

Application of Ionic Liquids in Solvent Extraction of Platinum Group Metals

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The advantageous properties of ionic liquids (ILs) have put them in the spotlight in recent years as durable and environmentally friendly solvents compared with conventional organic solvents. The applications of ILs have been expanding in various fields, including extraction and separation of metals. Platinum group metals (PGMs) are attractive targets for recovery using IL systems. In recent years, ILs have shown excellent performance for PGM extraction. In this review, we focus on the recent progress in solvent extraction using ILs for PGM recovery. Although application of ILs in PGM recovery is still in the early stages, research and development of ILs in this area are steadily advancing owing to the unique properties of ILs, such as their non-volatility, inflammability, low toxicity, and tunability. Fundamental approaches are expected to realize industrial applications of ILs in the future.

1. Introduction

Solvent wastes are one of the major issues in industry. They raise environmental and economic concern, and they account for a large part of the resources in industry and around 50% of post-treatment greenhouse gas emissions [1]. Therefore, solvent selection should be carefully considered to improve the synthesis conditions within the framework of green chemistry principles. Ionic liquids (ILs) have been attracting interest in recent years because of their variety of advantages as durable and environmentally friendly solvents. They have low vapor pressure, non-flammable nature, and excellent chemical, electrochemical, and thermal stability. However, this does not mean that ILs are inherently green. Some ILs are reported to be highly toxic and harmful when disposed in the environment [2].

ILs have been applied to various fields, such as polymer synthesis, catalysts, electrolytes of energy storage devices, biosensors, separation/extraction agents, lubricants, and so forth (Figure 1) [3-6]. In recent years, ILs have attracted much interest as solvents for nanomaterial synthesis and metal recovery. Even though the list of applications of ILs is diverse, it does not even begin to truly represent the wide range of areas affected by ILs. As more and more scientists become aware of the potential of ILs, their applications can be expected to expand even further. In this review, we focus on application of ILs to metal recovery through solvent extraction, particularly for recovery of platinum group metals (PGMs). We will first briefly review PGMs as resources and the general characteristic of ILs, and we will then discuss the capability of each IL group. Most of the ILs covered in this article are non-protic ILs. Consequently, several methods to

measure the physicochemical properties, the general synthesis procedures, and the extraction mechanisms of particular elements are reviewed.

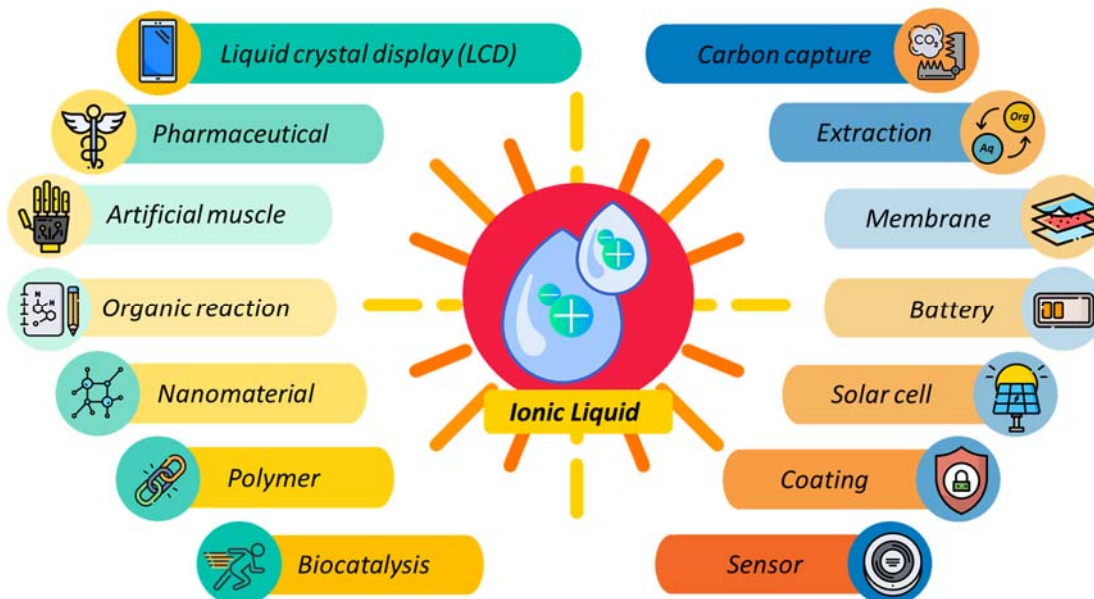


Figure 1. Applications of ILs in industry.

2. PGM resources

PGMs are six transitional metal elements that are chemically, physically, and anatomically similar. The PGMs are platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os). The top global producers of PGMs in 2018 are shown in Figure 2a. Currently, Southern Africa, namely, South Africa and Zimbabwe, are the top producers of PGMs, which is essential to meet the global demand of PGMs [7]. The top three companies (Anglo American, Impala Platinum, and Lonmin) that deal with PGMs are all located in South Africa [8]. The driving forces of the PGM market boom are their extraordinary and unique properties that sometimes make them irreplaceable in certain industries. The global demand of PGMs per industry sector for 2018 is shown in Figure 2b.

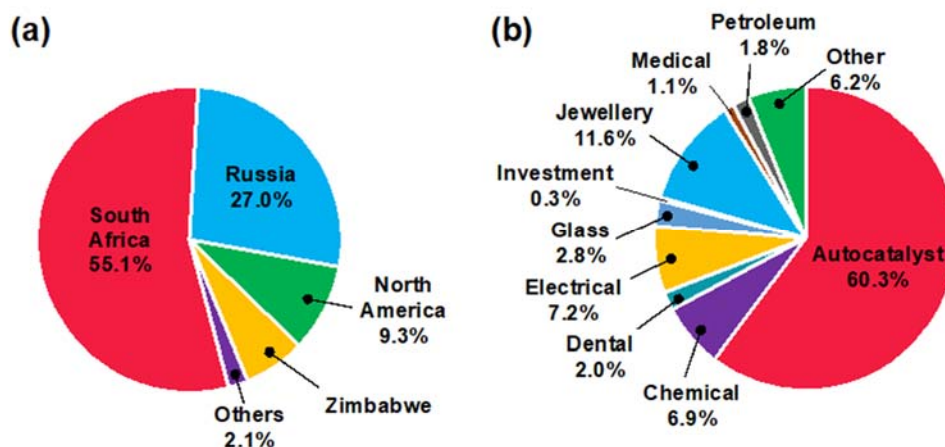


Figure 2. (a) Global production of PGMs per region and (b) global demand of PGMs per industry sector for 2018.

The largest consumers of Pt, Pd, and Rh are the automotive industry and jewelry market [9,10]. PGMs are mainly used in the three-way catalyst of the exhaust system. For several decades, Europe and North America have played an important role in this market because of their massive automotive industries. However, owing to environmental concerns, various countries, such as India, China, Russia, and Brazil, may push for stricter emission standards for most vehicles [11,12]. This action will further increase the demand for Pt, Pd, and Rh in the next decade. Moreover, the main drivers for PGMs in the jewelry market are India and China. With the economic development in both countries, the demand for PGMs in the jewelry industry will likely see a steady annual increase [13]. For Rh, the glass industry is one of the largest consumers after the automotive industry. However, Rh demand by the glass industry has been constantly fluctuating because Rh can be substituted with Pt [14]. Therefore, the main market for Rh is still the automotive industry. The demand for Rh is not going to decrease in the near future because it is necessary to perform nitrous oxide conversion in exhaust gas. For Ru and Ir, the electronics industry and mobile phone manufacturers are their largest consumers. The demand for Ir mainly comes from organic light-emitting diode producers for displays and touchscreens [15,16], and the demand for Ru comes from catalysts and electrical contacts owing to its unique properties [17]. However, the use of cheaper substitutes has resulted in a decrease in demand and a resulting price drop, putting a brake on the growth of demand in 2018. Competition among applications leads to increased pressure on supply. One way to ensure adequate supply is to increase exploration and extraction of geological deposits of PGMs. However, PGM supply has stagnated for over 5 years and producers do not expect a remarkable improvement in this situation in the near future [18]. The gap between the supply and demand for Pt, Pd and Rh in recent years is shown in Figure 3.

