Platinum group metals (PGMs) are industrially important elements because of their extensive use in electrical devices, dental materials, catalysts, and jewelry. Currently, rhodium (Rh) is the most expensive PGM and is mainly used in automotive catalysts alongside palladium (Pd) and platinum (Pt). The recycling of PGMs from secondary sources is in high demand, and the preferential and selective separation of Rh from PGM mixtures remains a great challenge. Here, a selective Rh separation method involving the precipitation of Rh from an HCl solution containing palladium (Pd), platinum (Pt), and Rh is reported. 4-Butylaniline and 4-hexylaniline were used as precipitants for Rh, and selective Rh precipitation was achieved at high HCl concentrations. We revealed that Rh in HCl selectively forms a unique and highly stable ion-pair complex comprising [RhCl6]3−/anilinium/chloride ions in a 1:6:3 ratio. The formation and high stability of the Rh complex were found to play important roles in the selective recovery of Rh from PGM mixtures.
RESULTS AND DISCUSSION

Precipitation Behavior of Rh(III). An overview of the metal separation experiments is shown in Figure 1. The precipitant, 4-butylaniline or 4-hexylaniline, was added to HCl solutions containing Pd(II), Pt(IV), and Rh(III) (1.0 mmol/L each), and then the mixtures were vigorously shaken. The precipitates formed in the mixtures were separated by centrifugation, and the percentages of the metals in the precipitates were evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) of the supernatant. Figure 2a,b shows the relationship between the metal precipitation percentages and the HCl concentrations. 4-Butylaniline was hardly able to precipitate Pd and Pt (<10%) in a wide range of HCl concentrations (1–8 M). On the other hand, it was observed that Rh was successfully precipitated and that the Rh precipitation percentages increased upon an increase in the HCl concentration. 4-Hexylaniline was also used as a metal precipitant. Most of Pd and Pt (>90%) were precipitated using 4-hexylaniline in 1–2 M HCl, and their precipitation percentages were found to drastically decrease upon an increase in the HCl concentration. In contrast, over 85% of Rh in the solutions was precipitated at high HCl concentrations (3–8 M).

As a result, a high Rh precipitation of over 85% and a high Rh selectivity (the Pd and Pt precipitation was <5%) were achieved at high HCl concentrations (6–8 M) using either 4-butylaniline or 4-hexylaniline as the precipitant. As shown in Figure 1, the resulting precipitate in 8 M HCl has a pinkish color, which corresponds to the color of the HCl solution of Rh(III).

In order to optimize the Rh precipitation conditions, metal precipitation experiments using 8 M HCl solutions were performed by changing the loading amounts of 4-alkylanilines used and the shaking time. The precipitation percentages of Rh after 3 h of shaking were observed to increase upon an increase in the 4-alkylaniline loading and reached a plateau at 4-butylaniline/Rh and 4-hexylaniline/Rh molar ratios of 20:1 and 9:1, respectively (see Figures 2c and S1 in the Supporting Information). In contrast, the precipitation percentages of Pd and Pt were found to be consistently below 5%, even at a high 4-alkylaniline/Rh molar ratio of 50:1. The optimized ratio of 4-alkylaniline/Rh for the Rh precipitation seems to depend on the hydrophobicity of 4-alkylanilines; the use of a smaller amount of 4-hexylaniline than 4-butylaniline results in the precipitation of more Rh. The effect of the shaking time on the metal precipitation was also investigated under the conditions with a 4-hexylaniline/Rh molar ratio of 30:1 in 8 M HCl (Figure 2d). The Rh precipitation was completed after just 10 min of shaking. Furthermore, the composition of the precipitated metals remained unaltered and was found to be independent of the shaking time.

Characterization of the Rh-Containing Precipitate. To elucidate the structure of the Rh-containing precipitate, single-crystal X-ray structure analysis was performed. Single crystals were prepared by the slow evaporation of a 1 M HCl solution of the precipitate prepared from a Rh-containing 8 M HCl and 4-hexylaniline solution. The structure determination revealed that six anilinium cations surround each Rh chloro-complex anion ([RhCl₆]₃⁻) and three chloride anions coexist to balance the total charge (see Figure 3a,b and the Supporting Information). Each anilinium cation faces a triangular face of the [RhCl₆]₃⁻ octahedron, and the distance between each anilinium cation and central Rh atom is almost constant at Rh···N 3.99–4.04 Å. In other words, one [RhCl₆]₃⁻ complex anion forms an ion-pair complex with six anilinium cations and three chloride anions.

