Selective and Mutual Separation of Palladium (II), Platinum (IV), and Rhodium (III) Using Aliphatic Primary Amines

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Abstract: The selective recovery of platinum-group metals (PGMs) remains a huge challenge. Although solvent extraction processes are generally used for PGM separation, the use of organic solvents is problematic because of their toxicity and environmental concerns. Here, we have developed a new PGM recovery method by precipitation from hydrochloric acid (HCl) solutions containing Pd(II), Pt(IV), and Rh(III) using aliphatic primary amines as precipitants. Pt(IV) was precipitated using the amines with alkyl chains longer than hexyl independent of HCl concentration. The precipitation of Pd(II) required longer alkyl amines than octyl, regardless of the HCl concentration. Rh(III) was recovered by precipitation at high HCl concentrations using the amines longer than hexyl. The mutual separation of Pt(IV), Rh(III), and Pd(II), in this order, was successfully achieved by changing the HCl concentrations and alkyl chain lengths of the amines. X-ray photoelectron spectroscopy and thermogravimetric analysis evidently showed that the metal-containing precipitates were ion-pair complexes composed of metal chloro-complex anions and ammonium cations.

Keywords: platinum-group metal; metal precipitation; ion-pair; aliphatic primary amine; hydrochloric acid

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1. Introduction

Platinum-group metals (PGMs), particularly Pd, Pt, and Rh, are of crucial importance because of their wide range of applications, such as automobile catalysts and electrical devices [1–5]. Despite the increasing demand for PGMs, their availability remains limited due to their scarcity in Nature and regional maldistribution. Therefore, efficient recovery and separation processes are necessary to recycle PGMs from post-consumer scrap. Typically, solvent extraction is regarded as a practical method to recover and separate PGM ions from metal-containing aqueous solutions. For example, tertiary amines [6,7], organophosphates [8–11], and organosulfides [12,13] have been reported to act as Pd(II) or Pt(IV) extractants. However, solvent extraction processes require organic solvents, which are used as diluents of extractants or extractants themselves, and the use of organic solvents is problematic because of their toxicity and environmental concern. Furthermore, the selective recovery of PGMs remains a massive challenge due to the similarity in their properties.

The recovery mechanisms of PGMs by solvent extraction are generally classified into two types, namely, ligand-metal coordination and ion-pair formation [14]. For the coordination mechanism, metal extraction generally occurs in the order of Pd(II) >> Rh(III) >> Pt(IV); and Rh(III) and Pt(IV) are regarded as kinetically inert [15]. Furthermore, the order of extractability via ion-pair formation for the PGM chloro-complexes formed in an aqueous hydrochloric acid (HCl) solution is reported to

be $[MCl_4]^{2-} \cong [MCl_6]^{2-} > [MCl_6]^{3-} >$ aqua species [16]; while the chloro-complex anions of PGMs formed in HCl are reported to be $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[RhCl_6]^{3-}$, as well as the chloro-aqua complexes of Rh(III) ($[RhCl_4(H_2O)_2]^-$ and $[RhCl_5(H_2O)]^{2-}$) [14]. Therefore, the extractability of PGMs in ligand-metal coordination and ion-pair formation evidently indicates the difficulty in the selective recovery of Pt(IV) in priority to Pd(II) as well as the Rh(III) recovery in advance of Pd(II) and Pt(IV) by conventional solvent extractions.

Recently, we developed PGM recovery methods based on precipitation using aromatic primary amines as precipitants [17–20]. The selective precipitation of Pt(IV) from HCl solutions containing Pd(II) and Pt(IV) was successfully achieved using 4-hexyloxyaniline at high HCl concentrations [17]. Furthermore, the preferential and selective Rh(III) recovery from the mixture of Pd(II), Pt(IV), and Rh(III) in HCl was successfully accomplished using aromatic primary monoamines [18] or diamines [19,20] as precipitants. The successful precipitation of Rh(III) was achieved based on the formation of unique ion-pair complexes comprising $[RhCl_6]^{3-}$ and anilinium cations of the amines. Although the potential of aromatic primary amines for PGM precipitants has been revealed, studies on the capability of aliphatic primary amines for PGM precipitants, as well as PGM extractants have been limited. Therefore, investigations of the availability of aliphatic primary amines for PGM recycling are valuable in the viewpoint of recycling industry.

