Mutual Separation of Palladium (II) and Platinum (IV) from Hydrochloric Acid Solutions Using *m*-Phenylene Diamine-Containing Agents

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m-Phenylene diamine-containing compounds were synthesized via a one-pot process and subsequently used as new precipitating agents (**PA1** and **PA2**). The precipitation of Pd and Pt was studied using **PA1** and **PA2** as metal precipitants. While **PA1** exclusively precipitated Pd from a HCl solution containing Pd, Pt, and base metals, **PA2** achieved precipitation of both Pd and Pt from the metal-containing HCl solution. Mutual separation of Pd and Pt was achieved by using **PA1** and **PA2** in the first and second precipitation steps, respectively. Separation tests at varying agent loadings revealed that Pd and Pt were precipitated by forming of an ion-pair composed of a metal chloro-complex anion (i.e., $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$) and one precipitating agent molecule (i.e., divalent cation). The stoichiometric ratio of the ion-pairs was in agreement with the atomic ratios estimated from X-ray photoelectron spectroscopy results. Since the precipitation mechanism herein was based on the formation of an ion-pair, the cations of the precipitating agents only recovered Pd and Pt chloro-complex anions when the cations of the base metals were present in the solution. The different hydrophobicities of the precipitating agents enabled mutual separation of Pd and Pt.

Keywords : platinum group metals / metal precipitate / mutual separation / precipitating agent

1. INTRODUCTION

Platinum group metals (PGMs), especially Pd and Pt, are important industrial elements owing to their extensive use in electrical devices, dental materials, catalysts, and jewelry [1,2]. Given the scarcity of the PGMs primary resources, the recycling of these metals from secondary sources or post-consumer scrap is essential [3]. Solvent extraction is regarded as a typical and practical method to recover PGM ions [4-8]. For example, Pd(II) and Pt(IV) can be extracted from hydrochloric acid (HCl) solutions with di-*n*-octyl sulfide [9] and tri-*n*-butyl phosphate [10] extractant agents, respectively. However, the use of volatile organic solvents as extractant diluents negatively affects the recovery process owing to their toxicity and environmental load.

Mutual separation of PGMs, which is required in the recovery process, is complicated because of the similar physical and chemical properties of the metal components. PGM ions are known to be recovered via coordination or ion-pair mechanisms [11]. Pd and Pt are typically recovered following a coordination mechanism with the trend Pd(II) >> Pt(IV) [12]. On the other hand, Pd and Pt chloro-complex anions (i.e., $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$) were extracted to a similar extent via an ion-pair mechanism [11,13]. Therefore, mutual separation of Pd and Pt is generally performed

by combining coordination and ion-pair recovery strategies, respectively. However, the utilization of different mechanisms within the recovery process requires several recovery agents specially designed for the corresponding recovery mechanism. In addition, the recovery of PGMs via a coordination mechanism is typically accompanied with base metals such as Cu, Fe, Al, and Zn [12].

In this study, we report on the selective precipitation and mutual separation of Pd and Pt using new precipitating agents (i.e., *m*-phenylene diamine-containing compounds). These precipitating agents were prepared by condensation of aniline or 4-phenoxyaniline with 3,5-bis(trifluoroacetamido)benzoyl chloride followed by deprotection with hydrazine. The precipitation behaviors of Pd and Pt with the as-prepared precipitating agents were examined by using Pd- and Pt-containing HCl solutions with or without base metals. The precipitating agents prepared in this study enabled mutual separation of Pd and Pt from a HCl solution containing base metals via an ion-pair mechanism.

2 EXPERIMENTAL

2.1 Materials

N,N-Dimethylacetamide (DMAc) was purchased from Wako Pure Chemical Industries Ltd. and distilled from calcium hydride

before use. Thionyl chloride, iron (II) chloride tetrahydrate, copper (II) acetate, and zinc powder were purchased from Kanto Chemical Co., Inc., and used as received. 4-Phenoxyaniline and aluminum (III) chloride were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. 3,5-Bis(trifluoroacetamido)benzoic acid was prepared following methods reported in the literature [14]. Pd(II) and Pt(IV) standard solutions (1000 ppm in 1 M HCl) were purchased from Wako Pure Chemical Industries, Ltd. The HCl solution containing base metals was prepared by dissolving copper (II) acetate, iron (II) chloride tetrahydrate, aluminum (III) chloride, and zinc powder in HCl.

