$ , with *cis*-diamminedichloroplatinum(II) in an aqueous solution is described. The complex was characterized by elemental analysis, thermogravimetric/differential thermal analysis (TG/DTA), Fourier transform infrared (FTIR), ultraviolet-visible (UV-vis), and solution <sup>1</sup>H, <sup>31</sup>P, and <sup>183</sup>W nuclear magnetic resonance (NMR) spectroscopy. The two *cis*-platinum(II) moieties,  $[cis-Pt(NH_3)_2]^{2+}$ , were coordinated each to two oxygen atoms in a mono-vacant site of  $[\alpha-PW_{11}O_{39}]^{7-}$  with *C<sub>s</sub>* symmetry, and the *cis*-conformation was highly stable in dimethylsulfoxide and water.

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 $(Me_4N-1)$  (Fig. 1), using cisplatin (*cis*-diamminedichloroplatinum(II)), a well-known antitumor compound [1]. Furthermore, the stability of the two platinum(II) moieties with *cis*-configuration in polyoxoanion 1 was investigated in dimethylsulfoxide (DMSO) and aqueous media.

# Experimental

### Materials and methods

K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>]·13H<sub>2</sub>O was prepared as described in the literature [8]. The number of solvated water molecules was determined by thermogravimetric/differential thermal analysis (TG/DTA). All reagents and solvents were obtained and used as received from commercial sources. The elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The sample was dried overnight at room temperature under 10<sup>-3</sup>-10<sup>-4</sup> torr before analysis. Infrared spectra were recorded on a Perkin-Elmer Spectrum100 Fourier transform infrared (FTIR) spectrometer using KBr disks at room temperature. TG and DTA data were obtained using a Rigaku Thermo Plus 2 series TG/DTA TG 8120. TG/DTA measurements were performed in air with a temperature increase of 4 °C per min between 20 and 500 °C. The <sup>1</sup>H (600.17 MHz) and  ${}^{31}P-{}^{1}H$ (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). <sup>1</sup>H NMR spectra were measured in DMSO-d<sub>6</sub> with reference to an internal 3-(trimethylsilyl)-1propanesulfonic acid, sodium salt (DSS). Chemical shifts are reported as positive for resonances downfield of DSS ( $\delta$  0). The <sup>31</sup>P NMR spectra were measured in DMSO- $d_6$  and  $D_2O$  with reference to an external standard of 85% H<sub>3</sub>PO<sub>4</sub> in a sealed capillary. Chemical shifts were

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**Fig. 1.** Polyhedral representation of  $[PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2]^{3-}$  with  $C_s$  symmetry. The WO<sub>6</sub> and PO<sub>4</sub> sites are represented by white octahedra and gray tetrahedra, respectively.

reported as negative on the  $\delta$  scale for resonance upfield of H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0). The <sup>183</sup>W NMR (25.00 MHz) spectrum was recorded in a tube (outer diameter: 10 mm) on a JEOL ECA-600 NMR spectrometer (Kyusyu University). The <sup>183</sup>W NMR spectrum measured in DMSO-*d*<sub>6</sub> was referenced to an external standard of saturated Na<sub>2</sub>WO<sub>4</sub>-D<sub>2</sub>O solution (substitution method). Chemical shifts were reported as negative for the resonance upfield of Na<sub>2</sub>WO<sub>4</sub> ( $\delta$  0). Solution ultraviolet-visible (UV-vis) spectra were recorded on a Perkin-Elmer Spectrum Lambda 650 spectrophotometer.

