

Article

Calix[4]arene-Based Amino Extractants Containing *n*-Alkyl Moieties for Separation of Pd(II) and Pt(IV) from Leach Liquors of Automotive Catalysts

Manabu Yamada ^{1,*} , Yu Kaneta ², Muniyappan Rajiv Gandhi ³, Uma Maheswara Rao Kunda ¹ and Atsushi Shibayama ³

¹ Research Center of Advanced Materials for Breakthrough Technology, Graduate School of Engineering Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan; drkuma8@gmail.com

² Graduate School of Engineering Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan; m8016002@s.akita-u.ac.jp

³ Graduate School of International Resource Sciences, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan; rajivgandhi85@gmail.com (M.R.G.); sibayama@gipc.akita-u.ac.jp (A.S.)

* Correspondence: myamada@gipc.akita-u.ac.jp; Tel./Fax: +81-18-889-3068

Received: 9 May 2018; Accepted: 2 July 2018; Published: 5 July 2018



Abstract: Pt, Pd, and Rh platinum group metals (PGMs) are utilized in automotive catalytic converters to reduce the level of harmful gas emissions. To evaluate the separation efficiencies of PGMs from the leach liquors of automotive catalysts, their extractabilities from both single-component solutions and leach liquors were determined using three *p*-dialkylaminomethylcalix[4]arenes (alkyl: *n*-hexyl~*n*-octyl; 3–5) as extractants, and the obtained results were compared with the data of acyclic *p*-di-*n*-octylaminomethyldimethylphenol (6) and those previously reported for macrocyclic calix[4]arene- and thiocalix[*n*]arene-based amine and amide extractants. Various extraction parameters, including the contact time, HCl concentration, and concentrations of Pd(II) and Pt(IV) ions, were examined, and the distributions and stoichiometry ratios of the recovered Pd(II) and Pt(IV) species were calculated. All macrocyclic extractants 3–5 exhibited high and selective extractabilities of Pd(II) and Pt(IV) ions contained in the leach liquors of automotive catalysts. The *E*% values of 3–5 from the leach liquors were 94.2, 93.0, and 97.7 for Pd(II) and 91.7, 94.0, and 92.5 for Pt(IV), respectively. Acyclic compound 6 did not perform well even though higher ratios of extractant used. Furthermore, the results of reusability testing demonstrated relatively large extractability values obtained for these two metals even after five extraction/stripping cycles.

Keywords: calixarene-based extractants; platinum-group metals; palladium; platinum; solvent extraction

1. Introduction

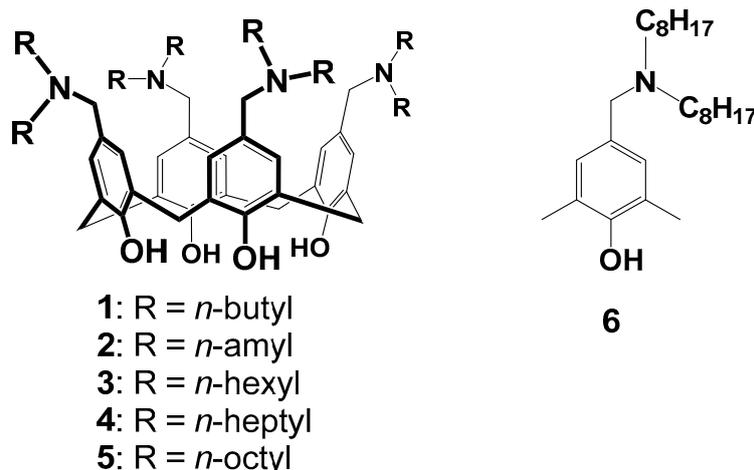
Calix[*n*]arenes have been used in catalysis, molecular recognition, ion separation, sensors, and so on [1–3]. Calixarene-based extractants have been widely utilized for the selective separation of alkali and rare earth metals, recovery of uranium ions from brine, and removal of heavy metals from aqueous solutions [4–9]. By performing chemical modifications of the functional groups located at the calixarene “upper” and “lower” rims, many functionalized calix[4]arenes were synthesized, and their ability to extract precious metals was intensively studied. Furthermore, as compared with the commercially available extractants, certain polydentate-functionalized calix[*n*]arenes can efficiently and selectively extract platinum group metals (PGMs) from solutions.

Owing to their scarcity in the Earth’s crust and eccentrically located resources, PGMs (Pd, Pt, Rh, Ru, Ir, and Os) represent valuable key components of many industrial applications. The demand

for PGMs remains very high as they are widely used in automotive and industrial catalysts, electronics, jewelry, dental materials, and electric/hybrid vehicles [10–12]. However, the existing imbalance between the limited supply of PGMs and their high demand causes significant price fluctuations. PGMs are mainly produced only in a few countries, including South Africa, Russia, USA, and Zimbabwe [12]. Therefore, the development of a PGM separation method from secondary resources is very important in terms of their effective recycling and sustainable use (typical secondary resources of PGMs include spent automotive catalysts, industrial catalysts, and electronic scraps [13]). The recovery of PGMs from spent automotive catalysts is very important because it contains appreciable amounts of Pd, Pt, and Rh than those of any other secondary resources (their typical amounts range from 1–2 g for a small car and 12–15 g for a big truck) [14]. In Japan, the extraction of PGMs from spent automotive catalysts is performed by combining various pyrometallurgical and hydrometallurgical processes [10,15–17]. Solvent extraction is a hydrometallurgical technique for the separation and purification of PGMs utilizing commercial extractants, such as 2-hydroxy-5-nonylacetophenone oxime (LIX-84A), di-*n*-octyl sulfide (DOS), and tri-*n*-butyl phosphate (TBP). LIX-84A and DOS are widely used for Pd(II) extraction and TBP for Pt(IV) extraction. Concomitantly, commercial extractants are oxidized upon extended contact with highly acidic aqueous phases, rendering them ineffective for metal separation [10,18–21]. LIX-84A is susceptible to hydrolysis under acidic conditions [19]. DOS is oxidized to di-*n*-octyl sulfoxide (DOSO) during extraction upon contact with oxidizing agents in the acidic aqueous phase [20]. Additionally, when TBP extracts Pt(IV) from the aqueous phase, adjusting over 5 M HCl in aqueous phase is required because of protonating TBP [10,21]. Further, they are characterized by relatively low selectivity, low stability in highly acidic media, and low extraction efficiency [10,21,22]. Therefore, the development of novel PGM extractants with high selectivity, high extraction rates, high separation efficiency, and high stability in acidic media is currently ongoing in many research groups [23–34].

Recently, we have reported that *n*-dialkylamino extractants based on acyclic thiodiphenols exhibited high extractabilities of Pd(II) and Pt(IV) ions [33]. In particular, their use resulted in rapid Pd(II) and Pt(IV) separation from the liquors of acid-leached automotive catalysts containing nine different metals (Pt, Pd, Rh, Al, Ba, Ce, La, Y, and Zr) with high selectivity through an ion-exchange extraction mechanism. Similarly, *n*-dialkylamino-modified calix[4]arene extractants (**1**: alkyl = butyl and **2**: alkyl = amyl; Scheme 1) were developed by our group to study their extractabilities towards PGMs [34]. By introducing gradually longer *n*-alkyl chains (alkyl = ethyl~amyl) in calix[4]arene skeletons, it has been observed that the extracted species consisting *n*-dialkylamino-modified calix[4]arene with chloro-PGM anions after PGM extraction showed an increase of solubility for chloroform as compared with the short alkyl chains having calixarene-based extractants with respect to our previous result [34]. These results prompted us to a further synthesis of higher chain length alkyl amino derivatives based on calix[4]arene. Additionally, influence of alkyl chain length and structure on copper(II) extraction by 5-alkyl-2-hydroxybenzaldoximes has also been reported [35,36]. The reports have shown that alkyl chain length affects the ability to function as useful extractants, that is, influence of an extraction rate of copper(II) and a solubility for hydrocarbon diluents.