2.2 Synthesis of precipitating agent 1 (PA1)

3,5-Bis(trifluoroacetamido)benzoic acid (2.20 g, 6.39 mmol) was refluxed in thionyl chloride (25 mL) for 2 h. After the removal of thionyl chloride by distillation, chloroform was added and subsequently distilled off to ensure complete removal of thionyl chloride. The resulting product was dried under vacuum and subsequently dissolved in DMAc (12 mL). To the former solution, aniline (0.54 g, 5.81 mmol) was added and the resulting mixture was stirred at room temperature for 12 h under nitrogen. After stirring at 50°C for a further 1 h, water (0.9 mL) was added to the mixture and stirred at 50°C for another 1 h. Hydrazine monohydrate (5.5 mL) was subsequently added and the mixture stirred at 50°C for 4 h. The mixture was subsequently poured into a 5% NaHCO₃ aqueous solution. The resulting precipitate was collected by filtration, washed with water, and subsequently dried at 80°C for 12 h under vacuum. The yield was 1.18 g (88%). ¹H NMR (DMSO-*d*₆, δ, ppm): 4.95 (s, 4 H), 6.01 (s, 1 H), 6.31 (d, 2 H), 7.04 (t, 1 H), 7.31 (t, 2 H), 7.76 (d, 2 H), 9.94 (s, 1 H). ¹³C NMR (DMSO-*d*₆, δ, ppm): 102.26, 102.33, 119.98, 123.11, 128.49, 136.91, 139.62, 149.13, 167.32. Anal. Calcd. for (C₁₃H₁₃N₃O): C, 68.70; H, 5.77; N, 18.49; Found: C, 68.68; H, 5.89; N, 18.31.

2.3 Synthesis of precipitating agent 2 (PA2)

PA2 was synthesized in the same manner as PA1 although 4-phenoxyaniline was used instead of aniline. The yield was 88%. ¹H NMR (DMSO-*d*₆, δ, ppm): 4.95 (s, 4 H), 6.02 (s, 1 H), 6.33 (d, 2 H), 6.98 (d, 2 H), 7.01 (d, 2 H), 7.10 (t, 1 H), 7.37 (t, 2 H), 7.78 (d, 2 H), 9.99 (s, 1 H). ¹³C NMR (DMSO-*d*₆, δ, ppm): 102.24, 102.29, 117.74, 119.32, 121.63, 122.87, 129.92, 135.59, 136.81, 149.12, 151.55, 157.48, 167.13. Anal. Calcd. for (C₁₉H₁₇N₃O₂): C, 71.46; H, 5.37; N, 13.16; Found: C, 71.36; H, 5.34; N, 13.03.

2.4 Precipitation procedure for Pd and Pt

To a 0.1 M HCl solution (5 mL) containing Pd(II) or Pt(IV) (0.94 mmol/L for Pd and 0.51 mmol/L for Pt, i.e., 100 ppm each) PA1 or PA2 were added and the mixture vigorously shaken at room temperature. The resulting solid was separated by centrifugation (7200 g, 10 min) and the metal concentration in the supernatant was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The metal separation experiments were carried out by varying the amount of precipitating agents and the shaking time.

2.5 Separation of Pd and Pt from solutions containing base metals

To a 0.1 M HCl solution (5 mL) containing Pd(II), Pt(IV), Cu(II), Fe(II), Al(III), and Zn(II) (50 ppm each) PA1 or PA2 (PA/Pd = 5 mol/mol, i.e., 23.5 μmol each) were added and the mixture

vigorously shaken for 3 h at room temperature. The resulting solid was separated by centrifugation (7200 g, 10 min) and the metal concentration in the supernatant was determined by ICP-AES.