#### $[(CH_3)_4N]_3[PW_{11}O_{39}{cis-Pt(NH_3)_2}_2] \cdot 10H_2O (Me_4N-1)$

A solution of cis-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.060 g; 0.2 mmol) dissolved in 75 mL of water was added to a solution of K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>]·13H<sub>2</sub>O (0.319 g; 0.1 mmol) dissolved in 10 mL of water. After stirring for 24 h at 25 °C, solid (CH<sub>3</sub>)<sub>4</sub>NBr (1.535 g; 10 mmol) was added and stirred for 24 h. Then, a yellow precipitate was collected by a membrane filter (JG 0.2 µm). At this stage, a crude product was obtained in a 0.251 g vield. For purification, the crude product (0.241 g) was dissolved in 17.0 mL of H<sub>2</sub>O at 60 °C, followed by standing in a refrigerator overnight. A yellow precipitate was collected by a membrane filter (IG  $0.2 \,\mu\text{m}$ ) and washed with ethanol. The obtained product was  $0.050 \,\text{g}$ (the yield calculated on the basis of [mol of Me<sub>4</sub>N-1]/[mol of K<sub>7</sub>  $[PW_{11}O_{39}] \cdot 13H_2O] \times 100$  was 14%). When the crude product (0.590 g) obtained by three cycles of preparation was dissolved in 36 mL of H<sub>2</sub>O at 60 °C, the yield was 23% (0.246 g). The obtained product was soluble in water and DMSO and insoluble in methanol, ethanol, acetone, and diethyl ether. Elemental analysis results showed: C, 4.32; H, 1.54; N, 2.92; P, 0.90; W, 59.1; Pt, 11.5; Cl, <0.02; K, <0.015%. Calculations for  $[(CH_3)_4N]_3[PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2] \cdot xH_2O(x=3) =$ H<sub>54</sub>C<sub>12</sub>N<sub>7</sub>Pt<sub>2</sub>O<sub>42</sub>P<sub>1</sub>W<sub>11</sub>: C, 4.22; H, 1.60; N, 2.87; P, 0.91; W, 59.27; Pt, 11.44%; Cl, 0%; K, 0%. A weight loss of 3.73% was observed during overnight drying at room temperature under  $10^{-3}$ - $10^{-4}$  torr before analysis, suggesting the presence of seven weakly solvated or adsorbed water molecules (3.56%). TG/DTA under atmospheric conditions showed a weight loss of 5.24% with endothermic points at 37 °C observed below 250 °C; calculations showed 5.09% for 10 water molecules. Additionally, a weight loss of 8.28% with two exothermic peaks at 290 and 317 °C was observed in the temperature range from 250 to 370 °C; calculations showed three [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> (calcd. 6.29%) and four NH<sub>3</sub> (calcd. 1.93%) molecules (total: 8.22%). IR (KBr disk) results in the 1300–400  $\text{cm}^{-1}$  region (polyoxometalate region) showed: 1101w, 1046w, 953vs, 917 m, 895 m, 861 s, 805vs, 753 s, 721 s, 595w, and 513w cm<sup>-1</sup>. NMR results gave <sup>1</sup>H NMR (DMSO- $d_6$ , 23.7 °C): 2.48–2.50 (DMSO), 3.13 (CH<sub>3</sub>), 3.32 (H<sub>2</sub>O), 4.18 (NH<sub>3</sub>), and 4.32 (NH<sub>3</sub>); <sup>31</sup>P NMR: (DMSO- $d_6$ , 23.8 °C):  $\delta$  – 12.85; <sup>183</sup>W NMR (DMSO- $d_6$ , 21.8 °C):  $\delta$  – 101 (2 W), – 102 (2 W), – 107 (1 W), – 116 (2 W), – 142 (2 W), and – 162 (2 W). UV–vis absorption (in H<sub>2</sub>O, 7.2 × 10<sup>-5</sup> M) showed:  $\lambda$  251 nm ( $\varepsilon$  40,120 M<sup>-1</sup>cm<sup>-1</sup>),  $\lambda$  324 nm ( $\varepsilon$  6787 M<sup>-1</sup>cm<sup>-1</sup>), and 405 nm ( $\varepsilon$  1346 M<sup>-1</sup>cm<sup>-1</sup>).

### **Results and discussion**

#### Synthesis and spectral characterization of Me<sub>4</sub>N-1

The polyoxoanion,  $[PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2]^{3-}$  (1), was formed by a 2:1 stochiometric reaction of cisplatin with mono-lacunary Keggin POM,  $[\alpha$ -PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>, in an aqueous solution at 25 °C under air, followed by reprecipitation from water. Faster formation of 1 was observed when excess cisplatin was used. During the reaction of cisplatin with  $[\alpha$ -PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> in aqueous solution, cationic aquaplatinum complexes, e.g., [cis-Pt(NH<sub>3</sub>)<sub>2</sub>Cl(H<sub>2</sub>O)]<sup>+</sup> and [cis-Pt(NH<sub>3</sub>)<sub>2</sub>  $(H_2O)_2]^{2+}$ , were initially formed by elimination of chloride ions [9]. Next, the two cationic aqua-platinum species coordinated to two oxygen atoms of the mono-lacunary site in  $[\alpha$ -PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>. The compound Me<sub>4</sub>N-1 was finally isolated as an analytically pure, yellow powder in a 14% yield. A control experiment was carried by suspending transplatin (trans-diamminedichloroplatinum(II)) (0.060 g; 0.2 mmol) in 75 mL of water (at this stage, only a small amount of transplatin was soluble in water). The suspension was added to an aqueous solution of  $K_7[\alpha-PW_{11}O_{39}]$  · 13H<sub>2</sub>O (0.32 g; 0.1 mmol) in 15 mL of water. After stirring for 24 h at 25 °C, solid (CH<sub>3</sub>)<sub>4</sub>NBr (1.546 g; 10 mmol) was added and stirred overnight. Then, a yellow precipitate was collected by a membrane filter (JG  $0.2 \,\mu\text{m}$ ). The <sup>31</sup>P NMR spectrum of the obtained product in DMSO-*d*<sub>6</sub> showed no signal, indicating that the polyoxometalate-coordinated platinum complex was not obtained using transplatin as a starting material under the present conditions.