In this work, the PGM extractabilities of three calix[4]arenes containing di-*n*-alkylamino moieties at the calixarene “upper” rims, *p*-di-*n*-alkylaminomethylcalix[4]arenes (*n*-hexyl~*n*-octyl = **3–5**; Scheme 1), were investigated, and the effects of the structural properties of macrocyclic calix[4]arene-based *n*-dialkylamino extractants (**3–5**) and acyclic *p*-di-*n*-octylaminomethyldimethylphenol (**6**) on the extraction of Pt(IV) and Pd(II) ions from HCl media were examined. Additionally, Pd(II) and Pt(IV) extraction percentages of the previous reported macrocyclic calix[4]arene- and thiacalix[*n*]arene-based amine and amide extractants were compared with the extractants **3–5**. Specifically, this study was aimed at determining the efficiencies of Pd(II), Pt(IV), and Rh(III) extraction from single-component PGM solutions and leach liquors of automotive catalysts, stripping of the extracted metal species, and reusability of the developed extractants.



Scheme 1. Chemical formula of *p*-di-*n*-alkylaminomethylcalix[4]arenes (1–5) and *p*-di-*n*-octylaminomethyldimethylphenol (6).

2. Experimental

2.1. Materials and Methods

p-*tert*-Butyl phenol, 2,6-dimethylphenol, dialkylamines, formaldehyde, acetic acid, phenol, AlCl₃, toluene, diethyl ether, and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Inc., Tokyo, Japan. Stock solutions of Pt(IV), Pd(II), and Rh(III) PGMs were prepared by dissolving PdCl₂ (Kanto Chemical Co., Inc., Tokyo, Japan), PtCl₄ (Acros Organics, NJ, USA), and RhCl₃·3H₂O (Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively, in HCl aqueous solution. Calix[4]arene was synthesized according to literature procedures [1,2]. The concentration of each metal ion in solution was measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (SPS-3000, Seiko Instruments Inc., Chiba, Japan). Fourier transform infrared (FT-IR) spectra of the extractants at 4000–600 cm⁻¹ by the attenuated total reflection (ATR) method were obtained using a Nicolet iS5 spectrophotometer (Thermo Fisher Scientific, MA, USA), whereas their nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 300 instrument (Bruker, MA, USA) and a JEOL JNM-ECA500 (JEOL, Tokyo, Japan).

2.2. Synthesis of 3–6

Extractant 3 was synthesized using the following procedure. Calix[4]arene (0.53 g, 1.25 mmol), THF (60 mL), dihexylamine (1.75 mL, 7.50 mmol), acetic acid (3 mL, 52.4 mol), and 37% formaldehyde solution (1.15 g, 38.3 mmol) were stirred for 24 h at room temperature. The solvent was removed under vacuum, and the resulting residue was dissolved in chloroform. The produced organic solution was washed with 0.01 M HCl and then neutralized with 10% K₂CO₃ solution. After that, the organic solvent was removed under vacuum, and the obtained oil was dried under vacuum at a temperature of 40 °C. The final yield was equal to 2.23 g (36.8%). ¹H NMR (300 MHz, CDCl₃) δ 6.96 (s, 8H, Ar), 4.20 (s, 4H, -Ar-CH₂-Ar-), 3.47 (s, 4H, -Ar-CH₂-Ar-), 3.30 (s, 8H, R₂-N-CH₂-Ar-), 2.33 (t, 16H, CH₃-(CH₂)₃-CH₂-CH₂-N-), 1.43 (s, 16H, CH₃-(CH₂)₃-CH₂-CH₂-N-), 1.25 (s, 48H, CH₃-(CH₂)₃-CH₂-CH₂-N-), and 0.88 (s, 24H, CH₃-(CH₂)₃-CH₂-CH₂-N-). IR (ν/cm): 2924, 2859, 1465, and 1216.

Extractant 4 was synthesized from diheptylamine using a procedure similar to that utilized for the preparation of extractant 3 (yield 41.7%). ¹H NMR (300 MHz, CDCl₃) δ 6.98 (s, 8H, Ar), 4.23 (s, 4H, -Ar-CH₂-Ar-), 3.46 (s, 4H, -Ar-CH₂-Ar-), 3.34 (s, 8H, R₂-N-CH₂-Ar-), 2.36 (t, 16H, CH₃-(CH₂)₄-CH₂-CH₂-N-), 1.43 (s, 16H, CH₃-(CH₂)₄-CH₂-CH₂-N-), 1.24 (s, 64H, CH₃-(CH₂)₄-CH₂-CH₂-N-), and 0.86 (s, 24H, CH₃-(CH₂)₄-CH₂-CH₂-N-). IR (ν/cm): 2924, 2854, 1466, and 1216.

Extractant **5** was synthesized from dioctylamine using a similar procedure (yield 34.3%). ¹H NMR (300 MHz, CDCl₃) δ 6.98 (s, 8H, Ar), 4.20 (s, 4H, -Ar-CH₂-Ar-), 3.42 (s, 4H, -Ar-CH₂-Ar-), 3.26 (s, 8H, R₂-N-CH₂-Ar-), 2.33 (t, 16H, CH₃-(CH₂)₅-CH₂-CH₂-N-), 1.42 (s, 16H, CH₃-(CH₂)₅-CH₂-CH₂-N-), 1.25 (s, 80H, CH₃-(CH₂)₅-CH₂-CH₂-N-), and 0.86 (s, 24H, CH₃-(CH₂)₅-CH₂-CH₂-N-). IR (ν/cm): 2922, 2853, 1456, and 1247.

Extractant **6** was synthesized via the following method. 2,6-Dimethylphenol (1.20 g, 10.0 mmol), THF (60 mL), dioctylamine (3.16 mL, 10.5 mmol), acetic acid (6 mL, 0.11 mol), and 37% formaldehyde solution (2.32 g, 14.16 mmol) were stirred for 24 h at room temperature. The solvent was removed under vacuum, and the resulting residue was dissolved in chloroform. The obtained organic solution was washed with 0.01 M HCl and then neutralized with 10% K₂CO₃ solution. After that, the organic solvent was removed under vacuum. The resulting oil was dried under vacuum at 40 °C, and its ultimate yield was equal to 1.26 g (33.6%). ¹H NMR (300 MHz, CDCl₃) δ 6.86 (s, 2H, Ar), 4.55 (s, 1H, Ar-OH), 3.37 (s, 2H, R₂-N-CH₂-Ar), 2.35 (t, 4H, CH₃-(CH₂)₅-CH₂-CH₂-N-), 2.19 (s, 6H, Ar-(CH₃)₂), 1.44 (s, 4H, CH₃-(CH₂)₅-CH₂-CH₂-N-), 1.25 (s, 20H, CH₃-(CH₂)₅-CH₂-CH₂-N-), and 0.86 (s, 6H, CH₃-(CH₂)₅-CH₂-CH₂-N-). IR (ν/cm): 2922, 2853, 1488, and 1303.