Herein, we present a new PGM separation method by precipitation from the mixed solution of Pd(II), Pt(IV), and Rh(III) in HCl using aliphatic primary amines as precipitants. Preferential and selective precipitation of Pt(IV) at low HCl concentrations was achieved using *n*-heptylamine and *n*-octylamine. Moreover, Rh(III) was recovered by precipitation in preference to Pd(II) at high HCl concentrations using *n*-heptylamine and *n*-octylamine. Thereafter, we successfully achieved the mutual separation of Pt(IV), Rh(III), and Pd(II) in this order by changing the HCl concentrations and the alkyl chain lengths of the amines. The mechanism of the selective precipitation of PGMs was studied by the analysis of the metal-containing precipitates.

2. Materials and Methods

2.1. Materials

n-Hexylamine, *n*-heptylamine, *n*-octylamine, *n*-nonylamine, *n*-decylamine, and *n*-dodecylamine were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used as received. Pd(II) and Pt(IV) standard solutions were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. Rh(III) standard solution was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used as received.

2.2. Metal Precipitation Experiments from Metal-Containing Solutions

To HCl solutions (1 mL) containing Pd(II), Pt(IV), and Rh(III) (1.0 mM each) were added aliphatic primary amine (0.05 mmol) and the mixtures were shaken vigorously for 30 min at room temperature. After centrifugation ($7200 \times g$, 10 min), the metal concentration in the supernatant was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Hitachi High-Tech Science Corp., Tokyo, Japan). The used aliphatic primary amines and the HCl concentrations were changed in the metal precipitation experiments.

The metal precipitation experiments from single metal-containing solutions (Pd(II), Pt(IV), or Rh(III): 1.0 mM, 6.0 M HCl) using *n*-nonylamine were performed by the similar procedure described above. The amount of *n*-nonylamine and the shaking time were changed in the metal precipitation experiments.

2.3. Mutual Separation of Pd(II), Pt(IV), and Rh(III)

To a 4 mL of 1.0 M HCl solution containing Pd(II), Pt(IV), and Rh(III) (1.0 mM each) was added *n*-octylamine (0.2 mmol) and the mixture was shaken vigorously for 30 min at room temperature. After

centrifugation (7200× *g*, 10 min), the metal concentration in the supernatant was determined by ICP-AES. Then, an 11 M HCl solution was added to the supernatant to yield a 6.0 M HCl solution containing Pd(II) and Rh(III) (ca. 0.5 mM each). To the resulting solution (4 mL) was added *n*-octylamine (0.05 mmol) and the mixture was shaken vigorously for 30 min at room temperature. After centrifugation (7200× *g*, 10 min), the metal concentration in the supernatant was determined by ICP-AES. Then, to the resulting supernatant (2 mL) was added *n*-decylamine (0.1 mmol) and the mixture was shaken vigorously for 30 min at room temperature. After centrifugation (7200× *g*, 10 min), the metal concentration in the supernatant was determined by ICP-AES.

2.4. Isolation of Metal-Containing Precipitate

To 10 mL of 6.0 M HCl solutions containing Pd(II), Pt(IV) or Rh(III) (2.0 mM) were added *n*-nonylamine (0.2 mmol, for Pd(II)) or *n*-octylamine (0.2 mmol, for Pt(IV) and Rh(III)) and the mixtures were vigorously shaken for 30 min at room temperature. The resulting solid was collected by filtration and washed five times with a 6.0 M HCl solution. The solid was dried at room temperature for 48 h under vacuum. The Rh(III)-containing precipitate using *n*-octylamine from a 2.0 M HCl solution was prepared in the similar manner.

2.5. Measurements

An ICP-AES instrument (SPS5510, Hitachi High-Tech Science Corp., Tokyo, Japan) was used for the metal concentration measurements. X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS-ULTRA X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, UK). Element quantification was performed using the relative sensitivity factors supplied with the instrument control software (N 1 s: 0.477, Cl 2 s: 0.493, Pd 3d: 5.356, Pt 4d: 4.637, Rh 3d: 4.822). Thermogravimetric measurements were carried out using a STA7300 (Hitachi High-Tech Science Corp., Tokyo, Japan) at a heating rate of 10 °C/min under air flow (200 mL/min).