Figure 1. Scheme of the experiments on Rh precipitation from HCl solutions containing Pd, Pt, and Rh. The photographs show the procedure under the following experimental conditions: 8 M HCl, 4-butylaniline/Rh molar ratio of 30:1, and 3 h of shaking.

Figure 2. Metal precipitation from HCl solutions containing Pd, Pt, and Rh (each at 1 mM) and the effect of HCl concentration on the metal precipitation using (a) 4-butylaniline and (b) 4-hexylaniline (amine/Rh molar ratio of 30:1, 3 h of shaking). (c) Effect of 4-hexylaniline loading on the metal precipitation (8 M HCl, 3 h of shaking). (d) Effect of the shaking time on the metal precipitation using 4-hexylaniline (8 M HCl, 4-hexylaniline/Rh molar ratio of 30:1).

Figure 3. (a,b) Crystal structure of the Rh-containing precipitate with 4-hexylaniline. (c) Chemical structure based on the single-crystal structure of the Rh-containing precipitate with 4-hexylaniline.
This result was not anticipated, as the trivalent $[\text{RhCl}_6]^{3-}$ anion is generally expected to form an ion-pair complex with three anilinium cations in terms of charge balance. To the best of our knowledge, this is the first report on unique ion-pair formation between Rh, anilinium, and chloride ions in the form of $[\text{RhCl}_6]^{3-}$/anilinium/chloride ions in a 1:6:3 ratio.

In order to determine whether the structure of the bulk Rh-containing precipitate was the same as its single-crystal structure or not, powder X-ray diffraction measurements were performed in the 2θ range of $5^\circ$–$25^\circ$ on a pristine precipitate prepared from 8 M HCl using 4-hexylaniline. As shown in Figure 4a, all of the peaks present in the measured patterns closely match the simulated pattern generated from the single-crystal diffraction data. This result indicates that the bulk pristine precipitate is made up of aggregated microcrystals comprising $[\text{RhCl}_6]^{3-}$/anilinium/chloride ions in a 1:6:3 ratio. The formation of the 1:6:3 complex in the bulk precipitate was further supported by thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopic (XPS) analysis. In the TGA, a weight loss was observed in the range of 150–480 °C because of the decomposition and volatilization of 4-hexylaniline and chloride, and the amount of ash at 750 °C was found to be 8.6% (Figure 4b). It is known that the combustion of RhCl$_3$ in an oxidative atmosphere yields Rh$_2$O$_3$ below a temperature of 900 °C. The expected weight fraction of Rh$_2$O$_3$ after combustion of the 1:6:3 complex was calculated to be 8.5%, which corresponds to the actual weight residue of the pristine precipitate measured.

XPS measurement was performed on the pristine precipitate, and the XPS spectrum was found to exhibit N 1s, Rh 3d, C 1s, and Cl 2p signals, indicating that the precipitate is a complex made up of Rh and 4-hexylaniline (Figure 4c). The N/Cl/Rh atomic ratio calculated from the XPS peaks was 6.1:8:8:1.0, which confirmed that the Rh-containing precipitate comprises one $[\text{RhCl}_6]^{3-}$ complex ion, six anilinium cations, and three chloride ions, in good agreement with the results of the powder X-ray diffraction measurements. The elemental analysis result of the pristine precipitate was also found to support the formation of a 1:6:3 complex (Table 1). It is noteworthy that the same unique complex with the same ratio of ions also formed when 4-butylaniline was used as the precipitant (see Figure S2 in the Supporting Information). This means that various aromatic primary amines have possibilities of working as Rh precipitants based on the formation of the unique Rh complexes.

**Effect of the Structure of Rh Chloro-Complex Anions.**

It is well-known that Rh(III) forms chloro-complex anions such as $[\text{RhCl}_4(\text{H}_2\text{O})]^{-2}$, $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, and $[\text{RhCl}_6]^{3-}$ in HCl solutions and that their compositions change according to the HCl concentration used. The distribution of Rh chloro-complex anions in various HCl concentrations was determined by UV--vis spectroscopy (Figures 5 and S3 in the Supporting Information).23,24 The predominant specie in high HCl concentrations was found to be $[\text{RhCl}_6]^{3-}$, whereas the amount of $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ present in the solution was observed to increase upon a decrease in the HCl concentration, until it became the major component of the solution at low HCl concentrations.