2.3. Liquid-Liquid Extraction Studies

2.3.1. Solvent Extraction of PGM by 3–6

Solvent extraction experiments were performed in triplicate at a temperature of 20 ± 1 °C to ensure that the obtained extractability values (*E*%) were reproducible within a range of ±5%. For this purpose, 1.0 mM CHCl₃ solutions of the extractants (10 mL) and 0.1 mM standard solutions containing single Pd(II), Pt(IV), and Rh(III) ions (10 mL) in 50 mL-glass bottles were used. The analyzed samples were shaken thoroughly at a speed of 300 rpm using a mechanical shaker for desirable time, and their aqueous and organic phases were separated in a separating funnel. The concentrations of Pd(II), Pt(IV), and Rh(III) ions in the aqueous phase were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS-3000; Seiko Instruments Inc., Chiba, Japan). Various extraction parameters, such as the contact time, metal/extractant ratio, and concentrations of extractants and HCl, have been examined. The obtained *E*% values and distribution ratios of Pd(II) and Pt(IV) species *D* were calculated using Equations (1)–(3):

$$E\% = [M]_{\text{org}} / [M]_{\text{aq,init}} \times 100 \quad (1)$$

$$[M]_{\text{org}} = ([M]_{\text{aq,init}} - [M]_{\text{aq}}) \quad (2)$$

$$D = [M]_{\text{org}} / [M]_{\text{aq}} \quad (3)$$

where $[M]_{\text{aq,init}}$ and $[M]_{\text{aq}}$ are the initial and final concentrations of metal ions in solution, respectively.

2.3.2. Solvent Extraction of Pd(II) and Pt(IV) Ions from Leach Liquors of Automotive Catalysts

Leached solutions were prepared by treating the automotive catalyst residue with HCl (11.6 M) and H₂O₂ (1 vol %) aqueous solutions [37]. The resultant mixture containing nine metal ions (Rh, Pd, Pt, Zr, Ce, Ba, Al, La, and Y) was diluted with water 25 times by volume for the purpose of liquid-liquid extraction (see Table S1). After dilution, the pH of the leach liquor was equal to 1.22. The concentration of each metal ion in solution was determined by ICP-AES. Subsequently, a chloroform solution of the extractants (10 mL, 1.0 mM) was added to 10 mL of the aqueous solution of metal ions. The resulting mixture was shaken at a speed of 300 rpm and temperature of 20 ± 1 °C for 60 min, and the concentrations of metal ions in the aqueous phase $[M]_{\text{aq}}$ were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS-3000; Seiko Instruments Inc., Chiba, Japan).

2.3.3. Stripping of Pt(IV) and Pd(II) Ions from Extractant Organic Phases

Stripping of Pt(IV) and Pd(II) ions from the two PGM-containing organic phases of the extractants was conducted by mixing 10 mL of each phase with 0.1 M thiourea in 0.1 M HCl solution (10 mL) as a stripping reagent. The obtained mixture was shaken at a speed of 300 rpm and temperature of 20 ± 1 °C, and the concentrations of Pt(IV) and Pd(II) ions in the aqueous phase after stripping $[M]_{\text{aq}}$ were determined by ICP-AES. The stripping efficiency ($S\%$) was calculated using the following equation:

$$S\% = [M]_{\text{aq}}/[M]_{\text{org}} \times 100, \quad (4)$$

where $[M]_{\text{aq}}$ is the concentration of Pt(IV) and Pd(II) ions in the aqueous solution after stripping, and $[M]_{\text{org}}$ is the concentration of these ions in the organic phase before stripping.

2.3.4. Reusability of Extractants

A fraction of the resulting organic phase (10 mL) after stripping was added to 20 mL of water and shaken for 10 min at a speed of 300 rpm. The resulting layers were separated using a separating funnel, and five extraction-stripping cycles of the liquid–liquid extraction process were performed under the conditions identical to those utilized for the leach liquors of automotive catalysts. Finally, the concentrations of all metal ions in the aqueous phase $[M]_{\text{aq}}$ were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS-3000; Seiko Instruments Inc., Chiba, Japan).

2.3.5. ^1H NMR and Attenuated Total Reflection (ATR)-FTIR Measurements of Native 3–5 and 0.1 M HCl-Treated 3–5

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL JNM-ECA500 (Tokyo, Japan) instruments at 20 ± 1 °C in CDCl_3 . Chemical shifts are quoted as parts per million (ppm) relative to the peak of tetramethylsilane (TMS) as an internal standard. ATR-FTIR spectra were measured at $4000\text{--}600\text{ cm}^{-1}$ using a Thermo Fisher Scientific Nicolet iS5 spectrophotometer (attenuated total reflection (ATR) method, MA, USA) with diamond mode by 16 scans. The internal reflections of ATR accessory is a Thermo Fisher Scientific Nicolet iD5 ATR accessory.

^1H NMR and ATR-FTIR spectra of the native extractants 3–5 and the acid-treated extractants 3–5 were measured directly by placing samples on the instruments. The sample preparation of the acid-treated extractants 3–5 for ^1H NMR and ATR-FTIR is given as follows: 10 mL of approximately 1 mM of 3–5 was diluted in CHCl_3 and 10 mL of 0.1 M HCl were shaken at a speed of 300 rpm and temperature of 20 ± 1 °C for 30 min. After that, organic phase was separated by a separating funnel, and then the CHCl_3 from organic phase were evaporated to give acid-treated extractants 3–5.

3. Results and Discussion

First, to examine the extraction behavior of extractants 3–5, extractions from three single-metal solutions (Pt, Pd, and Rh) in HCl media were performed at various contact times. These experiments were conducted using 1.0 mM solutions of extractants 3–5 and 0.1 mM standard solutions of Pd(II), Pt(IV), and Rh(III) ions in 0.1 M HCl. Figure S1 displays the effect of the contact time (0–60 min) on the extractions of Pd(II), Pt(IV), and Rh(III) ions with extractants 3–5. The extractabilities of all three single metal solutions reached equilibrium within 5 min, as was previously reported for extractants 1 and 2 [34]. The apparent extraction efficiency of 3–5 is similar to that of 1 and 2. Extractants 3–5 showed low efficiency on Rh(III) extraction, as well as 1 and 2, because the chloro-Rh(III) complex is an inert extractive species and is very stable in HCl media. Taking into account our previous work [34], Pd(II) extraction of 1–5 has almost same efficiency and differential ranges of the $E\%$ were 98.3–99.5%. Thus, extending alkyl chain lengths has not much effect on Pd(II) extraction. On the other hand, different phenomena, as is compared with Pd(II) extraction using 1–5, were observed on Pt(IV) and Rh(III) extractions. In the case of Pt(IV) extraction, differential ranges of the $E\%$ by 1–5 were 90.8–99.5%, but there is no regularity depending on the increases of the alkyl chain lengths of 1–5. In contrast,

the regularity between 3–5 on Rh(III) extraction was found, however, the same efficiency on Rh(III) extraction of 1 and 2 was proven. The extending of the alkyl chain lengths led to increase of the $E\%$; 9.6% in 3, 11.1% in 4, and 16.1% in 5. It might appear that the increase of efficiency on Rh(III) extraction attributes increases of hydrophobicity and basicity by extending alkyl chains in the extractants.