3. Results and Discussion

3.1. Metal Precipitation Experiments

The metal recovery experiments from the mixture of Pd(II), Pt(IV), and Rh(III) in HCl were carried out using aliphatic primary amines as metal precipitants. The aliphatic primary amines used herein have linear-chain alkanes (from hexyl to dodecyl). The precipitation percentages of the metals were determined by ICP-AES analysis of the supernatants after centrifugation. Figure 1a–e shows the relationship between the precipitation of metals and HCl concentration. *n*-Hexylamine, which has the shortest alkyl chain in this study, did not work as a precipitant for Pd(II), Pt(IV), and Rh(III) regardless of the HCl concentrations (i.e., no precipitation); however, *n*-heptylamine and *n*-octylamine precipitated most of Pt(IV) (over 80% except for *n*-heptylamine in 1.0 M HCl) in a wide range of HCl concentrations (1.0–8.0 M), whereas Pd(II) precipitation was below 5%. Notably, Rh(III) precipitation occurred using the aliphatic amines except for *n*-hexylamine at HCl concentrations exceeding 1.0 M, and the precipitation percentages increased with the HCl concentrations, resulting in precipitation percentages exceeding 80% at high HCl concentrations (> 4 M HCl). Thus, *n*-heptylamine and *n*-octylamine exclusively precipitated Pt(IV) in a 1.0 M HCl solution, while both Pt(IV) and Rh(III) were co-precipitated at higher HCl concentrations. The use of *n*-nonylamine, *n*-decylamine, and *n*-dodecylamine enabled the efficient precipitation of Pd(II) and Pt(IV) (over 80%) in the studied HCl concentrations. Moreover, the precipitation of Rh(III) increased with the HCl concentrations and exceeded 90% at high HCl concentrations (> 4 M HCl). Thus, *n*-nonylamine, *n*-decylamine, and *n*-dodecylamine can recover Pd(II), Pt(IV), and Rh(III) as precipitates in high yields at high HCl concentrations. These results evidently show that the HCl concentration did not particularly affect the precipitation behavior of Pd(II) and Pt(IV) irrespective of the used amine, whereas Rh(III) precipitation increased with the concentration of HCl. Figure 2a,b shows the effect of the alkyl chain length on

metal precipitation in 1.0 M HCl and 6.0 M HCl solutions. The precipitation of Pd(II) required a longer alkyl length than octyl in both 1.0 M HCl and 6.0 M HCl solutions, while the Pt(IV) precipitation occurred using amines with alkyl chains longer than hexyl in both 1.0 M HCl and 6.0 M HCl solutions. The precipitation percentages of Pt(IV) increased in proportion to the length of the alkyl chain and reached approximately 100% at octyl in 1.0 M HCl solutions, while high Pt(IV) precipitation percentages over 80% were achieved using the alkyl amines longer than hexyl in 6.0 M HCl solutions. For the Rh(III) precipitation, the precipitation percentages gradually increased with the length of the alkyl chain and reached 50% by using *n*-dodecylamine in 1.0 M HCl solutions. The percentages of Rh(III) precipitation in 6.0 M HCl solutions exceeded 60% by using the alkyl amines longer than hexyl, although those in the 1.0 M HCl solutions were below 10% except for when *n*-dodecylamine was used. It is noteworthy that a near-quantitative recovery of Rh(III) as precipitates was achieved when the amines had long alkyl chains and the concentration of HCl was high. Furthermore, the metal-containing precipitates obtained in this study were easily collected by filtration.
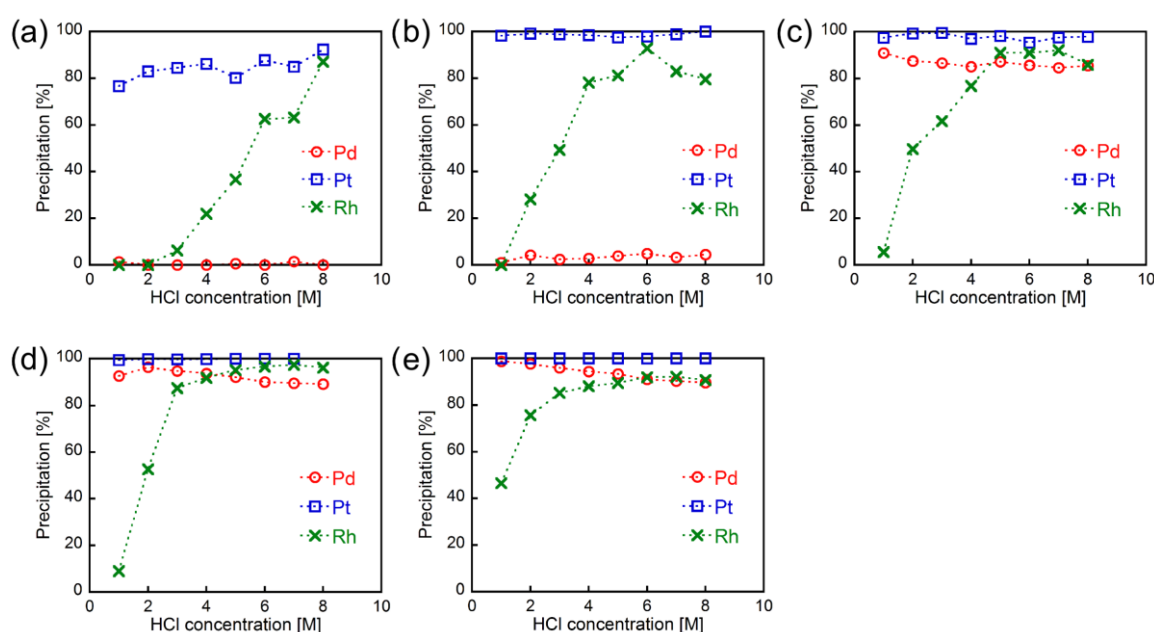