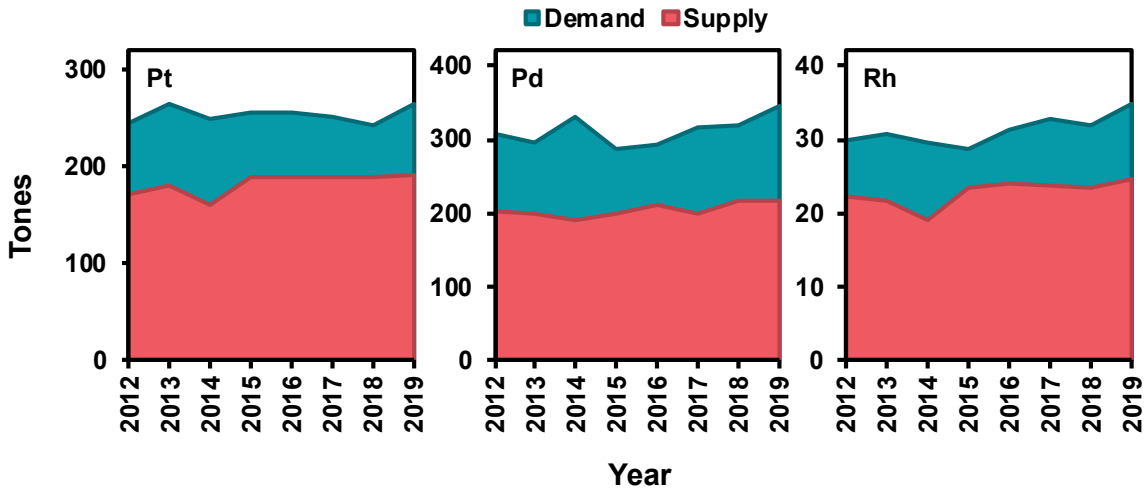


Figure 3. Supply and demand of Pt, Pd, and Rh in recent years The data were obtained from Johnson Matthey reports [9,10,19].

The historical data of PGM prices from 1992 to 2019 is shown in Figure 4. The price of Pt in United States dollars (USD) per ounce (oz) relatively constantly increased from 1998 to 2011. Subsequently, a continuous downward trend began. In general, the Pt price follows the gold price, and thereby more or less global economic development. This effect can be seen by the Pt price following the financial crisis in August

2007 [7]. The price of Pd also started to slightly increase in the early 2000s. Since 2009, the price greatly increased each year until it peaked in 2014. The Rh price hit its peak in 2008 because of an electrical shortage, which caused a severe shortage in PGM supply. During this period, the price of Pt increased to 2100 USD/oz, Pd increased from 390 to 560 USD/oz, and Rh hit an all time high of 7000 USD/oz. In recent years, Rh has continued to be the unsung hero of the precious metal market because the price has pushed above 3000 USD/oz, its highest level since early-October 2008. Currently, the price is up more than 35% since the start of the year with the spot price trading at a high of 3120 USD/oz. The Rh price also surpassed the gold price in early 2019, and it is expected to steadily increase [10]. Although the Rh price is extremely volatile because of its opaque marketplace, some reports predict higher prices as the market continues to be dominated by growing demand and shrinking supply [13].

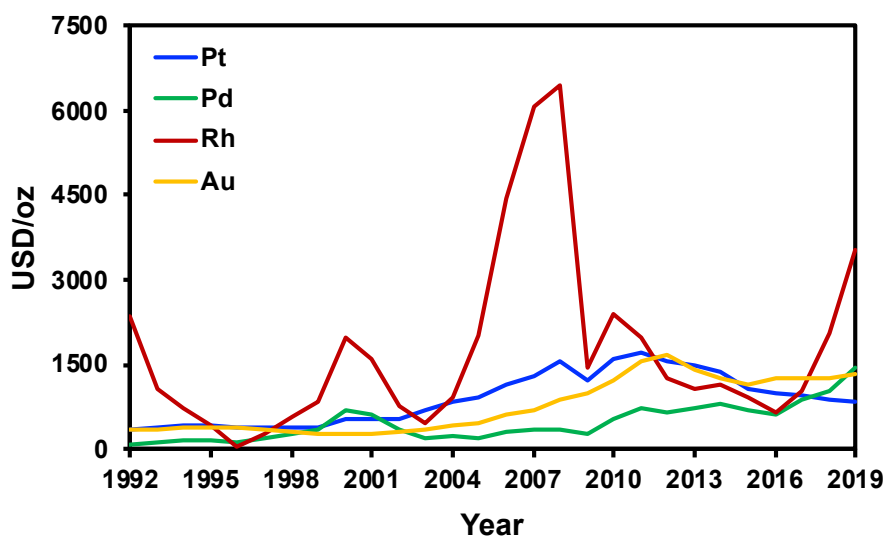


Figure 4. Historical data of PGM prices from 1992 to 2019 (data obtained from kitco.com).

3. Unique Properties of ILs

ILs are usually defined as salts that are in the liquid form at below 100°C. They are typically composed of a large asymmetric cation and an organic or inorganic anion. ILs have different physical properties from conventional liquids. Their remarkable properties and possible applications have made ILs a booming business in the past two decades, both in terms of research and industry. The number of publications on PGM extraction with ILs per year retrieved from the ISI Web of Knowledge-Science article database with the keywords of PGMs: TS = ("ionic liquid*" AND ("solvent extraction" OR "liquid liquid extraction") AND (platinum OR palladium OR rhodium OR iridium OR ruthenium OR osmium OR "platinum group metal*")) and Metals: TS = ("ionic liquid*" AND ("solvent extraction" OR " liquid-liquid extraction") AND metal*), is shown in Figure 5. The number of publications has increased in recent years.