Furthermore, a comparison of the structural effects observed for the macrocyclic extractants 3–5 and acyclic compound 6 was performed. Figure S2 shows the extractability values obtained for each single-component PGM solution using macrocyclic extractant 5 and acyclic compound 6. Although the concentration of 6 was four times higher than that of 5, the extractabilities of 5 and 6 determined for the three PGMs were significantly different: 66.9% for Pd(II), 80.4% for Pt(IV), and 0% for Rh(III). These results suggest that the macrocyclic extractant 5 and PGMs formed highly stable chemical species owing to assembly of metal recognition sites by modification of the amino moieties located along the annular structures of the calixarene upper rims.

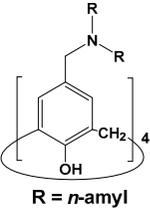
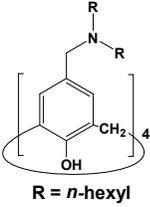
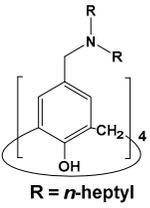
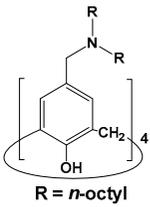
Generally, PGM extractability of amine-based extractants is affected by varying acid concentration [38]. Thus, to elucidate PGM extraction efficiency as a function of HCl concentration is also very important from an industrial point of view. Therefore, in order to examine the dependence of PGM extractability on the HCl concentration, extractions from single-metal PGM solutions with HCl concentrations ranging between 0.1 M and 8.0 M were conducted for 60 min using 1.0 mM solutions of extractants 3–5 and 0.1 mM standard Pd(II), Pt(IV), and Rh(III) solutions. Figure 1 shows the $E\%$ values obtained for the three PGMs at various HCl concentrations. After increasing the HCl concentration from 0.1 M to 8.0 M, the $E\%$ magnitudes determined for Pd(II) moderately decreased; $E\% = 99.3$ – 46.8% in 3, $E\% = 99.3$ – 49.7% in 4, and $E\% = 99.0$ – 42.3% in 5, at 0.1 M to 8.0 M HCl. On the other hand, those obtained for Pt(IV) decreased more rapidly; $E\% = 98.8$ – 26.7% in 3, $E\% = 99.4$ – 27.2% in 4, and $E\% = 90.4$ – 18.8% in 5, at 0.1 M to 8.0 M HCl. In the case of Rh(III) extraction, the obtained $E\%$ values were not very large (similar behavior was observed for 2). The maximum $E\%$ values for Pd(II) and Pt(IV) were obtained at an HCl concentration of 0.1 M, and the minimum ones at 8.0 M. In contrast, the maximum and minimum $E\%$ values determined for Rh(III) ions depended on the extractant composition. As was mentioned earlier, the HCl concentration produced a distinct effect on the Pd(II) and Pt(IV) extractions by 3–5, and the optimum condition for the extraction of these ions corresponded to the HCl concentration is 0.1 M.

A comparison of the $E\%$ for extractants 3–5 and calix[4]arene- and thiacalix[4]arene-based extractants previously reported in the literature for Pd(II) and Pt(IV) extraction from aqueous solutions is presented in Table 1 [24,34,39,40]. Extractants 3–5 possess an enhanced $E\%$, which confirms its increased selectivity toward Pd(II) and Pt(IV). Although various calix[4]arene- and thiacalix[4]arene-based extractants have been synthesized in the literature, the high efficiency was either Pd(II) or Pt(IV) extraction. Based on a literature review of thia- and calix[n]arene-based extractants, extractants 3–5 are confirmed to be the effective extractants for both Pd(II) and Pt(IV) from PGM included solutions comprising industrial wastes such as spent automotive catalysts.

Table 1. A comparison of Pd(II) and Pt(IV) extraction percentage of a few reported calix[4]arenes- and thiacalix[4]arene-based amine- or amide-extractants.

No.	Extractants	Structural Formulas	[Extractant] (M)	[Pd(II)] or [Pt(IV)] (M)	pH or [HCl] in Aqueous Solution	Pd(II) E (%)	Pt(IV) E (%)	Ref.
1	<i>p</i> -diethylamino-thiacalix[4]arene		1×10^{-3}	Pt(IV): 1×10^{-3}	pH 2.0	-	80.0	[24]
2	<i>p</i> - <i>tert</i> -butylthia-calix[4]aniline		5×10^{-4}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	pH 3.1	100	0	[39]
3	<i>p</i> - <i>tert</i> -butyl-tetra-kis[(diethylamide)methoxy]-thiacalix[4]arene		1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	pH 1.7	57.6	26.5	[40]
4	1	 R = <i>n</i> -butyl	1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	0.1 M HCl	98.3	94.7	[34]

Table 1. Cont.

No.	Extractants	Structural Formulas	[Extractant] (M)	[Pd(II)] or [Pt(IV)] (M)	pH or [HCl] in Aqueous Solution	Pd(II) E (%)	Pt(IV) E (%)	Ref.
5	2	 R = <i>n</i> -amyl	1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	0.1 M HCl	99.2	91.8	[34]
6	3	 R = <i>n</i> -hexyl	1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	0.1 M HCl	99.5	98.8	Present study
7	4	 R = <i>n</i> -heptyl	1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	0.1 M HCl	99.3	99.5	Present study
8	5	 R = <i>n</i> -octyl	1×10^{-3}	Pd(II): 1×10^{-4} Pt(IV): 1×10^{-4}	0.1 M HCl	99.0	90.8	Present study