Figure 1. Metal precipitation from HCl solutions containing Pd(II), Pt(IV), and Rh(III) (each at 1 mM) using (**a**) *n*-heptylamine, (**b**) *n*-octylamine, (**c**) *n*-nonylamine, (**d**) *n*-decylamine, and (**e**) *n*-dodecylamine (amine: 50 mM, 30 min of shaking).
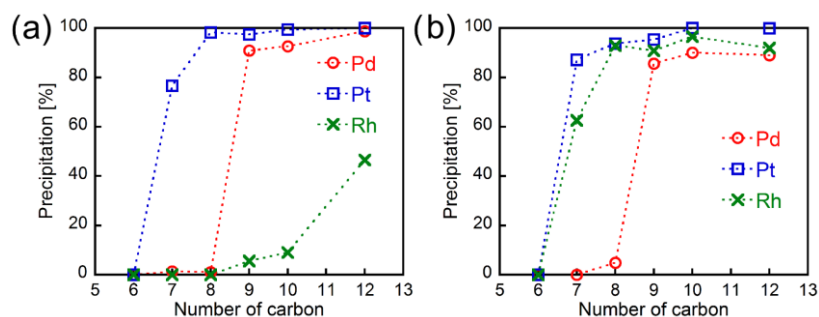

Figure 2. Relationship between metal precipitation and alkyl chain length of the amine in (**a**) 1.0 M HCl solutions and (**b**) 6.0 M HCl solutions (metal: 1 mM each, amine: 50 mM, 30 min of shaking).

3.2. Loading Amount and Shaking Time

The dependence of the metal precipitation percentages on the loading amount of *n*-nonylamine was investigated using 6.0 M HCl solutions containing individual metals (Pd(II), Pt(IV), and Rh(III)).

We selected *n*-nonylamine as a typical example because it can precipitate all the three PGMs as shown in Figure 1c. The precipitation percentages of each metal increased with the loading amount of *n*-nonylamine and reached a plateau at [*n*-nonylamine]/[metal] = 10 (mol/mol) when the single metal-containing solutions were used (Figure 3a). There was no significant difference in the precipitation behavior among the three metals.
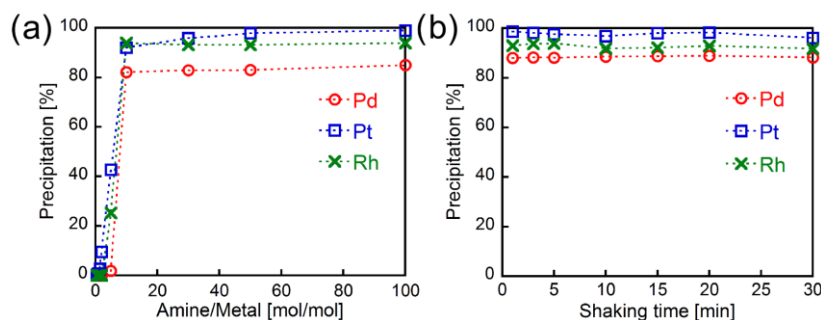

Figure 3. The effect of (**a**) *n*-nonylamine loading (30 min of shaking) and (**b**) shaking time on the metal precipitation (amine/metal = 50 mol/mol) from 6.0 M HCl solutions containing 1 mM individual metals (Pd(II), Pt(IV), and Rh(III)).