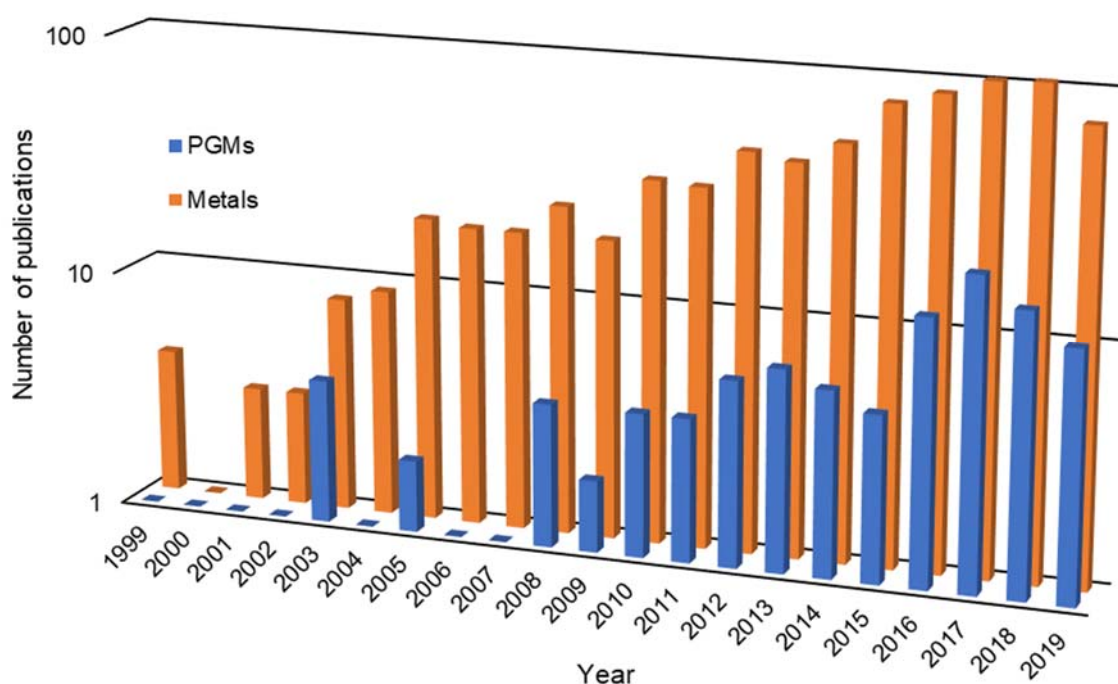


Figure 5. Number of publications concerning IL-based PGM extraction.

The melting point of ILs can be adjusted by changing the combination of anionic and cationic species. Moreover, a functional group can be added to the cation or anion to enhance the performance for a specific task. Because of the wide variety of cation and anion combinations, the potential of ILs is enormous. Thus, ILs are often considered to be designer solvents. The structures of the commonly used cations and anions of ILs are shown in Figure 6.

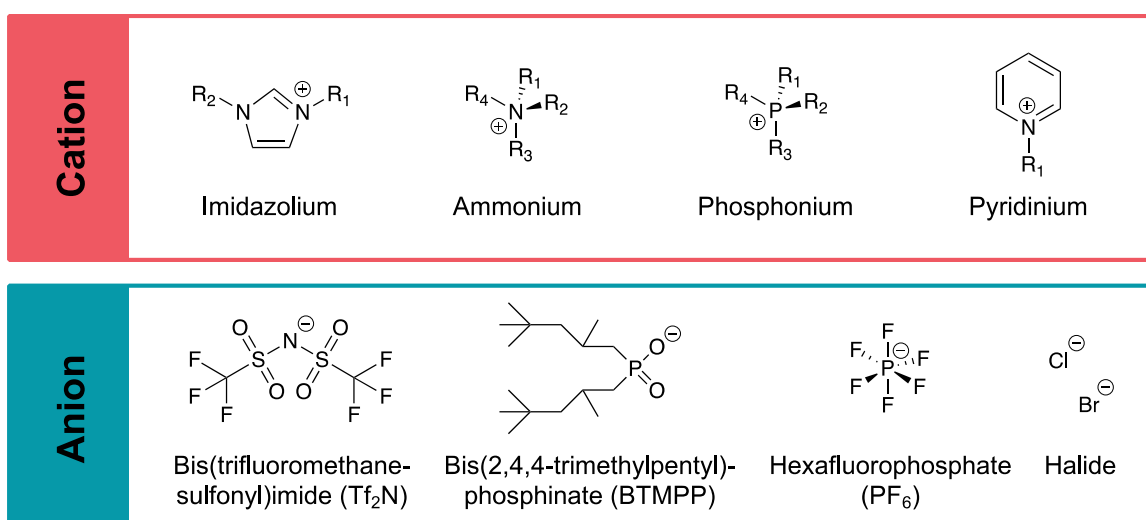


Figure 6. Commonly used IL cations and anions in PGM-related research.

Aside from their tunability, the properties of ILs are also remarkable compared with those of conventional liquids. ILs tend to have an extremely low vapor pressure that makes them non-volatile because of the reduced Coulombic interactions [20]. Moreover, ILs are inherently safer than conventional solvents because of their low flammability and good electrochemical stability and conductivity, which can prevent combustion from built-up static electricity. ILs also have low tendency for crystallization because of their wide liquidus ranges. In addition to the typical interactions of organic solvents, such as hydrogen bonding, dipole–dipole, and van der Waals interactions, ILs also have ionic interactions (mutual electrostatic attraction or repulsion of charged particles), which make them very miscible with polar substances [21]. Other physical properties, such as the viscosity, density, and surface tension, are adjustable according to the IL structure. For example, changing the anion from PF_6^- to BF_4^- can improve the IL solubility in water. Decreasing the degree of asymmetry of the IL can lead to lower viscosity, whereas increasing the degree of asymmetry can lead to a decrease in the density. The physical properties of several commonly used ILs are given in Table 1.

Table 1. Physical properties of commonly used ILs in PGM extraction.

Ionic liquid	Abbrev.	Melting point (°C)	Density (g/mL)	Viscosity (mPa.s)	Molecular weight
Trihexyltetradecylphosphonium chloride	$\text{P}_{66614}\text{Cl}$	-70	0.90	1820	519.3
Trihexyltetradecylphosphonium bromide	$\text{P}_{66614}\text{Br}$	-61	0.96	2090	563.8
Trihexyltetradecylphosphonium bis-(2,4,4-trimethylpentyl)phosphinate	P_{66614} BTMPP	N/A	0.90	806	773.3
1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	C_8MIM TF_2N	-50	1.32	92.5	457.5
1-octyl-3-methylimidazolium hexafluorophosphate	$\text{C}_8\text{MIM PF}_6$	N/A	1.24	714	340.3
1-hexyl-3-methylimidazolium hexafluorophosphate	$\text{C}_6\text{MIM PF}_6$	-74	1.29	497	312.2
1-butyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide	C_4MIM TF_2N	-4.0	1.43	51.0	419.4
1-butyl-3-methylimidazolium hexafluorophosphate	$\text{C}_4\text{MIM PF}_6$	-8.0	1.36	273	284.2
Trioctylmethylammonium nitrate	$\text{N}_{8881} \text{NO}_3$	N/A	0.93	1050	430.7
Trioctylmethylammonium chloride	$\text{N}_{8881} \text{Cl}$	-20	0.88	1500	404.2
Trioctylmethylammonium bis(trifluoromethylsulfonyl)imide	$\text{N}_{8881} \text{TF}_2\text{N}$	-81	1.11	608	648.8

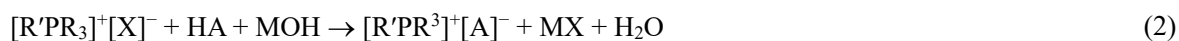
N/A : not available

ILs have been applied to leaching and solvent extraction processes for extraction of various metals.

Hydrophobic ILs can extract metal ions from aqueous solution and form IL–metal complexes, which are stable in a hydrophobic phase because hydrated metal ions tend to stay in the aqueous phase [22]. These results suggest favorable application of ILs in separation and recovery of PGMs considering that recovery in the conventional aqueous system is complex and difficult. ILs also act as either an inner diluent or an active extractant in the extraction systems, because their unique ion-exchange capability can offer an ideal solvation environment for extraction/separation of ionic metal species [23]. However, it should be stressed that IL-based extraction systems do not only have advantages, they also have some limitations [24]. The cations or anions of ILs can be transferred into the aqueous phase during the extraction operation when an extraction reaction occurs through the ion-exchange mechanism [25]. In addition, some of the anionic components, such as $[\text{PF}_6]^-$, have been reported to decompose in acidic media [26].