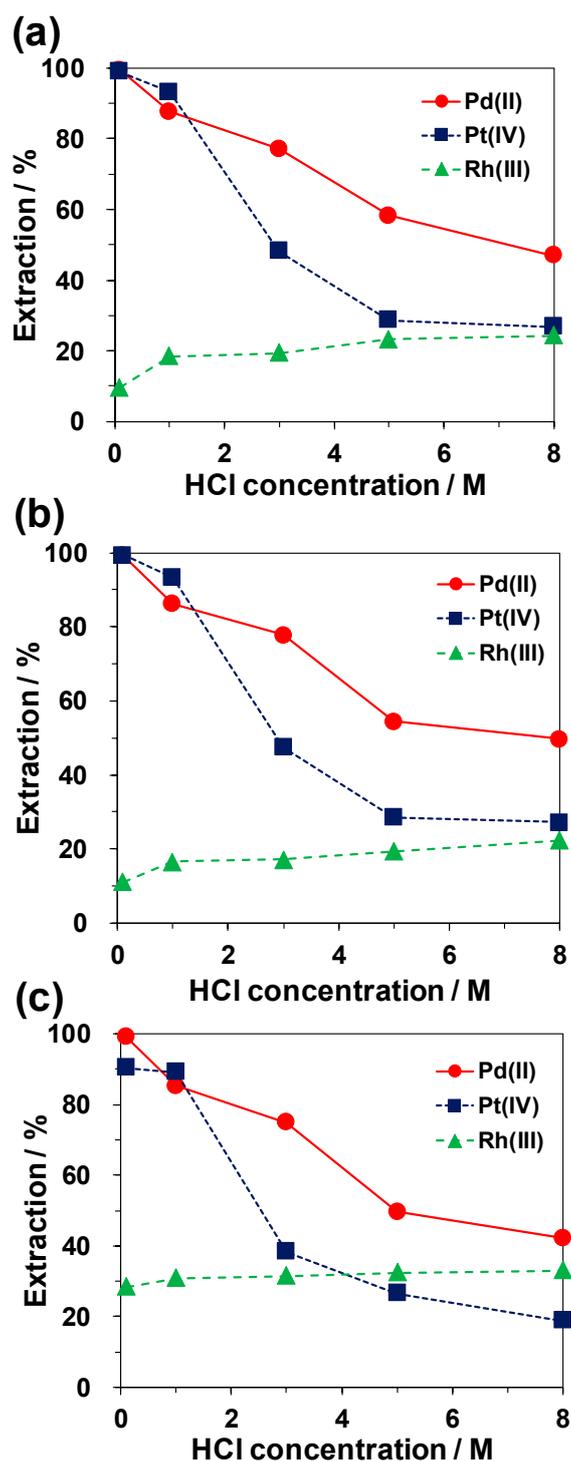


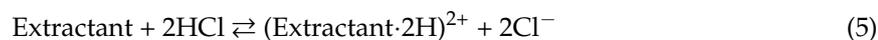
Figure 1. Extraction efficiency of three platinum group metals (PGMs) as a function of HCl concentration by extractants (a) 3, (b) 4, and (c) 5 from a single-component solution of Pd(II), Pt(IV), and Rh(III). Contact time = 60 min, [3–5] = 1.0 mM in CHCl_3 , [Pd(II)] = 0.1 mM (10.6 mg/L), [Pt(IV)] = 0.1 mM (19.5 mg/L), [Rh(III)] = 0.1 mM (10.2 mg/L), HCl = 0.1–8.0 M, temperature = 20 ± 1 °C.

In order to determine the stoichiometry of extractants 3–5 treated with Pd(II) and Pt(IV), the related $\log [D]$ versus $\log [E]$ plots were constructed. Similar to extractants 1 and 2, the slopes obtained for Pd(II) and Pt(IV) ions and extractants 3–5 were close to each other. As shown in Figure S3, the overall

slopes determined for extractants 3–5 were close to 1. Hence, the Pd(II)-extractant chemical species obtained after Pd(II) extraction likely exhibited a Pd(II)/extractant stoichiometry of 1:1. The three slope values obtained for the first five points located in the log [E] range between –5.5 and –4.0, were equal to 0.64 for 3, and 0.43 for 4 and 5. The other slopes determined for the last four points (in the log [E] range from –4.0 to –3.0) were 2.03 for 3, 2.06 for 4, and 2.00 for 5. From the constructed log-log plots, the existence of two different species with Pd(II)/extractant ratios of 2:1 and 1:2 in the organic phase can be suggested. Similar behavior was observed for the Pt(IV) extraction with extractants 3–5. In Figure S4, the slopes of the curves plotted for Pt(IV) species and three extractants were also close to 1; therefore, the produced species exhibited a Pt(IV)/extractant stoichiometric ratio of 1:1 in the organic phase. Furthermore, these curves can also be divided into two sections consisting of the first four and last five data points. The slopes of the first sections corresponding to the log [E] range from –5.5 to –4.0 were 0.64 for 3, 0.60 for 4, and 0.55 for 5. The slopes of the second sections lying in the log [E] range from –4.0 to –3.0 were 1.93 for 3, 1.87 for 4, and 2.21 for 5. Using the same logic, the existence of species with Pt(IV)/extractant stoichiometric ratios of 2:1 and a 1:2 in the organic phases can be assumed.

Further, in order to elucidate Pd(II) and Pt(IV) extraction mechanisms, native 3–5 and 0.1 M HCl-treated 3–5 were examined by means of ^1H NMR and ATR-FTIR spectroscopies. HCl extraction of 3–5 (10 mM) in CHCl_3 (10 mL) was carried out with a 0.1 M HCl (10 mL) for 30 min. ^1H NMR spectra of the native 3–5 and the acid-treated 3–5 were obtained as given in Figures S5–S7. Protons of methylene groups around nitrogen of amino moieties in 3–5 showed ~ 0.8 ppm downfield shift after being treated with 0.1 M HCl [41]. On the other, it was very difficult to exactly obtain integrated values of each chemical shift of acid-treated 3–5 because the chemical shifts were broad. However, the shift supports that 3–5 extracted HCl after treating with 0.1 M HCl by comparing the NMR spectra of the native and the acid-treated 3–5. Additionally, ATR-FTIR spectra of the native and the treated 3–5 also support the HCl extraction by amino groups of 3–5 and were given in Figure S8. In the case of 0.1 M HCl-treated 3–5, new peaks appeared around $2780\text{--}2730\text{ cm}^{-1}$, which might be attributed to a unique N–H stretching deriving from quaternary ammonium of extractants 3–5 [33].

From the log-log plots obtained for the Pd(II) and Pt(IV) extractions by 3–5 and the spectral analysis of ^1H NMR and ATR-FTIR after HCl extraction of 3–5, it can be concluded that the probable Pd(II) and Pt(IV) extraction mechanisms involve capturing one anionic Pd(II) or Pt(IV) chloro-complex by the two quaternary ammonium groups of cationic calix[4]arenes, according to Equations (5)–(7). The calixarene amino moieties of extractants 3–5 partially extract HCl molecules during the contact with the HCl media followed by exchanging Cl^- ions with $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$ complexes through the formation of an ion pair.



or



In this work, acyclic compound 6 was also used for the PGM extraction from the leach liquors of automotive catalysts. Pd(II), Pt(IV), and Rh(III) extractions were performed using the leach liquors (10 mL) and 1.0 mM of extractants 3–5 (10 mL) over a period of 60 min. In the case of acyclic compound 6, its 4.0 mM solution was used for extraction because each calix[4]arene-based extractant contained four di-*n*-alkylaminomethyl-modified aromatic units. Figure 2 displays the $E\%$ values obtained for the nine metal ions present in the liquors. The $E\%$ values of extractants 3–5 measured after the extraction of Pd(II) and Pt(IV) ions were 94.2% and 91.7% for 3, 93.0% and 94.0% for 4, and 97.7% and 92.5% for 5, respectively. The $E\%$ magnitudes determined for the seven other metal ions present in the leach liquors of automotive catalysts were below 6%. The results of the Pd(II) and Pt(IV) extractions performed using extractants 3–5 were similar to those obtained for the PGM extractions from the leach

liquors of automotive catalysts by extractants **1** and **2**. Although acyclic compound **6** exhibited high recognition abilities for Pd(II) and Pt(IV) ions, the $E\%$ values of Pd(II) and Pt(IV) species were lower than the numbers obtained for macrocyclic extractants **3–5** (56.2% for Pd(II) and 63.0% for Pt(IV)). The observed difference can be attributed to the presence of regularly arranged amino moieties along the annular structures of the calixarene upper rims. In other words, the macrocyclic structure can form highly stable metal species by assembling the functional groups characterized by high metal recognition ability. Meanwhile, the macrocyclic extractants **1–5** obtained by the modification of alkyl chains (*n*-propyl to *n*-octyl) have no remarkable difference for the $E\%$ on Pd(II) and Pt(IV) extractions. Hence, it is obvious that hydrophobicity of an extractant is not responsible for the extraction efficiency.