The effect of the shaking time on metal precipitation was also examined in the condition of [*n*-nonylamine]/[metals] = 50 (mol/mol) in 6.0 M HCl solutions containing individual metals (Pd(II), Pt(IV), and Rh(III)). Surprisingly, the precipitation percentages of the metals reached a maximum after shaking for 1 min (Figure 3b). This result clearly shows that PGM recovery by precipitation using aliphatic amines can be speedily completed.

3.3. Mutual Separation of Pd(II), Pt(IV), and Rh(III)

Based on the metal precipitation results relating to varying alkyl chain lengths and HCl concentrations, we performed a mutual separation of Pd(II), Pt(IV), and Rh(III) from a metal-mixed HCl solution. In the first precipitation step, *n*-octylamine was used as a precipitant because it can selectively precipitate Pt(IV) from 1.0 M HCl solutions (Figure 1b). As a result, Pt(IV) was recovered using *n*-octylamine from a 1.0 M HCl solution containing Pd(II), Pt(IV), and Rh(III) (1 mM each). Then, the HCl concentration of the resulting solution (Pd, Rh: 1 mM each, 1.0 M HCl) increased by adding an 11 M HCl solution and the 6.0 M HCl solution (Pd, Rh: 0.5 mM each) was obtained. In the second precipitation step, *n*-octylamine was added to the metal-containing 6.0 M HCl solution, and Rh(III) was recovered by precipitation. In the third precipitation step, the remaining Pd(II) was recovered using *n*-decylamine as a precipitant. As shown in Figure 4, each target metal is recovered as a precipitate over 75%, and co-precipitation of other metals is suppressed below 10%. Generally, Pt(IV) recovery in preference to Pd(II) is difficult according to the order of the PGM extractability [15,16]. Furthermore, Rh(III) in HCl cannot be extracted in preference to Pd(II) and Pt(IV) using conventional solvent extraction methods [14–16]. However, we achieved a mutual separation of Pt(IV), Rh(III), and Pd(II) in this order using aliphatic primary amines by changing the HCl concentration and alkyl chain length.

3.4. XPS Analysis of Metal-Containing Precipitates

XPS measurements of the metal-containing precipitates were carried out to analyze elemental composition. The precipitates were prepared by adding *n*-nonylamine (for Pd(II)) or *n*-octylamine (for Pt(IV) and Rh(III)) to the 6.0 M HCl solutions containing individual metals (Pd(II), Pt(IV), and Rh(III)). Prior to the measurements, the precipitates were washed with HCl to remove excess amine. The characteristic XPS peaks assigned to the Pd 3d, Pt 4d, and Rh 3d were observed for the Pd-, Pt-, and Rh-containing precipitates, respectively (Figure 5a–c). Furthermore, the peaks attributed

to the N 1s, C 1s, Cl 2s, and Cl 2p were also observed for all the three samples. The N:Cl:metal atomic ratios were calculated from the photoelectron peak areas using the atomic sensitivity factors. The atomic ratios (N:Cl:metal) were calculated to be 2.0:3.9:1.0 (Pd-containing precipitate), 2.0:6.1:1.0 (Pt-containing precipitate), and 6.0:9.1:1.0 (Rh-containing precipitate) (Figure 5a–c). Pd(II) and Pt(IV) exist as chloro-complex anions, $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$, in HCl solutions [14]. Since the aliphatic amines used herein form ammonium cations in HCl, the metal-containing precipitates will be the ion-pairs composed of metal chloro-complex anions and ammonium cations. The atomic ratios calculated from the XPS data are consistent with the expected composition of the Pd- and Pt-containing precipitates, as shown in Figure 6a,b. For Rh(III), the predominant species of Rh in 6.0 M HCl is $[RhCl_6]^{3-}$ [21]. Recently, we reported that aromatic primary amines selectively form Rh-containing precipitates comprising anilinium cation/chloride anion/$[RhCl_6]^{3-}$ at a 6:3:1 ratio (N:Cl:Rh = 6:9:1) [18]. The XPS result indicates that aliphatic primary amines also form unique ion-pair complexes composed of ammonium cation/chloride anion/$[RhCl_6]^{3-}$ in a 6:3:1 ratio (Figure 6c).
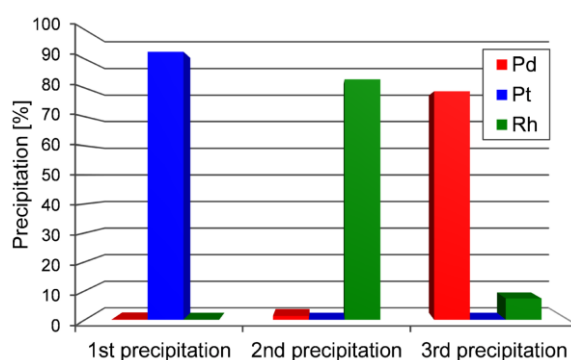