3.1 Phosphonium-based ILs

Phosphonium salts, especially halides, have been commercially available for many years. They are typically produced by quaternizing an alkylphosphine with a haloalkane in a 1:1 ratio under a nitrogen atmosphere. Bradaric et al. reported an alternate synthesis route to avoid any involvement of halide ions that is better to tailor the properties to match various application requirements [27]. This can be achieved through quaternization of tertiary phosphines with dialkylsulfates, dialkylphosphates, and alkylphosphonates. In addition, Adamova et al. reported that in synthesis of trioctylalkylphosphonium chloride (P_{888}RCl), a different set of reaction time and temperature is required depending on the alkyl-chain length [28]. This study showed that the physicochemical properties change by alteration of temperature and reaction time. The phosphonium-based ILs synthetic pathways are as follows:



Examples are synthesis of trihexyl(tetradecyl)phosphonium bis(trifluorosulfonyl)imide ($\text{P}_{66614}\text{Tf}_2\text{N}$) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate ($\text{P}_{66614}\text{BMTPP}$) [27], which follow Eqs. (1) and (2), respectively (Figure 7).

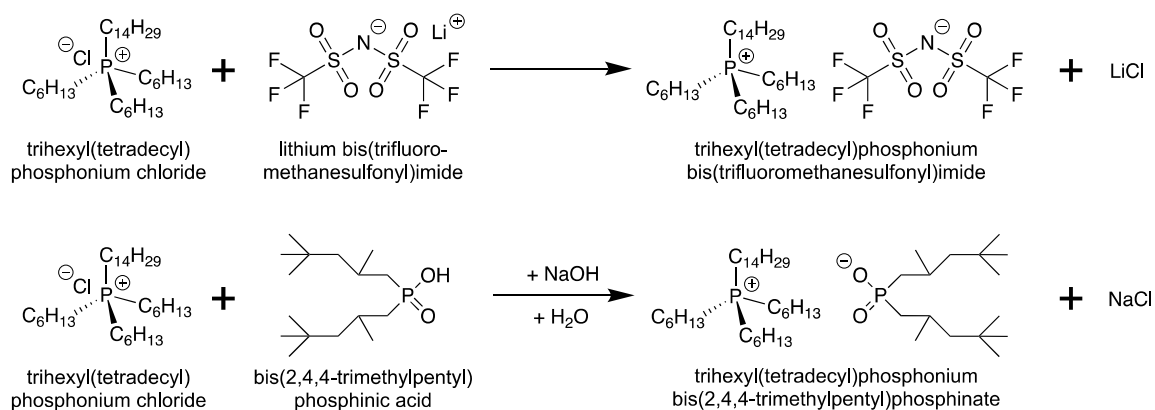


Figure 7. Synthetic pathways of $\text{P}_{66614}\text{Tf}_2\text{N}$ and $\text{P}_{66614}\text{BMTPP}$.

The set of phosphonium-based ILs $\text{P}_{66614}\text{Cl}$ (Cyphos IL101), $\text{P}_{66614}\text{BMTPP}$ (Cyphos IL 104), and $\text{P}_{66614}\text{Tf}_2\text{N}$ (Cyphos IL 109) has attracted attention in metal extraction and separation fields. The initial report

on extraction of PGMs with phosphonium-based ILs was by Cieszynska et al. in 2007 [29]. This study offered insight into the performance of phosphonium-based ILs in PGM extraction. In addition to P₆₆₆₁₄Cl, P₆₆₆₁₄BMTTP and P₆₆₆₁₄Br also show excellent performance in Pd extraction [30-33]. However, the results are inferior to recent reports, with one of the reasons being the use of a solvent in the extraction system, such as toluene. The extraction efficiencies of Pd with P₆₆₆₁₄Cl and P₆₆₆₁₄BMTTP are still high despite the presence of many other metals, such as Ni, Fe, and Cu, especially for low HCl concentration [34]. Moreover, most studies have reported a decrease in the selectivity of Pd in the presence of Pt owing to the competition between complex formation of [PtCl₆]²⁻ and [PdCl₄]²⁻ [34]. Papaiconomou et al. combined phosphonium-based ILs and imidazolium-based ILs to solve the selectivity issue. With two stages of extraction, separation of Pt and Pd was achieved using 1-octyl-3-methylimidazolium bis(trifluorosulfonyl)imide (C₈mimTf₂N) and P₆₆₆₁₄Br. C₈mimTf₂N was indifferent towards Pd at any HCl concentration and quite selective for Pt at low Pt concentration, which was assumed to be because of the lower Gibbs energy of solvation of [PtCl₆]²⁻ than [PdCl₄]²⁻. Thus, initial extraction of Pt was performed with C₈mimTf₂N, followed by Pd extraction with P₆₆₆₁₄Br [32]. Although separation of Pt and Pd was achieved, recovery of both PGMs from the loaded ILs was difficult. Nguyen et al. reported a different approach for Pt and Pd separation through selective stripping. Quantitative extraction of Pt and Pd from a mixture of Pt, Pd, and Rh was achieved using P₆₆₆₁₄Cl. Selective stripping of Pt and Pd was performed using NaSCN and CS(NH₂)₂ as stripping reagents for Pt and Pd, respectively. Moreover, it has been reported that extraction of PGMs in chloride media is mainly influenced by the chloride ion concentration rather than the acidity of the feed solution [35].

Rhodium is more difficult to extract than Pt and Pd. Extraction of Rh with IL systems has only been investigated and reported in recent years. Despite successful recovery of Pt and Pd from aqueous solution, Nguyen et al. was not able to extract Rh under any conditions [35]. However, Svecova et al. reported successful extraction of Rh using a similar system, in which the main difference was the absence of diluent [36]. Three different ILs, namely, P₆₆₆₁₄Cl, P₆₆₆₁₄Br, and P₆₆₆₁₄ dicyanamide (DCA), were able to extract Rh with high efficiency in low chloride concentration solution, with P₆₆₆₁₄Br showing the highest efficiency (98.7%), even in the presence of Pd. A similar trend was observed in Rh extraction by our group, where high extraction ability was achieved in low chloride concentration solution [37]. This was attributed to the dominant species of the chloro complex in low chloride concentration, which is [RhCl₅]²⁻. While [RhCl₆]³⁻ was dominating in high chloride concentration. However, Svecova et al. reported the presence of an additional Rh-chloro complex species in low chloride concentration: [RhCl₄]⁻ [38]. This species played an important role in enhancing extraction of Rh in low chloride concentration than [RhCl₅]²⁻. Extraction of other PGMs, such as ruthenium, osmium and iridium, has rarely been explored with ILs systems, especially osmium. An initial report on Ru extraction by Rzelewska et al. in 2016 showed the excellent performance of P₆₆₆₁₄Br in Ru extraction [39]. In comparison with Rh, Ru extraction is generally better with quaternary phosphonium ILs, especially at high HCl concentration. An interesting point in the report by Rzelewska et al. [40] was that the complexes of Ru changed after being left in aqueous solution for 2 weeks, which affected their extraction performance. However, the exact reason for this change still requires further investigation. Rzelewska et al. also investigated Ru extraction using P₆₆₆₁₄BMTTP and tributyl(tetradecyl)phosphonium chloride (P₄₄₄₁₄Cl). P₄₄₄₁₄Cl showed the highest efficiency in Ru extraction, followed by P₆₆₆₁₄Cl and P₆₆₆₁₄BMTTP. However, because of the higher hydrophilicity of P₄₄₄₁₄Cl than P₆₆₆₁₄Cl and P₆₆₆₁₄BMTTP,

emulsion formation resulting in slow phase separation was observed [41].