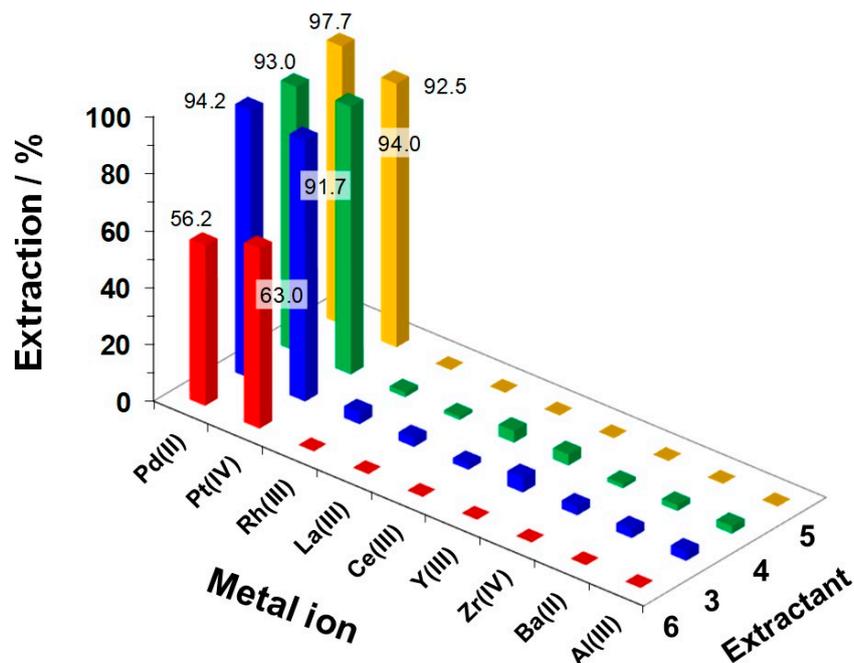


Figure 2. Liquid-liquid extraction from the 25 times-diluted leach liquors of automotive catalysts by three macrocyclic extractants **3–5** and acyclic compound **6**. Contact time = 60 min; [**3–5**] = 1.0 mM in CHCl_3 ; [**6**] = 4.0 mM in CHCl_3 ; metal ions = Pd(II), Pt(IV), Rh(III), La(III), Ce(III), Y(III), Zr(IV), Ba(II), and Al(III); pH = 1.22 (~ 0.06 M HCl); temperature = 20 ± 1 °C.

The stripping of the extracted Pd(II) and Pt(IV) ions from the organic phase was examined utilizing a 0.1 M thiourea/1.0 M HCl mixed solution (10 mL) as a stripping reagent [23,26,30] and reusability of the used extractants **3–5** on Pd(II) and Pt(IV) extractions from the leach liquors of automotive catalysts. A total of five Pd(II) and Pt(IV) stripping/extraction cycles were performed. As shown in Figure 3, the $S\%$ values obtained for Pd(II) and Pt(IV) ions after the first stripping cycle were 99.9% and 96.3% for **3**, 96.6% and 96.7% for **4**, and 95.3% and 95.4% for **5**, respectively. After this step, each organic phase containing extractants **3–5** (10 mL) was washed with distilled water (20 mL) to remove the unreacted thiourea species that had been transferred during the stripping process, and the extraction procedure was repeated. The $E\%$ magnitudes determined for the reused extractants and Pd(II) and Pt(IV) ions were 93.2% and 93.0% for **3**, 90.1% and 90.7% for **4**, and 97.5% and 92.5% for **5**, respectively. After five extraction/stripping cycles, the results similar to those obtained after the first cycle were produced. Additionally, the accumulation of the other metals in the solvent after the five extraction/stripping cycles was within $\sim 5\%$ of each. The reusability check indicated that the reused extractants **3–5** could be utilized continuously for the separation of Pd(II) and Pt(IV) ions from PGM-containing secondary resources (including the leach liquors of automotive catalysts).

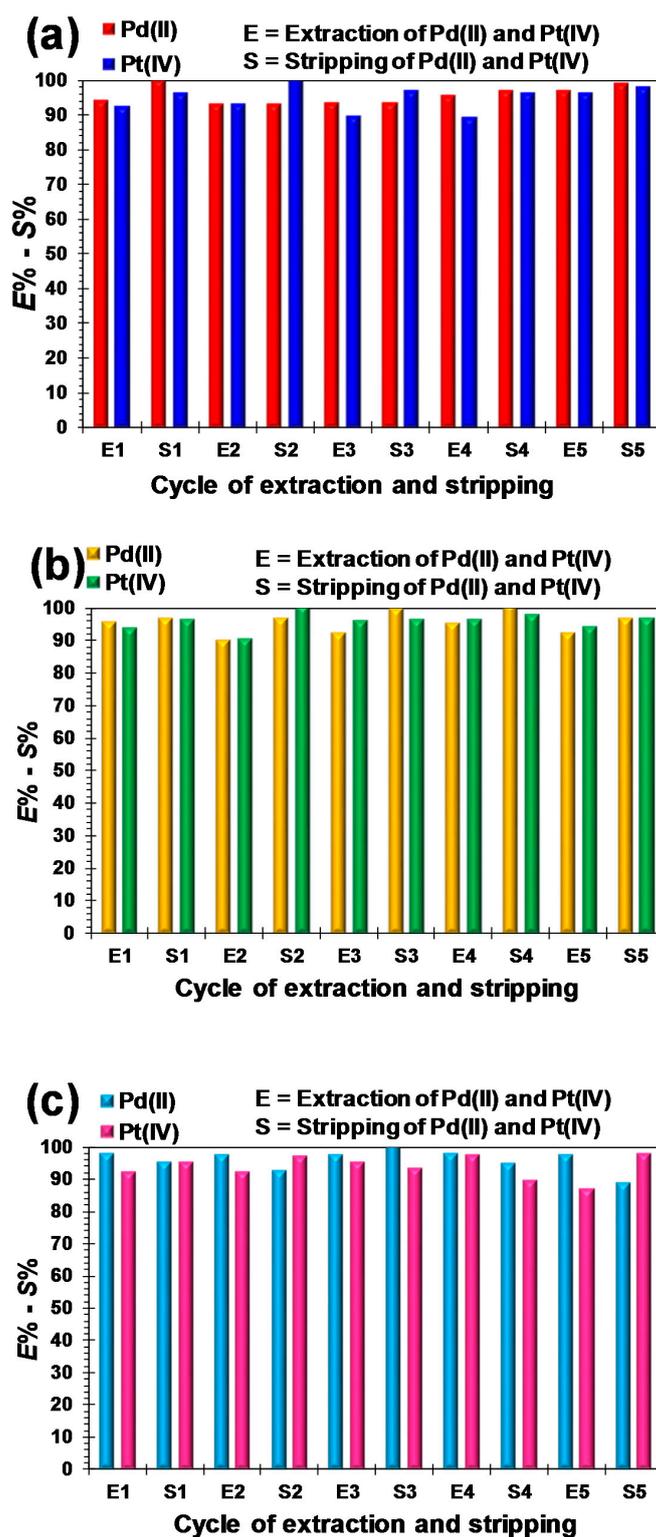


Figure 3. *E%* and *S%* in extraction and stripping cycles of extractants (a) 3, (b) 4, and (c) 5. Condition: contact time = 60 min for extraction and stripping; shaking speed = 300 rpm for extraction and stripping; organic phase: [3–5] = 10 mM in chloroform, aqueous phase: the leach liquors of automotive catalysts, stripping reagent = 0.1 M thiourea/1.0 M HCl, A/O = 1 (10 mL × 10 mL) for extraction and stripping, A/O = 2 (20 mL × 10 mL) for washing with water; temperature = 20 ± 1 °C.