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, Pt, P, and W were in good agreement with the calculated values for the chemical formula of Me<sub>4</sub>N-1 with three hydrated water molecules (see Experimental). It should be noted that Cl analysis showed no contamination of unreacted cisplatin. The weight loss observed during drying before analysis was 3.73% for Me<sub>4</sub>N-1, corresponding to seven weakly solvated or adsorbed water molecules. On the other hand, during TG/DTA under atmospheric conditions, a weight loss of 5.24% was observed below 250 °C, corresponding to 10 water molecules. Therefore, the number of water molecules (10) observed by TG/DTA under atmospheric conditions was consistent with the sum of the hydrated water molecules (3) indicated by elemental analysis and the number of water molecules (7) corresponding to the weight loss observed during drying before analysis. In addition, a weight loss of 8.28% was observed in the temperature range from 250 to 370 °C, corresponding to the sum of three tetramethylammonium ions and four ammonia molecules.

The FTIR spectrum of Me<sub>4</sub>N-1 measured as a KBr disk is shown in Fig. S1. The spectral pattern of Me<sub>4</sub>N-1 (1101, 1046, 953, 917, 895, 861, 805, 753, and 721 cm<sup>-1</sup>) was different from that of K<sub>7</sub>[ $\alpha$ -PW<sub>11</sub>O<sub>39</sub>]<sup>-1</sup>3H<sub>2</sub>O (1086, 1043, 953, 903, 862, 810, and 734 cm<sup>-1</sup>) and that of Na<sub>3</sub>[ $\alpha$ -PW<sub>12</sub>O<sub>40</sub>]<sup>-1</sup>2H<sub>2</sub>O [10] (1080, 984, 893, and 808 cm<sup>-1</sup>), suggesting that the two platinum(II) moieties were coordinated to the vacant site of [ $\alpha$ -PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup>.

The <sup>31</sup>P NMR spectrum of Me<sub>4</sub>N-1 in DMSO- $d_6$  at ~25 °C showed a clear single-line spectrum at -12.85 ppm due to the internal phosphorus atom, confirming the purity and homogeneity of the sample (Fig. S2). The signal was shifted compared with the signals of



**Fig. 2.**  $^{183}$ W NMR spectrum of 1 in DMSO-*d*<sub>6</sub>. The spectrum was referenced to an external standard of saturated Na<sub>2</sub>WO<sub>4</sub>-D<sub>2</sub>O solution (substitution method).

 $K_7[\alpha\text{-PW}_{11}O_{39}]^\cdot13H_2O~(\delta-10.12)$  and  $Na_3[\alpha\text{-PW}_{12}O_{40}]^\cdot12H_2O~[10]~(\delta-14.67).$ 

The <sup>1</sup>H NMR spectrum of Me<sub>4</sub>N-1 in DMSO- $d_6$  showed two signals at 4.18 ppm and 4.32 ppm (Fig. S3). These signals were assigned to the two NH<sub>3</sub> ligands coordinated to each platinum(II) atom. No signals due to cisplatin or transplatin were observed. These results suggested that non-equivalent platinum sites were formed by the coordination of  $[cis-Pt(NH_3)_2]^{2+}$  to the oxygen atoms in a vacant site of  $[\alpha-PW_{11}O_{39}]^{7-}$ , as shown in Fig. 1. The <sup>183</sup>W NMR spectrum of Me<sub>4</sub>N-1 in DMSO- $d_6$  showed six signals at -101, -102, -107, -116, -142, and -162 ppm with 2:2:1:2:2:2 intensities, resulting in  $C_s$  symmetry (Fig. 2). A clear <sup>195</sup>Pt NMR spectrum could not be obtained due to the low solubility of Me<sub>4</sub>N-1 in DMSO- $d_6$ ; however, two broad signals were observed. These results were consistent with the <sup>1</sup>H NMR spectrum of Me<sub>4</sub>N-1 in DMSO- $d_6$ , as mentioned above.