Extraction of PGMs from more complex systems has been reported by our group and Rzelewska-Piekut et al. and an extraction framework to successfully recover Pt, Pd, Ru, and Rh using P₆₆₆₁₄Cl has been established [42]. Separation of Pt and Pd was achieved by stripping and Rh remained in the raffinate. Our group reported successful recovery of Pd and Rh from an automotive catalyst leachate using trioctyl(dodecyl)phosphonium chloride (P₈₈₈₁₂Cl), which was first reported for extraction of PGMs [43]. Separation of Pd and Rh was achieved through HCl concentration adjustment. A high HCl concentration was effective for Pd extraction and a low HCl concentration was suitable for Rh extraction. Removal of any impurities in the process was also successfully performed. Regeneration of P₈₈₈₁₂Cl was achieved by contact with high concentration HCl solution. A summary of the performance of phosphonium-based ILs for PGM extraction is given in Table 2.

Table 2. Performance of phosphonium-based ILs in PGM extraction.

Cation	Anion	Diluent	D	E(%)	Author and year	Ref.
P ₆₆₆₁₄ ⁺	Cl ⁻	Toluene		Pd(97)	Ciezyńska et al., 2007	[29]
	Cl ⁻	Toluene		Pd(97)	Ciezyńska et al., 2010	[30]
	Cl ⁻	Toluene		Pd(97), Pt(60), Rh(8), Ru(8)	Ciezyńska et al., 2011	[34]
	BTMPP ⁻			Pt(70), Pd(61)		
	BTMPP ⁻	Toluene		Pd(96)	Ciezyńska et al., 2012	[31]
	Br ⁻	Toluene	Pt(3400)		Papaiconomou et al., 2015	[32]
	Br ⁻	Toluene		Pd(100)	Regel-Rosocka et al., 2015	[33]
	Cl ⁻	Xylene		Pt(99), Pd(98), Rh(0)	Nguyen et al., 2016	[35]
	Br ⁻	Toluene		Pt(90), Rh(50), Ru(60)	Rzelewska et al., 2016	[39]
	Cl ⁻		Pd(2532), Rh(47)	Pd(99), Rh(96)		
	Br ⁻		Pd(3000), Rh(95)	Pd(99), Rh(96)	Svecova et al., 2016	[36]
	Dca ⁻		Pd(3000), Rh(2.3)	Pd(99), Rh(32)		
	Cl ⁻	Toluene	Rh(1.25), Ru(2.7)		Rzelewska et al., 2017	[40]
	BTMPP ⁻		Rh(1.25), Ru(2.1)			
Cl ⁻		Ru(2.28)				
BTMPP ⁻		Ru(2.1)		Rzelewska et al., 2017	[41]	
P ₄₄₄₁₄ ⁺	Cl ⁻		Ru(2.72)			
P ₈₈₈₁₂ ⁺	Cl ⁻		Pt(99), Pd(99), Rh(88)	Firmansyah et al., 2018	[37]	

	Cl ⁻		Pt(99), Pd(95), Rh(15), Ru(30)		
P ₆₆₆₁₄ ⁺	Br ⁻	Toluene	Pt(99), Pd(95), Rh(15), Ru(30)	Rzelewska-Piekut et al., 2019	[42]
	BTMPP ⁻		Pt(99), Pd(95), Rh(10), Ru(30)		
	Cl ⁻	Toluene	Rh(62)	Rh(95)	Svecova et al., 2019 [38]
P ₈₈₈₁₂ ⁺	Cl ⁻		Pd(99), Rh(80)	Firmansyah et al., 2019	[43]

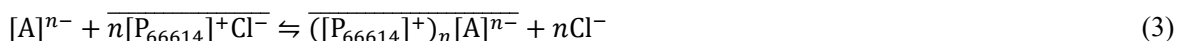
D: distribution ratio

P₆₆₆₁₄⁺: trihexyl(tetradecyl)phosphonium

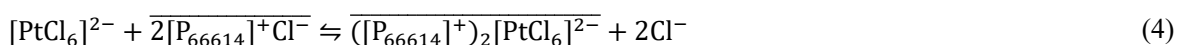
P₄₄₄₁₄⁺: tributyl(tetradecyl)phosphonium

P₈₈₈₁₂⁺: trioctyl(dodecyl)phosphonium

Extraction of PGMs by phosphonium-based ILs occurs by an anion-exchange mechanism:

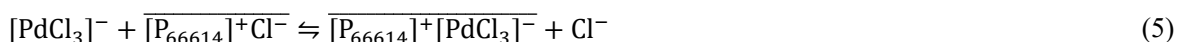


where the overbars denote the species in the organic phase and $[A]^{n-}$ is the anionic metal species to be extracted. For Pt, $[PtCl_6]^{2-}$ is the predominant species at most HCl concentrations. From several studies [35,37,42], extraction of Pt(IV) with phosphonium-based ILs occurs by the following equation:

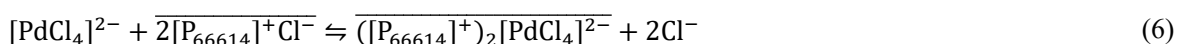


However, the Pd extraction mechanism is different from the Pt extraction mechanism. In hydrochloric acid/chloride media, Pd can form four chloro complexes: $[PdCl]^+$, $PdCl_2$, $[PdCl_3]^-$, and $[PdCl_4]^{2-}$. In most cases, $[PdCl_4]^{2-}$ is the predominant species, and it is in rapid equilibrium with $[PdCl_3]^-$, which is more labile and its relative concentration is significant at low chloride concentration. Thus, the extraction mechanism of Pd is generally governed by the chloride concentration [35].

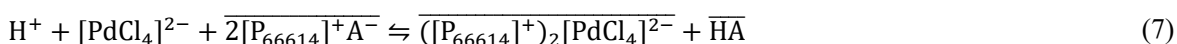
- At low HCl concentration,



- At high HCl concentration,

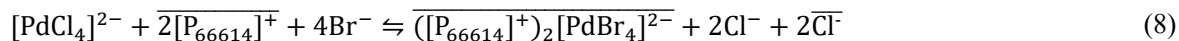


Ciezyńska et al. and Papaiconomou et al. reported the extraction mechanisms of Pd using P₆₆₆₁₄BTMPP and P₆₆₆₁₄Br, respectively [31,32]. Ciezyńska et al. discovered the presence of a dimer for bis(2,4,4-trimethylpentyl)phosphinic acid, which verified formation of this acid species during extraction. Thus, extraction of Pd using P₆₆₆₁₄BTMPP occurs by

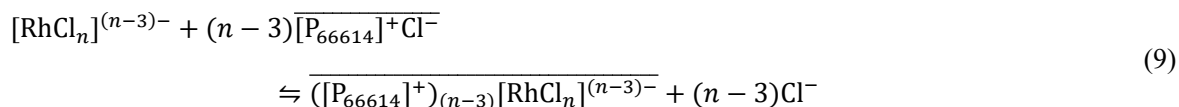


Pd extraction with P₆₆₆₁₄Br has been investigated by ultraviolet–visible (UV–Vis) spectroscopy. Prior to extraction, the color of the aqueous phase was light orange. The UV–Vis spectrum showed the presence of a