4. Conclusions

In the present work, the most effective extractions of Pd(II) and Pt(IV) species by extractants 3–5 were observed at an HCl concentration of 0.1 M, and their PGM extraction capabilities could be ranked in the order Pd(II) > Pt(IV) >>> Rh(III). The PGMs extractabilities of 3–5 reached equilibrium within 5 min. After studying the effects of the structural factors of macrocyclic and acyclic extractants on PGM extraction, it was found that acyclic compound 6 exhibited high selectivities for Pd(II) and Pt(IV) ions, whereas macrocyclic extractants 1–5 demonstrated higher extractabilities of Pd(II) and Pt(IV) species as compared with those of acyclic compound 6. The proposed extraction mechanism consists of the following steps: (1) extraction of HCl from solution by extractants 3–5 and (2) exchange of the Cl[−] ions attached to the quaternary ammonium moieties of calixarene-based extractants with Pd(II) and Pt(IV) chloro-anions. The stoichiometries of extractants 3–5 containing Pd(II) and Pt(IV) species likely corresponded to the metal/extractant ratio of 1:1; however, chemical species with ratios of 1:2 and 2:1 were observed as well. During the extraction from the leach liquors of automotive catalysts, extractants 3–5 exhibited higher extractabilities of Pd(II) and Pt(IV) ions, while the values obtained for other metal ions were below 6%. The effective stripping of Pd(II) and Pt(IV) species after five extraction/stripping cycles was achieved using a thiourea/HCl solution. By performing the reusability studies of extractants 3–5, it was found that the *E*% values determined for Pd(II) and Pt(IV) ions extracted from the leach liquors remained constant even after five continuous extraction/stripping cycles.

From the results of the current study, it can be concluded that extractants 3–5 may be potentially used as novel extracting reagents for the separation of Pd(II) and Pt(IV) ions from other secondary resources. The developed calixarene-based extractants by our group are expected to exhibit high solubility in hydrocarbon-based diluents because of their non-polar nature resulting from the long alkyl chains. Currently, we are investigating the possibility of PGM extraction from leach liquors using extractants 1–5 with various hydrocarbon diluents to achieve their successful commercialization.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/8/7/517/s1>, Table S1: The concentrations of metal ions in the leached liquors of automotive catalysts after 25-times dilution, Figure S1: Effects of contact time on the extraction of (a) Pd(II), (b) Pt(IV), and (c) Rh(III) by extractants 3–5, Figure S2: Comparative study of three platinum group metals (PGM) extractabilities from each single-component PGM solution using macrocyclic 5 and acyclic 6, Figure S3: Log-log plot by varying concentration of extractants 3–5 on Pd(II) extraction, Figure S4: Log-log plot by varying concentration of extractants 3–5 on Pt(IV) extraction, Figure S5: Proton nuclear magnetic resonance (¹H NMR) spectra of native extractant 3 and 0.1 M HCl-treated 3, Figure S6: ¹H NMR spectra of native extractant 4 and 0.1 M HCl-treated 4, Figure S7: ¹H NMR spectra of native extractant 5 and 0.1 M HCl-treated 5, Figure S8: Comparison of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of 0.1 M HCl-treated 3–5 with those of native extractants 3–5.

Author Contributions: Conceptualization, M.Y.; Validation, M.Y., K.Y., M.R.G. and U.M.R.K.; Formal Analysis, M.Y., K.Y. and M.R.G.; Investigation, M.Y., K.Y., M.R.G. and U.M.R.K.; Resources, A.S.; Data Curation, M.Y. and Y.K.; Writing-Original Draft Preparation, M.Y., K.Y. and M.R.G.; Writing-Review & Editing, M.Y., K.Y., M.R.G., U.M.R.K. and A.S.; Visualization, M.Y., K.Y., M.R.G. and U.M.R.K.; Supervision, M.Y.; Funding Acquisition, M.Y. and A.S.

Funding: This research was funded by “Mukai Science and Technology Foundation,” Japan.

Acknowledgments: This work was mainly supported by the “Mukai Science and Technology Foundation”, Japan. This work was partially supported by the “JSPS KAKENHI” (Grant Numbers 16K17941, 16H04182, and 18K11705) and “Discretionary Funds of the President of Akita University”.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Vicens, J.; Böhmer, V. (Eds.) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; ISBN 0-7923-0714-3.
2. Gutsche, C.D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, UK, 1998; ISBN 0-85404-502-3.
3. Neri, N.; Sessler, J.L.; Wang, M.-X. (Eds.) *Calixarene and Beyond*; Springer: Cham, Switzerland, 2016; ISBN 978-3-319-31865-3.

4. Shinkai, S.; Shiramama, Y.; Satoh, H.; Manabe, O. Selective extraction and transport of UO_2^{2+} with calixarene-based uranophiles. *J. Chem. Soc. Perkin Trans. II* **1989**, 1167–1171. [[CrossRef](#)]
5. Deligöz, H.; Yilmaz, M. Liquid-liquid extraction of transition metal cations by calixarene-based cyclic ligands. *Solvent Extr. Ion Exch.* **1995**, *13*, 19–26. [[CrossRef](#)]
6. Deligöz, H.; Erdem, E. Comparative studies on the solvent extraction of transition metal cations by calixarene, phenol and ester derivatives. *J. Hazard. Mater.* **2008**, *154*, 29–32. [[CrossRef](#)] [[PubMed](#)]
7. Kim, J.Y.; Morisada, S.; Kawakita, H.; Ohto, K.; Kim, Y. Relationship between chemical structure and extraction efficiency toward palladium with ketonic derivatives of *p*-tert-octylcalix[4]arene in nitric acid media. *J. Incl. Phenom. Macrocycl. Chem.* **2015**, *82*, 25–32. [[CrossRef](#)]
8. Tanaka, M.; Morisada, S.; Kawakita, H.; Inoue, K.; Ohto, K. Synthesis of a cross phosphonic acid type calix[4]arene with two different spacers and its extractive separation of rare earth metals. *J. Incl. Phenom. Macrocycl. Chem.* **2015**, *82*, 33–42. [[CrossRef](#)]
9. Atanassova, M.; Kurteva, V. Synergism as a phenomenon in solvent extraction of 4f-elements with calixarenes. *RSC Adv.* **2016**, *6*, 11303–11324. [[CrossRef](#)]
10. Crundwell, F.; Moats, M.; Ramachandran, V.; Robinson, T.; Davenport, W.G. *Extractive Metallurgy of Nickel, Cobalt, and Platinum Group Metals*; Elsevier: Oxford, UK, 2011; ISBN 978-0-08-096809-4.
11. Zaera, F. The long and winding road to catalysis. *Nature* **2017**, *541*, 37–38. [[CrossRef](#)] [[PubMed](#)]
12. Johnson Matthey. *Summary of Platinum Supply & Demand in 2017*; PGM Market Reports February 2018; Johnson Matthey: Royston, UK, 2018.
13. Fornalczyk, A. Industrial catalysts as a source of valuable metals. *J. Achiev. Mater. Manuf. Eng.* **2012**, *55*, 864–869.
14. Tollefson, J. Worth its weight in Platinum. *Nature* **2007**, *450*, 334–335. [[CrossRef](#)] [[PubMed](#)]
15. Kolliopoulos, G.; Balomenos, E.; Giannopoulou, I.; Yakoumis, I.; Pantias, D. Behavior of platinum group metals during their pyrometallurgical recovery from spent automotive. *Open Access Libr. J.* **2014**, *1*, e735. [[CrossRef](#)]
16. Nogueira, C.A.; Paiva, A.P.; Oliveira, P.C.; Costa, M.C.; da Costa, A.M.R. Oxidative leaching process with cupric ion in hydrochloric acid media for recovery of Pd and Rh from spent catalytic converters. *J. Hazard. Mater.* **2014**, *278*, 82–90. [[CrossRef](#)] [[PubMed](#)]
17. Steinlechner, S.; Antrekowitsch, J. Potential of a hydrometallurgical recycling process for catalysts to cover the demand for critical metals, like PGMs and cerium. *JOM* **2015**, *67*, 406–411. [[CrossRef](#)]
18. Okuda, A.; Sawai, H.; Ichiishi, S.; Shibata, J. Extractions of Pd(II) and Pt(IV) from hydrochloric acid solution by dihexyl sulfide and the degradation of dihexyl sulphide. *J. MMIJ (Shigen-to-Sozai)* **2000**, *116*, 929–933. [[CrossRef](#)]
19. Cox, M. Solvent extraction in hydrometallurgy. In *Principles and Practices*, 2nd ed.; Rydberg, J., Cox, M., Musikas, C., Choppin, G.R., Eds.; Marcel Dekker Inc.: New York, NY, USA, 2004; pp. 455–505, ISBN 0-8247-5063-2.
20. Rajiv Gandhi, M.; Yamada, M.; Haga, K.; Shibayama, A. Synthesis of pincer-type extractants for selective extraction of palladium from PGMs: An improved liquid-liquid extraction approach to current refining processes. *Sci. Rep.* **2017**, *7*, 8709. [[CrossRef](#)] [[PubMed](#)]
21. Narita, H.; Suzuki, T.; Motokawa, R. Recent research in solvent extraction of Platinum group metals. *J. Jpn. Inst. Met. Mater.* **2017**, *81*, 157–167. [[CrossRef](#)]
22. Narita, H.; Morisaku, K.; Tamura, K.; Tanaka, M.; Shiwaku, H.; Okamoto, Y.; Suzuki, S.; Yaita, T. Extraction properties of palladium(II) in HCl solution with sulfide-containing monoamide compounds. *Ind. Eng. Chem. Res.* **2014**, *53*, 3636–3640. [[CrossRef](#)]
23. Traeger, J.; König, J.; Städtke, A.; Holdt, H.-J. Development of a solvent extraction system with 1,2-Bis(2-Methoxyethylthio)Benzene for the selective separation of Palladium(II) from secondary raw materials. *Hydrometallurgy* **2012**, *127–128*, 30–38. [[CrossRef](#)]
24. Yamada, M.; Rajiv Gandhi, M.; Kondo, Y.; Hamada, F. Synthesis and characterisation of *p*-diethylaminomethylthiacalix[4]arene for selective recovery of platinum from automotive catalyst residue. *Supramol. Chem.* **2014**, *26*, 620–630. [[CrossRef](#)]
25. Ortet, O.; Paiva, A.P. Liquid-liquid extraction of palladium(II) from chloride media by *N,N*-dimethyl-*N,N*-dicyclohexylthiodiglycolamide. *Sep. Purif. Technol.* **2015**, *156*, 363–368. [[CrossRef](#)]