The UV-vis spectrum of Me<sub>4</sub>N-1 in water showed three absorption bands at 251 nm (extinction coefficient:  $\epsilon$  40120 M<sup>-1</sup>cm<sup>-1</sup>), 324 nm



**Fig. 3.** Time course for the relative amount (%) of the *cis*-platinum(II) moiety in 1 ( $\bigcirc$ ) and a *cis*-isomer that was the sum of cisplatin and the species formed by a ligand exchange reaction with DMSO ( $\triangle$ ). The relative amount was calculated using the integrated value of a signal at 4.36 ppm for 1 and (3.97 ppm and 4.65 ppm) for cisplatin. Experimental conditions: Me<sub>4</sub>N-1 (ca. 20 mg) or cisplatin (ca. 10 mg) was dissolved in 3 mL of DMSO-*d*<sub>6</sub> containing 0.021 mmol of DSS. These solutions were kept in a water bath at 30 °C for 92 h. The time course of these solutions was monitored by <sup>1</sup>H NMR spectroscopy after 0.5, 2, 5, 12, 23.5, and 92 h.

( $\epsilon$  6787 M<sup>-1</sup>cm<sup>-1</sup>), and 405 nm ( $\epsilon$  1346 M<sup>-1</sup>cm<sup>-1</sup>), as shown in Fig. S4. The broad bands at 251 nm and 324 nm were assigned to the charge transfer (CT) bands of W–O and a broad band at 405 nm due to the two platinum(II) atoms, which was red-shifted relative to that of cisplatin ( $\lambda$  = 366 nm).

Stability of the two platinum(II) species of 1 with cis-configuration in DMSO and aqueous media

It has been reported that cisplatin undergoes rapid ligand exchange reactions and slow isomerization to the trans-isomer in dimethylsulfoxide and water [1,11-14]. In addition, significant inhibition of the isomerization of cisplatin in an aqueous solution by addition of Cl<sup>-</sup> ions has been reported [12]. In our experiments, <sup>1</sup>H NMR spectra of cisplatin in DMSO- $d_6$  showed that the *cis*-isomers, including species formed by the ligand exchange reaction with DMSO, were slowly isomerized to trans-isomers at 30 °C. The cis-isomers remained after 12 h (77%) and 92 h (50%), as shown in Figs. 3 and S5. The <sup>31</sup>P NMR spectra of Me<sub>4</sub>N-1 (Fig. S6) in DMSO- $d_6$  showed a signal at -12.84 ppm after 12 h, indicating that polyoxoanion 1 was stable after 12 h; however, a new signal at -12.96 ppm appeared after 23.5 h, and the intensity increased with time. The <sup>1</sup>H NMR spectra (Fig. S7) in DMSO- $d_6$  showed two signals due to the *cis*-platinum(II) moieties in 1 at 4.21 ppm and 4.36 ppm, and 95.1% of *cis*-platinum(II) moieties remained after 12 h; thus, 1 was more stable than cisplatin under the same conditions (Fig. 3). However, new signals at 4.26 ppm and 4.43 ppm appeared in the <sup>1</sup>H NMR spectra after 23.5 h, and the intensities increased with time. No signals due to the cis- (3.97 ppm and 4.65 ppm) and *trans*- (3.50 ppm and 4.39 ppm) platinum(II) species eliminated from the vacant site of 1 were observed in <sup>1</sup>H NMR spectra. This was also supported by the result that no signal due to the Keggin-type mono-lacunary polyoxotungstate (-10.12 ppm) was observed in <sup>31</sup>P NMR spectra. Thus, the new signals might be due to the ligand exchange reaction of one or two ammonia molecules of platinum(II) sites with DMSO [13]. For the <sup>31</sup>P NMR spectra of 1 in  $D_2O$ , a signal at -12.66 ppm due to the central phosphorous atom in 1 was observed after one week at ca. 25 °C, suggesting that *cis*-platinum (II) species in 1 were quite stable in aqueous solution with no additives (Fig. S8).

## Summary

A Keggin-type polyoxotungstate-coordinated diplatinum(II) complex was synthesized. A tetramethylammonium salt,  $[(CH_3)_4N]_3$  $[PW_{11}O_{39}{cis-Pt(NH_3)_2}_2]$  (Me<sub>4</sub>N-1), was obtained as an analytically pure, yellow powder in 35% yield. The characterization of compound Me<sub>4</sub>N-1 was accomplished by elemental analysis, TG/DTA, FT-IR, UVvis, and (<sup>1</sup>H, <sup>31</sup>P and <sup>183</sup>W) NMR spectroscopy. The two *cis*-platinum (II) moieties,  $[cis-Pt(NH_3)_2]^{2+}$ , were coordinated each to two oxygen atoms in a mono-vacant site of  $[\alpha-PW_{11}O_{39}]^{7-}$  with  $C_s$  symmetry, and the *cis*-configuration of platinum(II) moieties in 1 was highly stable in DMSO and water with no additives.

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#### Appendix A. Supplementary data

Supplementary data for this article can be found online at doi:10.1016/j.inoche.2011.03.049.

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