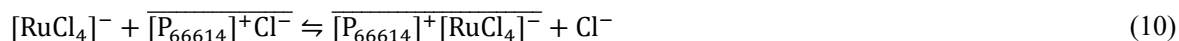
[PdCl₄]²⁻ complex. After extraction with P₆₆₆₁₄Br, the color turned red [32]. The UV–Vis spectrum showed the presence of the [PdBr₄]²⁻ complex in the IL phase. Thus, the mechanism of Pd extraction using P₆₆₆₁₄Br is as follows [32]:



Various rhodium complexes can be present in chloride media, namely, [RhCl₄]⁻, [RhCl₅]²⁻, and [RhCl₆]³⁻. We reported the presence of [RhCl₅]²⁻ as the main species in the aqueous phase at low HCl concentration [37], whereas [RhCl₆]³⁻ was the main species at high chloride concentration. However, Svecova et al. reported the presence of [RhCl₄]⁻ at low chloride concentration [38]. Consequently, it can be expected that [RhCl₅]²⁻ and [RhCl₆]³⁻ could proceed according to the extraction mechanisms

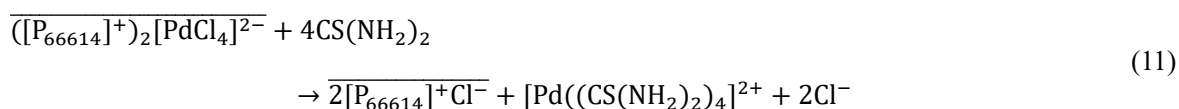


The chemistry of Ru(III) species in chloride solution is complex. For [Cl⁻] < 6 mol L⁻¹, [RuCl₅]²⁻ and [RuCl₄]⁻ are present in the solution [44]. Moreover, some RuCl₃, cis- and trans-[RuCl₂]⁺ ions, and [RuCl]²⁺ ions can be present. For anionic chloro complexes of Ru(III), the mechanism of extraction with phosphonium-based ILs is similar to that proposed for Pd extraction [41]:

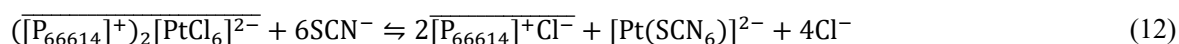


Pt(IV), Rh(III), and Ru(III) form octahedral complexes with a coordination number of 6 in aqueous chloride solution, whereas complexes of palladium in the +2 oxidation state are planar (coordination number 4). Taking into account the size or density of the charge of the chloro complex, the following order reflects the ability of PGM chloro complexes to be extracted by anion exchangers: [PdCl₄]²⁻ > [PtCl₆]²⁻ > [RuCl₅]²⁻ > [RuCl₆]³⁻ > [RhCl₆]³⁻ [45]. Chloro complexes of PGMs with low charge density (e.g., [PdCl₄]²⁻ and [PtCl₆]²⁻) show remarkable ability to form ion pairs with anion exchangers, unlike complexes with higher charge density (e.g., [RhCl₆]³⁻). In addition, planar chloro complexes (e.g., [PdCl₄]²⁻) are more available to an extractant than octahedral chloro complexes. Having a large hydration layer, complexes with high density of charge are characterized by a smaller interaction with counterions than complexes with a small hydration layer [42]. For this reason, extraction of Rh(III) to the IL phase is negligible and it remains in the raffinate. This is advantageous from a separation point of view, and it makes it possible to separate Rh(III) from other PGM ions present in the mixture feed solution.

Stripping of PGMs from phosphonium-based ILs has been investigated with various types of stripping reagents. CS(NH₂)₂ has been reported to be an effective stripping reagent for Pd in several studies. The effectiveness of CS(NH₂)₂ as a Pd(II) removal reagent is related to its soft ligand properties [43]. According to hard–soft acid base theory, Pd(II) is categorized as a soft metal and thus forms a water-soluble complex with CS(NH₂)₂ (Pd(CS(NH₂)₂)). Dissociation of Pd from the Pd–CS(NH₂)₂ complex can be achieved by several steps [35,43]. In alkaline solution, [Pd(CS(NH₂)₂)₄]²⁺ is hydrolyzed to the metastable intermediate complex [Pd(OH)₂(CS(NH₂)₂)], which rapidly decomposes and forms PdS, followed by reaction with the HCl solution to form the palladium–chloro complex PdCl₂:



NH₄OH also shows good performance in stripping Pt. However, NH₄OH is not particularly selective for Pt. In addition, NH₄OH is excellent in removing Pd, Zn, and Cu from ILs [35,43]. We reported effective stripping of Pt from loaded ILs using HNO₃. A similar finding was also reported by Rzelewska-Piekut et al. for stripping of Pt from a model solution using HNO₃ [42]. Nguyen et al. showed that NaSCN is effective and selective for Pt stripping over Pd [35]. The percentage stripping of Pt(IV) increased as the NaSCN concentration increased. The presence of the stable [Pt(SCN)₆]²⁻ complex in the aqueous phase has been reported. Therefore, the stripping mechanism of Pt(IV) with NaSCN can be expressed as follows:



There are a limited number of studies that deal with stripping of Ru and Rh. According to Rzelewska et al. CS(NH₂)₂ is effective as a stripping solution for Ru, with almost 90% efficiency [41]. For Rh, our group discovered that HCl is an efficient stripping solution. However, further investigation is required to determine the extraction mechanisms for both Ru and Rh.

3.2 Imidazolium-based ILs

The use of imidazolium-based ILs in separation has mainly been for butyl (C₄), hexyl (C₆), and octyl (C₈) methylimidazolium (mim) with various types of anions, such as hexafluorophosphate (PF₆⁻), tetrafluoroborate (BF₄⁻), and bis(trifluoromethanesulfonyl)imide (Tf₂N⁻). A typical imidazolium-based IL can be prepared by a relatively simple method (Figure 8). The synthesis steps are sequentially performed as follows: quaternization of the amine, solvent removal, anion exchange with a metal salt, solvent/salt removal, and refining [46-48]. Using this typical method, ILs with a wide range of physicochemical properties can be obtained by different functionalization (through variation of alkyl-X) and anion species (through variation of the metal salt). Burrell et al. reported the pathway for large-scale synthesis of imidazolium-based ILs [49]. According to their report, ILs should be colorless because the presence of color is a clear indication of impurities. To produce high-quality ILs, the precursors need to be purified prior to synthesis of the ILs. This can be simply achieved by using decolorizing charcoal in water followed by either heating to the reflux temperature for 3–5 min or heating at 65°C for 24 h [49]. UV-Vis and fluorescence spectroscopy are the simplest and most useful tools to determine the purity of ILs.

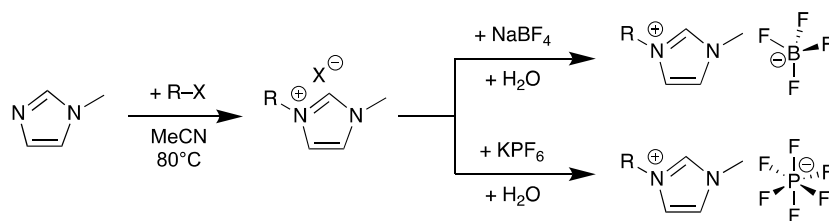


Figure 8. Synthetic pathways for imidazolium-based ILs.

Extraction of metals with imidazolium ILs is well described and has been widely investigated. In most cases, the ILs replace typical solvent extraction diluents. An initial study on metal extraction with

imidazolium-based ILs was reported by Visser et al. in 2001, which explored the feasibility of ILs for extraction of Na⁺, Sr⁺ and Cs⁺ [50]. However, extraction of PGMs with imidazolium-based ILs was first reported in 2013 [51]. The performance of imidazolium-based ILs in PGM extraction is summarized in Table 3. Most of the studies with imidazolium-based ILs did not use any diluents because most imidazolium-based ILs have low viscosity.