Figure 4. Mutual separation of Pd(II), Pt(IV), and Rh(III) from a 1.0 M HCl solution containing Pd(II), Pt(IV), and Rh(III) (1 mM each).
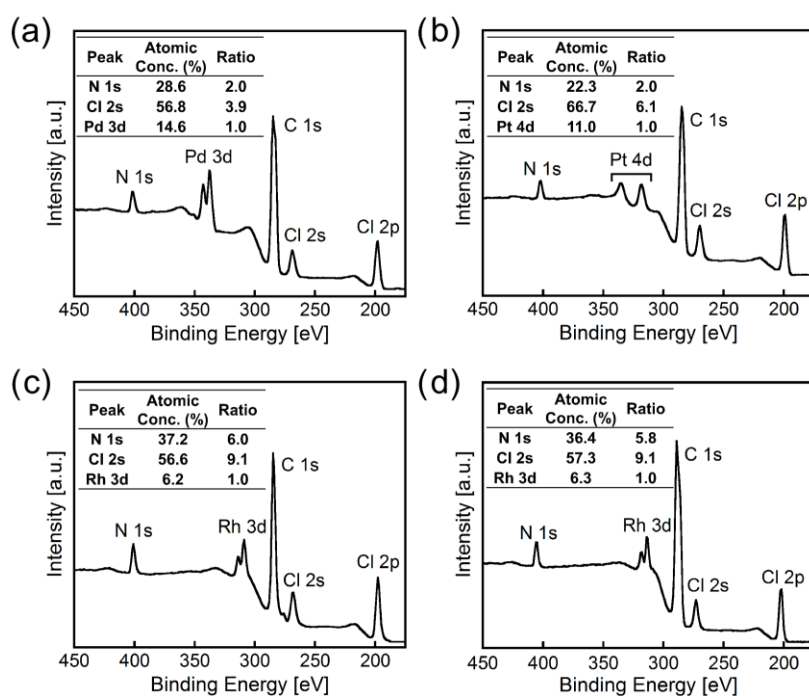

Figure 5. XPS spectra of the precipitates of (**a**) Pd(II) with *n*-nonylamine, (**b**) Pt(IV) with *n*-octylamine, and (**c**) Rh(III) with *n*-octylamine prepared from 6.0 M HCl solutions, and (**d**) the precipitate of Rh(III) with *n*-octylamine prepared from a 2.0 M HCl solution.
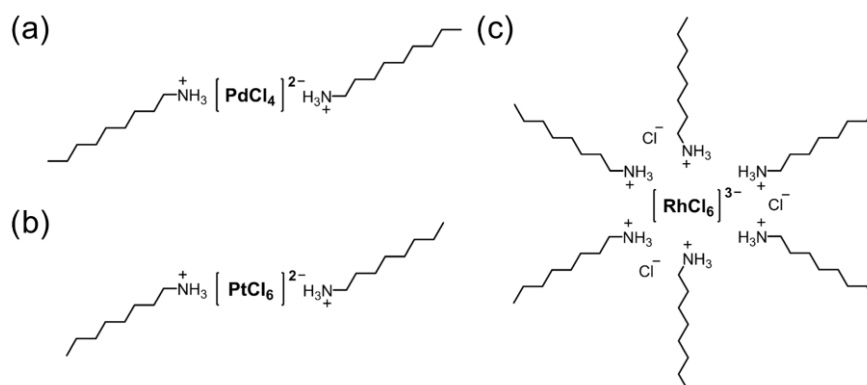
Figure 6. Expected chemical structures of the ion-pair complexes of (**a**) Pd(II) with *n*-nonylamine, (**b**) Pt(IV) with *n*-octylamine, and (**c**) Rh(III) with *n*-octylamine.