2.6 Mutual separation of Pt and Pd

PA1 (5.3 mg, 23.5 μmol) was added to a 0.1 M HCl solution (10 mL) containing Pd(II), Pt(IV), Cu(II), Fe(II), Al(III), and Zn(II) (50 ppm each) and the mixture was vigorously shaken for 1 h at room temperature. The resulting solid was separated by centrifugation (7200 g, 10 min) and the metal concentration in the supernatant was determined by ICP-AES. PA2 (2.0 mg, 6.4 μmol) was subsequently added to the supernatant (5 mL). After vigorous shaking for 3 h at room temperature, the mixture was centrifuged and the metal concentration in the supernatant determined by ICP-AES.

2.7 X-ray photoelectron spectroscopy (XPS) measurements

To a 0.1 M HCl solution (10 mL) containing Pd(II) (100 ppm) PA1 (1.1 mg, 4.7 μmol) was added and the mixture vigorously shaken for 1 h at room temperature. The resulting solid was collected by centrifugation (7200 g, 10 min) and dried at 80°C for 12 h under vacuum to yield the Pd-containing solid sample. In a similar manner, the Pt-containing solid sample was prepared using PA2 (0.8 mg, 2.6 μmol) and a 0.1 M HCl solution (10 mL) containing Pt(IV) (100 ppm). The resulting Pt- and Pd-containing solid samples were used for XPS measurements.

2.8 Measurements

¹H and ¹³C NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer. The metal concentrations were measured on an ICP-AES instrument (SPS5510, SII Nanotechnology Inc.). XPS measurements were conducted on an AXIS-ULTRA X-ray photoelectron spectrometer (Kratos Analytical Ltd.). The saturated concentrations of PA1 and PA2 in 0.1 M HCl were determined by UV absorption at 300 nm ($\epsilon = 4.25 \times 10^3$ and $7.55 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for PA1 and PA2, respectively).

3. RESULTS AND DISCUSSION

3.1 Synthesis of the precipitating agents

m-Phenylene diamine-containing compounds (i.e., PA1 and PA2) were synthesized following the procedure described previously (Scheme 1) [14] and used as new precipitating agents for PGMs. PA1 and PA2 were obtained in high yields by condensation of aniline or 4-phenoxyaniline with 3,5-bis(trifluoroacetamido)benzoyl chloride followed by deprotection via transamidation with hydrazine. Remarkably, PA1 and PA2 were obtained in a one-pot process without tedious purification steps (e.g., column chromatography). The simple synthesis and purification used herein to prepare the precipitating agents are advantageous for practical use.

Figure 1 shows the ¹H NMR spectra of PA1 and PA2. The characteristic signals derived from the amine and amide protons were observed, and all the aromatic proton signals were well

Scheme 1 Synthesis of *m*-phenylene diamine-containing agents.

 Figure 1 ^1H NMR spectra of **PA1** and **PA2** in $\text{DMSO}-d_6$.

assigned. In addition, the elemental analysis results supported the formation of the desired *m*-phenylene diamine-containing compounds. From these characterization data, we concluded that **PA1** and **PA2** were successfully synthesized.

PA1 and **PA2** were soluble in polar aprotic solvents such as DMAc and dimethyl sulfoxide (DMSO) as well as in aqueous HCl. The saturated concentrations of **PA1** and **PA2** in 0.1 M HCl at 20°C were 23.4 and 4.0 mg/mL, respectively. Since the metal separation experiments were carried out at **PA1** or **PA2** concentrations in 0.1 M HCl below 1.5 mg/mL, these compounds were completely soluble in the metal-containing HCl solution at the initial stage.

3.2 Precipitation behavior of Pd and Pt

The metal separation experiments using **PA1** and **PA2** were carried out as follows. To 0.1 M HCl solutions containing Pd(II) or Pt(IV) were added **PA1** or **PA2**, and the resulting mixtures were vigorously shaken. In the separation experiments, Pd and Pt were precipitated out as solid mixtures of metals and precipitating agents. The precipitation percentages of Pd and Pt were determined by ICP-AES analysis of the supernatants after the removal of the precipitates. A precipitation percentage of 100% indicates that all the metals were precipitated out from the metal-containing solutions by attaching on the dissolved precipitating agents. Figures 2 and 3 show the relationship between the metal precipitation and the precipitating agent feed ratios. **PA1** exclusively precipitated Pd under the studied conditions (Figures 2a and b). On the other hand, both Pd and Pt were precipitated using **PA2** (Figures 3a and b). Except in the case of Pt precipitation with **PA1**, the precipitation of Pd and Pt proportionally increased with the amount of the precipitating agents and reached 100% at ca. [precipitating agent]/

 Figure 2 Effect of the **PA1** loading on the precipitation of Pd (a) and Pt (b). Shaking time = 3 h.