26. Ortet, O.; Paiva, A.P. Development of tertiary thioamide derivatives to recover Palladium(II) from simulated complex chloride solutions. *Hydrometallurgy* **2015**, *151*, 33–41. [[CrossRef](#)]
27. Paiva, A.P.; Martins, M.E.; Ortet, O. Palladium(II) recovery from hydrochloric acid solutions by *N,N'*-dimethyl-*N,N'*-dibutylthiodiglycolamide. *Metals* **2015**, *5*, 2303–2315. [[CrossRef](#)]
28. Yamada, M.; Rajiv Gandhi, M.; Kunda, U.M.R.; Hamada, F. Thiacalixarenes: Emergent supramolecules in crystal engineering and molecular recognition. *J. Incl. Phenom. Macrocycl. Chem.* **2016**, *85*, 1–18. [[CrossRef](#)]
29. Yamada, M.; Rajiv Gandhi, M.; Sato, D.; Kaneta, Y.; Kimura, N. Comparative study on Palladium(II) extraction using thioamide-modified acyclic and cyclic extractants. *Ind. Eng. Chem. Res.* **2016**, *55*, 8914–8921. [[CrossRef](#)]
30. Rajiv Gandhi, M.; Yamada, M.; Kondo, Y.; Shibayama, A.; Hamada, F. Rapid and selective extraction of Pd(II) ions using the SCS type pincer ligand 1,3-Bis(dimethylthiocarbamoyloxy)benzene, and its Pd(II) extraction mechanism. *RSC Adv.* **2016**, *6*, 1243–1252. [[CrossRef](#)]
31. Paiva, A.P.; Ortet, O.; Carvalho, G.I.; Nogueira, C.A. Recovery of Palladium from a spent industrial catalyst through leaching and solvent extraction. *Hydrometallurgy* **2017**, *171*, 394–401. [[CrossRef](#)]
32. Paiva, A.P. Recycling of Palladium from spent catalysts using solvent extraction- some critical points. *Metals* **2018**, *7*, 505. [[CrossRef](#)]
33. Yamada, M.; Rajiv Gandhi, M.; Kaneta, Y.; Kimura, N.; Katagiri, H. Thiodiphenol-based *n*-dialkylamino extractants for selective Platinum group metal separation from automotive catalysts. *Ind. Eng. Chem. Res.* **2018**, *57*, 8914–8921. [[CrossRef](#)]
34. Yamada, M.; Rajiv Gandhi, M.; Kaneta, Y.; Hu, Y.; Shibayama, A. Calix[4]arene-based *n*-dialkylamino extractants for selective Platinum group metal separation from automotive catalysts. *ChemistrySelect* **2017**, *2*, 1052–1057. [[CrossRef](#)]
35. Stepniak-Biniakiewicz, D.; Szymanowski, J. Influence of the structure of alkyl derivatives of salicylaldehyde oxime upon the extraction rate of copper from diluted acidic solutions. *Polyhedron* **1987**, *6*, 197–203. [[CrossRef](#)]
36. Ainscow, T.A.; Aldalur, I.; Beezer, A.E.; Connor, J.A.; Garbett, N.C.; Mitchell, J.C.; Page, A.L.; Tindale, N.; Turner, K.A.; Willson, R.J. Influence of alkyl chain length and structure on the extraction of Copper(II) from aqueous acid by 5-alkyl-2-hydroxybenzaldoximes in hydrocarbon solvents: Diffusion coefficients of extractants and their complexes. *J. Colloid Interface Sci.* **1999**, *213*, 87–91. [[CrossRef](#)] [[PubMed](#)]
37. Harjanto, S.; Cao, Y.; Shibayama, A.; Naitoh, I.; Nanami, T.; Kasahara, K.; Okumura, Y.; Liu, K.; Fujita, T. Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions. *Mater. Trans.* **2006**, *47*, 129–135. [[CrossRef](#)]
38. 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. [[CrossRef](#)]
39. Katagiri, H.; Iki, N.; Matsunaga, Y.; Kabuto, C.; Miyano, S. 'Thiacalix[4]aniline' as a highly specific extractant for Au(III) and Pd(II) ions. *Chem. Commun.* **2002**, 2080–2081. [[CrossRef](#)]
40. Fontàs, C.; Anticó, E.; Vocanson, F.; Lamartine, R.; Seta, P. Efficient thiacalix[4]arenes for the extraction and separation of Au(III), Pd(II) and Pt(IV) metal ions from acidic media incorporated in membranes and solid phases. *Sep. Purif. Technol.* **2007**, *54*, 322–328. [[CrossRef](#)]
41. Chamberlain, N.F. *The Practice of NMR Spectroscopy with Spectra-Structure Correlations for Hydrogen-1*; Springer: New York, NY, USA, 1974; Chapter 2; pp. 15–43.