Table 3. Performance of imidazolium-based ILs in PGM extraction.

Cation	Anion	D	E(%)	Author and year	Ref.
C ₈ mim ⁺		Pt(4.3)	Pt(41)		
C ₈ dmim ⁺	Tf ₂ N ⁻	Pt(0.8)	Pt(8.9)	Genand-Pinaz et al., 2013	[51]
C ₁₂ (mim) ₂ ⁺		Pt(5.7)	Pt(37)		
C ₈ mim ⁺	Tf ₂ N ⁻	Pt(4.2)		Papaiconomou et al., 2013	[52]
C ₈ dmim ⁺		Pt(0.8)			
C ₈ mim ⁺		Ir(71)			
C ₈ dmim ⁺	Tf ₂ N ⁻	Ir(8.0)		Papaiconomou et al., 2014	[53]
C ₄ mim ⁺		Ir(3.2)			
C ₄ mim ⁺	Tf ₂ N ⁻		Pt(80), Pd(8)	Yang et al., 2014	[54]
C ₄ mim ⁺	PF ₆ ⁻		Pt(20), Pd(5)		
C ₄ mim ⁺			Pt(22), Pd(5)		
C ₆ mim ⁺	Tf ₂ N ⁻		Pt(60), Pd(8)	Yang et al., 2014	[57]
C ₈ mim ⁺			Pt(80), Pd(8)		
C ₁₂ mimCl + C ₈ mimPF ₆			Pt(82)		
C ₁₄ mimCl + C ₈ mimPF ₆			Pt(87)	Tong et al., 2015	[59]
C ₁₆ mimCl + C ₈ mimPF ₆			Pt(94)		
C ₈ mim ⁺	Tf ₂ N ⁻	Pt(6.4), Pd(0.1)		Papaiconomou et al., 2015	[32]
C ₈ mim ⁺	Tf ₂ N ⁻	Pt(18)		Papaiconomou et al., 2016	[56]
C ₄ mim ⁺	Br ⁻		Pt(99), Pd(99)	Liu et al., 2017	[58]
C ₈ mimTf ₂ N + P ₆₆₆₁₄ Cl			Pt(92), Pd(10)		
C ₈ mimTf ₂ N + P ₆₆₆₁₄ Tf ₂ N			Pt(59), Pd(8)	Kubota et al., 2017	[60]
C ₈ mim ⁺	Tf ₂ N ⁻		Pt(40), Pd(8)		

D: distribution ratio

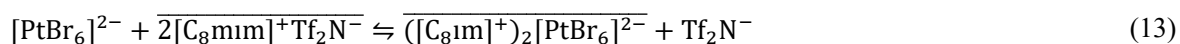
C_{*n*}mim⁺: *n*-alkylmethylimidazolium

C_{*n*}dmim⁺: *n*-alkyldimethylimidazolium

C_{*n*}bim⁺: *n*-alkylbenzimidazolium

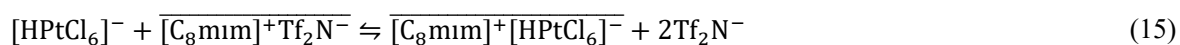
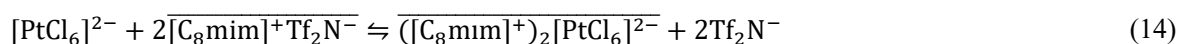
Papaiconomou et al. reported extraction and separation of Pt from Au using 1,2-dimethyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (C₈dmimTf₂N) and 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₈mimTf₂N) [52]. They found that efficient separation of Au and Pt is achievable using a simple two-step process based solely on ILs. In the first step, [AuCl₄]⁻ is extracted by

liquid–liquid extraction with the aid of C₈mimTf₂N. In the second step, Pt is extracted from water as [Pt(SCN)₆]²⁻ using C₈mimTf₂N. A similar approach was applied to separate Pt and Pd by a two-step process using the combination of P₆₆₆₁₄Br and C₈mimTf₂N [32]. In the first step, Pt was extracted as [PtCl₆]²⁻ using C₈mimTf₂N, and then extraction of [PdCl₄]²⁻ was performed with P₆₆₆₁₄Br. Genand-Pinaz et al. also reported the efficient extraction of Pt using water-soluble ILs such as C₈mimCl and C₁₂(mim)₂Br₂, which showed the effect of different ligands (Cl⁻, Br⁻ and SCN⁻) on the extraction efficiency of Pt [51]. [Pt(SCN)₆]²⁻ showed higher efficiency than [PtCl₆]²⁻ and [PtBr₆]²⁻ because of the presence of soft sulphur and hard nitrogen atoms, which favorably interact with the imidazolium ring [51]. Moreover, because of the smaller size of Cl⁻ compared with Br⁻, metal–chloro complexes have lower solvation energies than metal–bromo complexes. Thus, [PtBr₆]²⁻ exhibited higher efficiency than [PtCl₆]²⁻. The extraction mechanism between C₈mimTf₂N and [PtBr₆]²⁻ is as follows:



Papaiconomou et al. also reported extraction of Ir using imidazolium-based ILs [53]. A similar set of ILs was used in addition to 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C₄mimTf₂N). They reported that a longer alkyl chain gives a higher distribution coefficient. The study suggested that replacing the labile hydrogen on the imidazolium ring with a methyl group decreases the extraction efficiency because of the efficiency difference between C₈dmimTf₂N and C₈mimTf₂N [53].

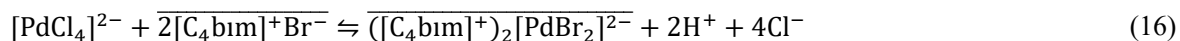
Yang et al. first reported extraction of Pt and Pd using an undiluted system of imidazolium-based ILs [54]. C₄mimTf₂N showed poor performance for Pt and Pd extraction. However, the PF₆⁻ anion significantly enhanced the extraction efficiency of Pt. For C₆mim and C₈mim, [PtCl₆]²⁻ favors ion pair formation with the cation part of the ILs owing to its relatively low charge density. In contrast, [PdCl₄]²⁻ with a larger hydration shell has less interdependency with the counterion, resulting in a lower preference for extraction via ion pair formation. Because the alkyl-chain length contributes to the ion pair stability, the cation with a longer alkyl chain resulted in better performance for Pt extraction. Extraction was expected to occur via an anion-exchange reaction, that is, the chloro complex anions transferred to the IL phase, while the Tf₂N⁻ anions were released into the aqueous feed solution. The anion-exchange equations for Pt extraction are as follows:



An in-depth study of the Pt extraction mechanism was reported by Papaiconomou et al. in 2016 [56]. They investigated the extraction mechanism of Pt using hydrophobic imidazolium-based ILs (e.g., C₈mimTf₂N). They found that the mechanism of metal extraction is typically mainly based on either ion exchange or ion-pair formation, with the latter being more favorable because it avoids undesirable loss of the ILs in the aqueous phase [55]. They also found that both the ion exchange and ion-pair formation mechanisms are equally applicable to metal extraction [56]. This uncertainty principle can also be applied to extraction of charged metal complexes with any hydrophobic IL.