 Figure 3 Effect of the **PA2** loading on the precipitation of Pd (a) and Pt (b). Shaking time = 3 h.

 Figure 4 Effect of the shaking time on the precipitation of Pd (a) and Pt (b) using **PA2**. **PA2**/Pd = 5 mol/mol and **PA2**/Pt = 5 mol/mol.

[metal] = 1.0 (mol/mol). This result clearly indicates that the precipitation of Pd and Pt were achieved via formation of metal-containing precipitates composed of metals and precipitating agents in equimolar amounts.

Figure 4 shows the time-dependence of the precipitation at **PA2**/metal = 5 (mol/mol) in 0.1 M HCl solutions. Pd was rapidly precipitated (within 10 min) with **PA2**. On the other hand, the precipitation of Pt with **PA2** reached a plateau after 3 h of shaking. This result revealed that the Pd-containing precipitates formed faster as compared to the Pt-containing solids.

3.3 Separation of Pd and Pt from base metals

In actual recovery processes, it is significantly important to separate PGMs from base metals such as Cu, Fe, Al, and Zn typically found in the leaching solution of scraps. The precipitation selectivities of Pd and Pt were examined using a HCl solution containing Cu(II), Fe(II), Al(III), and Zn(II) along with Pd(II) and Pt(IV). As shown in Table 1, **PA1** and **PA2** quantitatively precipitated Pd and/or Pt without dragging any of the base metals. It should be noted that the presence of the base metals produced no discernible impact on the precipitation behaviors of Pd and Pt. Thus, **PA1** selectively precipitated Pd in contrast to **PA2** that precipitated both Pd and Pt. Based on this result, we concluded that the precipitating agents used herein are feasible because of their high selectivity toward Pd and Pt in a base metal-containing solution.

3.4 Mutual separation of Pd and Pt

Based on the precipitation results mentioned above, **PA1** exclusively and selectively precipitated Pd, while **PA2** precipitated both Pd and Pt. Therefore, we attempted to separately precipitate Pd and Pt from a HCl solution containing both Pd and Pt as well as base metals by using **PA1** and **PA2** in combination. First, selective

Table 1 Precipitation of Pd and Pt from HCl solutions containing base metals.

Precipitating agent	Precipitation (%)					
	Pd(II)	Pt(IV)	Cu(II)	Fe(II)	Al(III)	Zn(II)
PA1	94.6	3.4	0.8	< 0.5	0.8	< 0.5
PA2	99.5	97.8	0.8	< 0.5	< 0.5	< 0.5

Table 2 Mutual separation of Pd and Pt from a HCl solution containing base metals.

Precipitation step	Precipitation (%)					
	Pd(II)	Pt(IV)	Cu(II)	Fe(II)	Al(III)	Zn(II)
1st	92.7	6.7	< 0.5	< 0.5	< 0.5	< 0.5
2nd	7.3	92.5	< 0.5	< 0.5	< 0.5	< 0.5

Pd precipitation from a mixed solution containing Pd, Pt, and base metals in 0.1 M HCl was performed using **PA1**. After the removal of the Pd-containing precipitates, Pt precipitation from the residual solution was carried out with **PA2**. As a result, Pd and Pt were selectively and efficiently precipitated in the first (92.7% for Pd and 6.7% for Pt) and second (7.8% for Pd and 92.5% for Pt) steps, respectively (Table 2). This process was advantageous in that the mutual separation of Pd and Pt was achieved without the need for any other additives except for **PA1** and **PA2** and without changing the solution conditions (e.g., acid concentration).