As previously mentioned, the Rh-containing precipitate prepared from 8 M HCl formed a 1:6:3 complex of $[\text{RhCl}_6]^{3-}$/anilinium/chloride ions. In order to examine the structure of the Rh-containing precipitate prepared from low-concentration HCl solutions, where $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ is the major component, powder X-ray diffraction, TG, and XPS measurements were performed on the precipitate prepared from 2 M HCl using 4-hexylaniline. All of the obtained results, the diffraction patterns, the amount of weight residue, and the atomic ratio, were found to correspond to those of the precipitate from the 8 M HCl solution, indicating that the precipitate obtained from the 2 M HCl solution also has an ion-pair complex structure comprising $[\text{RhCl}_6]^{3-}$/anilinium/chloride ions in a 1:6:3 ratio (Figure S4 in the Supporting Information). On the basis of the above results, it was concluded...
that 4-alkylanilines selectively precipitate [RhCl₆]³⁻ by forming an ion-pair complex, regardless of the HCl concentration used. Figure 6a shows the composition of [RhCl₆]³⁻ determined by UV−vis spectroscopy and the precipitation percentages of Rh using 4-hexylaniline at different HCl concentrations. As shown in Figure 6a, the precipitation percentages of Rh exceed the abundance ratio of [RhCl₆]³⁻ at low HCl concentrations, even though only [RhCl₆]³⁻ can form a precipitate. The influence of the shaking time on the Rh precipitation from 2 and 8 M HCl using 4-hexylaniline was examined, and the results are shown in Figure 6b. The Rh precipitation from the 8 M HCl solution was completed after a mere 10 min of shaking. On the other hand, the precipitation percentages of Rh from the 2 M HCl solution were found to gradually increase upon an increase in the shaking time and reached 78% after 24 h of shaking, despite the composition ratio of [RhCl₆]³⁻ in 2 M HCl being only 7.5%. This precipitation behavior from 2 M HCl is considered to be the result of an equilibrium shift from [RhCl₄(H₂O)₂]⁻ and [RhCl₆(H₂O)₃]⁻ to [RhCl₆]³⁻.

Mechanism of Selective Precipitation of Rh(III). It is widely recognized that Rh(III) in HCl cannot be extracted using conventional solvent extraction methods and that the extremely low extractability of Rh(III) via the ion-pair mechanism is considered to be due to the large hydration shell of [RhCl₆]³⁻. Generally, conventional extractants, containing secondary, tertiary, and quaternary ammonium cations, show hydrophobic behavior because the hydrophilic ammonium cations are generally surrounded by hydrophobic aromatic rings or long alkyl chains. As a consequence, they cannot overcome the large hydration shell of [RhCl₆]³⁻, resulting in the failure to form an ion pair. 4-Alkylanilines used in this study are primary amines and show amphiphilic properties because the hydrophilic ammonium cations in the ion pairs are stable even in high HCl concentrations. Consequently, the preferential and selective precipitation of Rh was successfully achieved based on the unique Rh-containing ion-pair structure that results in peculiar high stability of the Rh/4-alkylaniline ion pairs in high HCl concentrations. It is worth noting that our strategy concept for Rh-selective separation was successfully achieved based on the formation of a unique and highly stable ion-pair complex has the possibility of the selective recovery of industrially important Ru(III) and Ir(III) from the other PGMs because the structures of chloro-complexes of Ru(III) and Ir(III), [RuCl₆]³⁻ and [IrCl₆]³⁻, are similar to that of [RhCl₆]³⁻. The investigation of applicable metals and amines as well as the detailed analysis on the stability of the ion-pair complexes is still in progress.

CONCLUSIONS

In conclusion, a new way of separating Rh from the HCl solutions containing Pd(II), Pt(IV), and Rh(III) based on the preferential and selective precipitation of Rh(III) using 4-alkylanilines has been developed. Selective Rh precipitation was achieved at high HCl concentrations using either 4-butylaniline or 4-hexylaniline. Structural analysis of the resulting Rh-containing precipitates revealed the formation of a unique ion-pair complex comprising [RhCl₆]³⁻/anilinium/chloride ions in a 1:6:3 ratio. Rh-selective precipitation at high HCl concentrations is due to the unusual high stability of Rh/4-alkylaniline ion pairs. It is hoped that this method will be promising for use in practical Rh recovery processes and will open up the field of PGM recycling.

MATERIALS AND METHODS

Materials. 4-Butylaniline and 4-hexylaniline were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Pd(II) and Pt(IV) standard solutions (1000 ppm in 1 M HCl) were purchased from Wako Pure Chemical Industries, Ltd. Rh(III) standard solution (1000 ppm in 1 M HCl) was purchased from Kanto Chemical Co., Inc.