3.5. Thermogravimetric Analysis of Metal-Containing Precipitates

The ratios of metals and aliphatic primary amines in the metal-containing precipitates were also examined by thermogravimetric analysis (TGA). The precipitates used for the evaluation were prepared using *n*-nonylamine (for Pd(II)) or *n*-octylamine (for Pt(IV) and Rh(III)) and individual metal-containing 6.0 M HCl solutions. The weight loss observed in the range of 200–500 °C for all the three samples is attributed to the decomposition and volatilization of amines and chlorine (Figure 7a–c). The residual weights of Pd-, Pt-, and Rh-containing precipitates after heating at 750 °C were found to be 22.5%, 28.7%, and 10.3%, respectively. $PdCl_2$, $PtCl_4$, and $RhCl_3$ form Pd oxide (PdO), zerovalent Pt, and Rh oxide (Rh_2O_3) after combustion below 800 °C, respectively [22]. The expected weight fractions after the combustion of ion-pair complexes shown in Figure 6a–c are consistent with the experimental results of the TGA, as summarized in Table 1. The TGA results strongly support that the metal-containing precipitates consist of the ion-pairs depicted in Figure 6a–c.
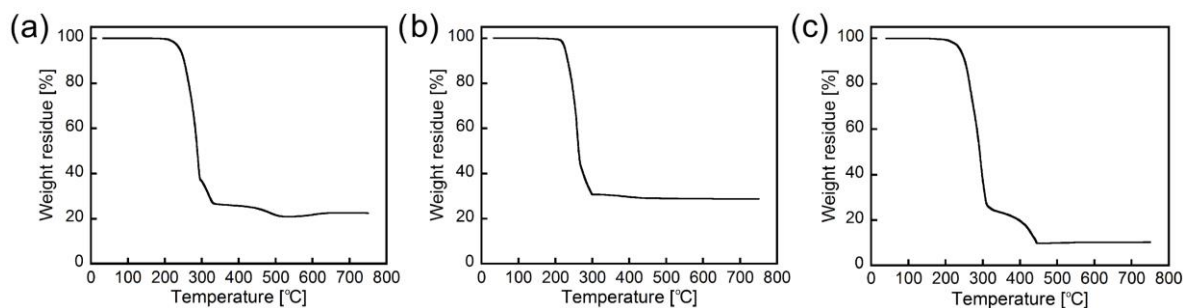

Figure 7. TG curves of the precipitates of (**a**) Pd(II) with *n*-nonylamine, (**b**) Pt(IV) with *n*-octylamine, and (**c**) Rh(III) with *n*-octylamine at a heating rate of 10 °C/min under air flow (200 mL/min).

Table 1. Weight fractions after the combustion of the precipitates.

Metal	Ash at 750 °C [a]	Expected Weight Fraction [b]
Pd(II)	22.8%	22.5%
Pt(IV)	28.7%	29.2%
Rh(III)	10.3%	10.5%

[a] Weight fractions of ash after TGA shown in Figure 7. [b] Expected weight fractions after combustion of ion-pair complexes shown in Figure 6.

3.6. Metal Precipitation Behavior

Figure 2a,b show that the metal precipitation of Pd(II) highly depends on the alkyl chain length of the amines. Since all the amines used herein are primary and have linear alkane chains, there is

no difference in the properties of their amine groups, such as electron density and proton affinity. Therefore, the difference among the amines is only their hydrophobicity, i.e., their solubility in HCl. It is assumed that the hydrophobicity of the short alkyl amines (hexyl, heptyl, and octyl) is insufficient to precipitate the ion-pair composed of one Pd chloro-complex anion ($[PdCl_4]^{2-}$) and two ammonium cations, whereas Pt(IV) can be recovered as precipitates using the alkyl amines longer than hexyl. To investigate the difference in the solubility of the metal-containing precipitates, the saturating concentrations were measured for the ion-pairs composed of $[PdCl_4]^{2-}$ or $[PtCl_6]^{2-}$ and *n*-octylammonium cations. The ion-pairs were prepared by evaporating the 1:2 (mol/mol) mixed solution of the metal chloro-complex anions and *n*-octylamine in 1.0 M HCl solutions. The saturating concentrations of the Pd- and Pt-containing ion-pairs in 6.0 M HCl were 5.6 and 0.94, respectively. This result clearly shows that the hydrophilicity of the Pd-containing ion-pairs is higher than that of the Pt-containing ones. Consequently, the amines with alkyl chains longer than octyl are necessary to form Pd-containing precipitates. The difference in the solubility of the Pd- and Pt-containing ion-pairs is derivable from the difference in the number of Cl: the Pd-containing ion-pair possessing only four Cl would be less hydrophobic than the Pt-containing one with six Cl.