3.5 Study of the precipitation mechanism

It is known that Pd(II) and Pt(IV) form chloro-complexes (i.e., $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_6]^{2-}$) in aqueous HCl solutions [15,16]. The recovery mechanisms of metal chloro-complex anions are generally classified into two types: ligand-metal coordination and ion-pair formation. To discuss the recovery mechanism followed herein, we obtained the ^1H NMR spectra of **PA1** in water and 0.1 M HCl. The proton signals at 6.50 and 6.73 ppm were assigned to the aromatic protons of the *m*-phenylene diamine moiety in water down-field shifted in 0.1 M HCl by 1.17 and 1.22 ppm, respectively (Figure 5). These down-field shifts indicate that the two amine groups in the precipitating agents were transformed into ammonium cations in 0.1 M HCl. Since Pd, Pt, and the precipitating agents exist as ionic species under the studied conditions, an ion-pair formation mechanism between Pd and Pt chloro-complex anions and the precipitating agent cations was considered herein during the precipitation process. According to the data presented in Figures

Figure 5 ^1H NMR spectra of **PA1** in water and 0.1 M HCl.

2 and 3, the ion-pairs formed in the precipitation process were composed of one metal chloro-complex and one precipitating agent molecule. The equimolar stoichiometry of the ion-pair components fulfilled the charge-balanced conditions (i.e., one divalent anion and two monovalent cations). The selective precipitation of Pd and Pt from base metals was also explained via ion-pair formation since the base metal cations cannot form ion-pairs with the precipitating agent anions.

We analyzed the metal-containing precipitates generated in the precipitation process by XPS measurements with the aim to confirm the ion-pair forms. Figure 6a shows the XPS spectrum of the precipitate composed of Pd and **PA1**. The characteristic Pd3d and N1s peaks were observed and the N/Pd atomic ratio was calculated to be 2.88. Similarly, the precipitate composed of Pt and **PA2** showed the characteristic Pt4d and N1s peaks and a N/Pt atomic ratio of 2.97 (Figure 6b). These XPS results strongly supported the formation of ion-pairs consisting of one metal chloro-complex anion and one precipitating agent molecule which contains three N atoms. Therefore, we concluded that Pd and/or Pt can be precipitated using **PA1** and **PA2** via formation of ion-pairs composed of metal chloro-complexes (i.e., divalent anions) and precipitating agents (i.e., divalent cations) in a 1:1 stoichiometric ratio (Figure 7).

Although **PA2** achieved precipitation of both Pd and Pt, **PA1** exclusively precipitated Pd under the same conditions. The difference between the two precipitating agents is hydrophobicity, which is derived from their chemical structures. Thus, **PA1** is less hydrophobic than **PA2** because of the lower number of hydrophobic aromatic rings. This difference in the hydrophobicity of **PA1** and **PA2** was also confirmed by the different saturated

Figure 6 XPS spectra of Pd-containing (a) and Pt-containing (b) precipitates.

Figure 7 Proposed ion-pair structures composed of metal chloro-complex anions and precipitating agent cations.

concentrations in 0.1 M HCl of both agents. Thus, the solubility of **PA1** (23.4 mg/mL) was higher than that of **PA2** (4.0 mg/mL). The selective precipitation of Pd on **PA1** can be explained in terms of the hydrophobicity of the Pt chloro-complex–**PA1** ion-pair. Thus, the hydrophobicity of this ion-pair was not high enough to precipitate out of the HCl solution.

4 CONCLUSION

Two new precipitating agents, **PA1** and **PA2**, were successfully prepared in a one-pot process with high yields. The precipitation of Pd and Pt were studied using **PA1** and **PA2** as metal precipitants. While **PA1** exclusively precipitated Pd from a HCl solution containing Pd, Pt, and base metals, both Pd and Pt were precipitated from the same solution by using **PA2**. The precipitation tests performed by varying the loadings of the precipitating agents revealed that the metal-containing precipitates were composed of chloro-complex anions ($[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$) and precipitating agents in equimolar amounts. The stoichiometric ratio of the ion-pairs was in good agreement with the atomic ratios estimated by XPS. Since the precipitation mechanism followed herein was ion-pair formation, the precipitating agent cations only precipitated chloro-complex anions of Pd and Pt in the absence of base metal cations. The different hydrophobicity of the precipitating agents allowed mutual separation of Pd and Pt.

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