Metal Precipitation Experiments Using 4-Butylaniline and 4-Hexylaniline. To HCl solutions (1 mL) containing Pd(II), Pt(IV), and Rh(III) (1.0 mmol/L each) were added 4-butylaniline or 4-hexylaniline, and the mixtures were vigorously shaken at room temperature. The resulting solution was separated by centrifugation (7200g, 10 min), and the metal concentration in the supernatant was determined by ICP−AES. The metal precipitation experiments were carried out by varying the concentration of HCl, the amount of precipitating agents, and the shaking time.

Isolation of the Rh-Containing Precipitate. To a HCl solution (2 or 8 M, 10 mL) containing Rh(III) (1.0 mmol/L each) was added 4-hexylaniline (35 mg, 0.2 mmol) or 4-butylaniline (30 mg, 0.2 mmol), and the mixture was vigorously shaken for 3 h at room temperature. The resulting solid was collected by filtration and washed five times with a 3 M HCl solution. The solid was dried at room temperature for 48 h under vacuum.
Preparation of a Single Crystal. The Rh-containing precipitate (10 mg) prepared from 8 M HCl using 4-hexylaniline was dissolved in 1 M HCl (ca. 50 mL), and the resulting solution was left to stand for 1 month. The single crystal was obtained as a red-colored crystal.

Measurements. 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 relative sensitivity factors supplied with the instrument control software were used for element quantification (N 1s: 0.477, Cl 2s: 0.493, Rh 3d: 4.822). UV–vis absorption spectra were collected using a UV–vis spectrophotometer (Model V-550, Jasco co., Tokyo, Japan). TGA measurements were carried out using a STA7300 (Hitachi High-Tech Science Co., Tokyo, Japan) at a heating rate of 10 °C/min under air flow (200 mL/min).

The powder X-ray diffraction measurements were carried out with a Rigaku Ultima IV. Elemental analysis was conducted on an elemental analyzer (CE-440M, Exeter Analytical Inc., North Chelmsford, MA). The single-crystal X-ray diffraction data were collected using a Rigaku Saturn 724 charge-coupled device (CCD) diffractometer with Mo Kα radiation (λ = 0.71075 Å). The crystal data and structure refinement are listed in Table S1. Data collection, cell refinement, and data reduction were conducted using the CrysAlisPro software. The structure was solved by direct methods using the program SHELXT28 and refined by full-matrix least-squares methods on F2 using SHELXL2014.29 All materials for publication were prepared by Yadokari-XG 2009 software.30 Tables of positional and thermal parameters, bond lengths and angles, torsion angles, and figures may be found from the Cambridge Crystallographic Centre by referencing CCDC number 1863100.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03435.

Additional experimental data for the metal precipitation and the analysis of the Rh-containing precipitate (PDF)

Single-crystal structure of the Rh-containing precipitate with 4-hexylaniline (CIF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: kmatsu@gipc.akita-u.ac.jp.

ORCID

Kazuya Matsumoto: 0000-0001-9036-0365
Hiroshi Katagiri: 0000-0003-4100-9995

Author Contributions
The article was written through contributions of all authors.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (Grant-in-Aid for Young Scientists (B) 17K12835).