The precipitation percentages of Rh(III) increase with the HCl concentrations, although those of Pd(II) and Pt(IV) are quite independent of the HCl concentrations. Rh(III) forms several anion species in HCl, such as $[RhCl_4(H_2O)_2]^-$, $[RhCl_5(H_2O)]^{2-}$, and $[RhCl_6]^{3-}$, and the abundance ratio of $[RhCl_6]^{3-}$ increases with HCl concentrations [18,20,21]. For example, $[RhCl_6]^{3-}$ dominantly exists in 6.0 M HCl ($[RhCl_6]^{3-}$: 91%) [18,20]. From the results of the XPS and TGA of the Rh-containing precipitate using a 6.0 M HCl solution, $[RhCl_6]^{3-}$ is precipitated to form an ion-pair complex shown in Figure 6c. Therefore, we assumed that the preferential precipitation of $[RhCl_6]^{3-}$ occurred independently of the HCl concentrations by the ion-pair formation. To examine the precipitated Rh species, the XPS measurement was carried out for the precipitate formed by adding *n*-octylamine to a Rh-containing 2.0 M HCl solution. From the XPS spectrum of the precipitate composed of *n*-octylamine and Rh, the atomic ratio of N:Cl:Rh was calculated to be 5.8:9.1:1.0, indicating that the Rh-containing precipitate prepared from a 2.0 M HCl solution had the same composition as that from a 6.0 M HCl solution (Figure 5d). Since the distribution of the Rh species in 2.0 M HCl is reported to be 78% of $[RhCl_5(H_2O)]^{2-}$ and 8% of $[RhCl_6]^{3-}$ [18,20], the XPS result evidently shows the selective precipitation of $[RhCl_6]^{3-}$ in 2.0 M HCl using *n*-octylamine. The precipitation percentage of Rh(III) in 2.0 M HCl using *n*-octylamine (28%) was higher than the abundance ratio of $[RhCl_6]^{3-}$ (8%), which would be consequent of an equilibrium shift from $[RhCl_4(H_2O)_2]^-$ and $[RhCl_5(H_2O)]^{2-}$ to $[RhCl_6]^{3-}$. The precipitation behavior of Rh(III) using aliphatic primary amines is similar to that using 4-alkylanilines [18]. On the other hand, only aliphatic primary amines can precipitate Pd(II) and Pt(IV) even at high HCl concentrations: 4-alkylanilines do not form Pd(II)- and Pt(IV)-containing precipitates at high HCl concentrations (> 5 M HCl). Although 4-alkylanilines are advantageous from the viewpoint of Rh(III)-selective precipitation, aliphatic primary amines have the advantages of the capability in the mutual separation of Pd(II), Pt(IV), and Rh(III) as well as in the recovery by precipitation of Pd(II) and Pt(IV) at high HCl concentrations.

4. Conclusions

The recovery of Pd(II), Pt(IV), and Rh(III) by precipitation was achieved using aliphatic primary amines with linear-chain alkanes as precipitants. Pt(IV) was precipitated using the amines with alkyl chains longer than hexyl independent of HCl concentration, while the precipitation of Pd(II) required the longer alkyl amines than octyl, regardless of the HCl concentration. However, Rh(III) was recovered by precipitation at high HCl concentrations using amines longer than hexyl. The mutual separation of Pt(IV), Rh(III), and Pd(II), in this order, was successfully achieved by changing the HCl concentrations and alkyl chain lengths of the amines. XPS and TGA results clearly showed that the metal-containing precipitates are ion-pair complexes composed of metal chloro-complex anions and ammonium cations. It is noteworthy that Rh(III) formed a unique ion-pair complex comprising ammonium cations of

aliphatic amines/chloride anions/$[RhCl_6]^{3-}$ = 6:9:1. This PGM precipitation method, using aliphatic primary amines, is a promising application in the PGM recycling.

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