REFERENCES

(1) Alonso, E.; Field, F. R.; Kirchain, R. E. Platinum availability for future automotive technologies. Environ. Sci. Technol. 2012, 46, 12986–12993.
(2) Khaliq, A.; Rhamdhani, M.; Brooks, G.; Masood, S. Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 2014, 3, 152–179.
(3) Fröhlich, P.; Lorenz, T.; Martin, G.; Brett, B.; Bertau, M. Valuable metals—recovery processes, current trends, and recycling strategies. Angew. Chem., Int. Ed. 2017, 56, 2544–2580.
(4) Kaipar, J.; Fomashiero, P.; Hickey, N. Automotive catalytic converters: current status and some perspectives. Catal. Today 2003, 77, 419–449.
(5) Hagleliken, B. C. Recycling the platinum group metals: a European perspective. Platinum Met. Rev. 2012, 56, 29–35.
(6) Lokhande, T. N.; Anuse, M. A.; Chavan, M. B. Extraction and separation studies of platinum(IV) with N-n-octylaniline. Talanta 1998, 47, 823–832.
(7) Lee, J. Y.; Raju, B.; Nagaphani Kumar, B.; Rajesh Kumar, J.; Park, H. K.; Ramachandra Reddy, B. Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst. Sep. Purif. Technol. 2010, 73, 213–218.
(8) Swain, B.; Jeong, J.; Kim, S.-k.; Lee, J.-c. Separation of platinum and palladium from chloride solution by solvent extraction using Alamine 300. Hydrometallurgy 2010, 104, 1–7.
(9) Gupta, B.; Singh, I. Extraction and separation of platinum, palladium and rhodium using Cyanex 923 and their recovery form real samples. Hydrometallurgy 2013, 134–135, 11–18.
(10) Jha, M. K.; Gupta, D.; Lee, J.-c.; Kumar, V.; Jeong, J. Solvent extraction of platinum using amine based extractants in different solutions: a review. Hydrometallurgy 2014, 142, 60–69.
(11) Baba, Y.; Eguchi, T.; Inoue, K. Solvent extraction of palladium with dihexyl sulfide. J. Chem. Eng. Jpn. 1986, 19, 361–366.
(12) Ishimori, T.; Watanabe, K.; Nakamura, E. Inorganic extraction studies on the system between tri-n-butyl phosphate and hydrochloric acid. Bull. Chem. Soc. Jpn. 1960, 33, 636–644.
(13) Crundwell, F. K.; Moats, M. S.; Ramachandran, V.; Robinson, T. G.; Davenport, W. G. Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals; Elsevier: Amsterdam, 2011.
(14) Bernardis, F. L.; Grant, R. A.; Sherrington, D. C. A review of methods of separation of the platinum-group metals through their chloro-complexes. React. Funct. Polym. 2005, 65, 205–217.
(15) Rydberg, J.; Cox, M.; Muskas, C.; Choppin, G. R. Solvent Extraction Principles and Practice, 2nd ed.; Marcel Dekker, Inc.: New York, 2004.
(16) Nikolosi, A. N.; Ang, K.-L. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. Miner. Process. Extr. Metall. Rev. 2013, 35, 369–389.
(17) Narita, H.; Morisaku, K.; Tanaka, M. The first effective extractant for trivalent rhodium in hydrochloric acid solution. Chem. Commun. 2008, 5921–5923.
(18) Narita, H.; Morisaku, K.; Tanaka, M. Highly efficient extraction of rhodium(III) from hydrochloric acid solution with amide-containing tertiary amine compounds. Solvent Extr. Ion Exch. 2015, 33, 407–417.
(19) Suzuki, T.; Ogata, T.; Narita, H. Selective precipitation of palladium(II) over platinum(IV) in hydrochloric acid solution by 2-chloropyridine. Chem. Lett. 2018, 47, 389–391.
(20) Matsumoto, K.; Yamakawa, S.; Jikei, M. Selective recovery of platinum(IV) from palladium(II)-containing solution using 4-(hexyloxy)aniline. Chem. Lett. 2017, 46, 22–24.
(21) Benguerel, E.; Demopoulos, G. P.; Harris, G. B. Speciation and separation of rhodium (III) from chloride solutions: a critical review. Hydrometallurgy 1996, 40, 135–152.
(22) Józwiak, W. K.; Maniecki, T. P. Influence of atmosphere kind on temperature programmed decomposition of noble metal chlorides. Thermochim. Acta 2005, 435, 151–161.
(23) Endo, K.; Saikawa, M.; Sugimoto, M.; Hada, M.; Nakatsuji, H. Theoretical study of the transition energies of the visible absorption
spectra of $[\text{RhCl}_6]^{3-}$ and $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ complexes in aqueous solution. *Bull. Chem. Soc. Jpn.* 1995, 68, 1601–1605.

(24) Wolsey, W. C.; Reynolds, C. A.; Kleinberg, J. Complexes in the rhodium (III)-chloride system in acid solution. *Inorg. Chem.* 1963, 2, 463–468.

(25) Naidoo, K. J.; Klatt, G.; Koch, K. R.; Robinson, D. J. Geometric hydration shells for anionic platinum group metal chloro complexes. *Inorg. Chem.* 2002, 41, 1845–1849.

(26) Matsumoto, K.; Yamakawa, S.; Aoyagi, T.; Haga, K.; Iikei, M.; Shibayama, A. Mutual separation of palladium (II) and platinum (IV) from hydrochloric acid solutions using m-phenylene diamine-containing agents. *Int. J. Soc. Mater. Eng. Resour.* 2017, 22, 15–19.

(27) CrysAlisPro CCD, CrysAlisPro RED and ABSPACK in CrysAlisPro RED; Oxford Diffraction Ltd.: Abingdon, England, 2006.

(28) Sheldrick, G. M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* 2015, 71, 3–8.

(29) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, 71, 3–8.

(30) (a) Wakita, K. Yadokari-XG: Software for Crystal Structure Analyses, 2001. (b) Kabuto, C.; Akine, S.; Nemoto, T.; Kwon, E. Release of software (Yadokari-XG 2009) for crystal structure analyses. *J. Crystallogr. Soc. Jpn.* 2009, 51, 218–224.