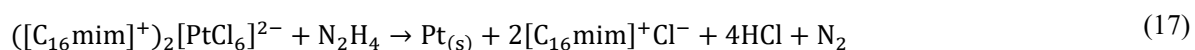
Most reports on PGM extraction using imidazolium-based ILs have tended to focus on extraction of Pt. Yang et al. investigated the extraction behavior of Pd in the extraction system [57]. However, extraction of Pd with C_nmim (n = 4, 6, or 8) X (X = Tf₂N⁻ or PF₆⁻) was poor. In 2017, Liu et al. reported a high Pd

extraction efficiency using 1-butyl-3-benzimidazolium bromide (C₄bimBr) [58]. Through the one-step separation method, high-purity Pd and Pt were recycled. The extraction efficiencies of both Pt and Pd were nearly 100%. Low concentration hydrochloric acid was favorable for Pd extraction. From X-ray diffraction, the mechanism of Pd extraction was considered to be the complexation mechanism in which one Pd(II) atom shared two bonding nitrogen atoms provided by two isolated C₄bimBr molecules. The extraction mechanism of Pd using the C₄bimBr system can be expressed as [58]:



Several reports on PGM extraction using mixed IL systems have been published in recent years. Tong et al. reported a mixed system of (C_nmimCl, *n* = 12, 14, and 16) and (C_nmimPF₆, *n* = 4, 6, and 8) imidazolium-based ILs for Pt extraction [59]. Under the optimum conditions, the C₁₆mimCl/C₈mimPF₆ system showed high extractability and selectivity for Pt over base metals (Mn, Cu, Co, Ni, Fe, and Al). We reported a mixed system of imidazolium- and phosphonium-based ILs for extraction of Pt and Pd. The mixture of P₆₆₆₁₄Cl and C₈mimTf₂N was used in the system. P₆₆₆₁₄Cl showed high extraction efficiencies for both Pt and Pd [60]. In addition, C₈mimTf₂N showed selectivity for Pt, albeit with lower extraction efficiency than P₆₆₆₁₄Cl. By mixing both ILs, the extraction efficiency drastically increased and the selectivity for Pt markedly improved.

Stripping of PGMs from imidazolium-based ILs has rarely been investigated. Most of the previously mentioned studies did not include a stripping step as part of the study. An initial study on PGM stripping was performed by Liu et al. in 2017 [58]. They reported efficient stripping of Pt and Pd from C₄bimBr using a mixture of CS(NH₂)₂ and HCl. The stripping percentage of Pd(II) was almost 100% because CS(NH₂)₂ has stronger ability to combine with Pd(II) than with the extractant C₄bimBr. Hydrazine has also been reported to be an effective stripping agent for Pt because it can reduce Pt in IL–Pt complexes to platinum powder [59]:



We investigated the stripping processes of Pt and Pd from a mixture of P₆₆₆₁₄Cl and C₈mimTf₂N. Stripping tests of Pt and Pd in the mixed IL system were performed using several different stripping agents, including HNO₃, HCl, NaCl, NH₄Cl, and ammonia [60]. Effective stripping performance was obtained with acids, such as HCl and HNO₃. HNO₃ showed higher stripping efficiency than HCl. Moreover, the degree of Pt stripping increased with increasing acid concentration. Papaiconomou et al. reported efficient stripping of Ir from C₄mimTf₂N and C₈dmimTf₂N using 8 or 12 mol L⁻¹ HCl, whereas HNO₃ was efficient to strip Ir from C₈mimTf₂N [53]. Despite various reports on PGM stripping from imidazolium-based ILs, there is no clear agreement on the stripping mechanism from imidazolium-based ILs.

3.3 Ammonium-based ILs

The fundamental procedure for synthesis of all quaternary ammonium and phosphonium salts is based on the Menshutkin reaction, in which a tertiary amine nucleophile replaces a leaving group in an aliphatic or aromatic nucleophilic substitution reaction [61]. The original nucleophile becomes the counterion in the quaternary salt. The most active alkylating reagents are alkyl fluorosulfonates, tosylates, and iodides, but for practical purposes bromides and chlorides are the most popular reagents. Other forms of quaternary ammonium-based ILs are usually produced by ion exchange with ammonium halide ILs (Figure 9). Mikkola et al. reported a number of straight-forward easy-to-perform recipes following the guidelines of published

methods, such as precipitation, evaporation, and microwave-assisted synthesis, for modification of existing ammonium-based ILs [62].

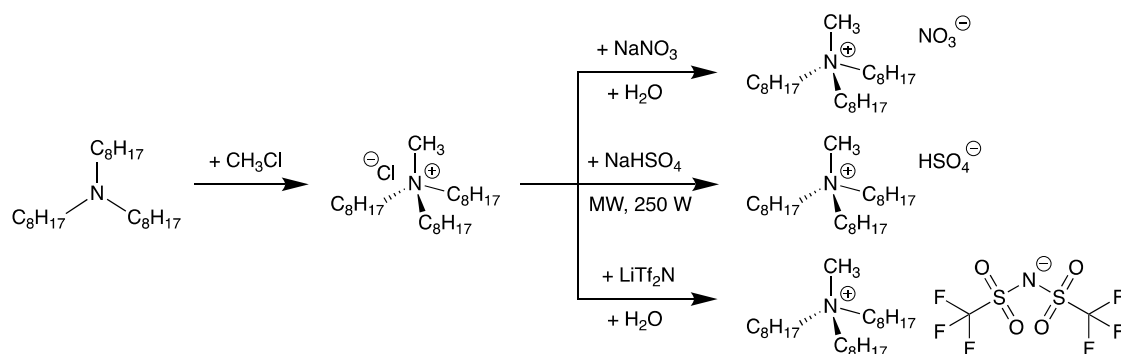


Figure 9. Synthetic pathways for various types of ammonium-based ILs.

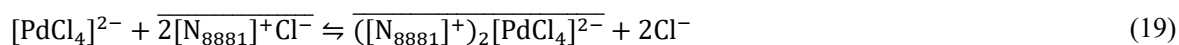
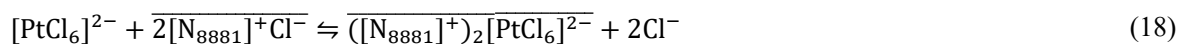
Quaternary ammonium salts, such as trioctylmethylammonium chloride ($N_{8881}Cl$), have been applied to solvent extraction of metals since 1978. McDonald et al. reported extraction of lead using $N_{8881}Cl$ [63]. However, $N_{8881}Cl$ was first recognized and mentioned as an IL by Giridhar et al. in 2005 [64]. Coincidentally, the first PGM extraction by ammonium-based ILs was performed in the same study. The performance of ammonium-based ILs is summarized in Table 4.

Table 4. Performance of ammonium-based ILs in PGM extraction.

Cation	Anion	D	E(%)	Author and year	Ref.
N_{8881}^+	Cl^-	Pd(20)		Giridhar et al., 2006	[64]
	NO_3^-	Pd(1.3)			
N_{8881}^+	Cl^-		Pt(96), Pd(37)	Lee et al., 2009	[71]
N_{8881}^+	Tf_2N^-	Pt(2.5), Pd(3.2)			
N_{888H}^+	NO_3^-	Pt(9600), Pd(24000), Rh(15)	Pt(91), Pd(99), Rh(13)	Katsuta et al., 2011	[65]
	Tf_2N^-	Pt(16), Pd(6.3)			
N_{8881}^+	Cl^-		Pt(99), Pd(99)	Wei et al., 2016	[67]
N_{8881}^+	HSO_4^-		Pt(99), Pd(5)	Kumar et al., 2017	[68]
N_{8881}^+	Cl^-		Pd(92)	Mohdee et al., 2018	[69]
N_{8888}^+	Tf_2N^-	Pt(0)		Boudesocque et al., 2019	[70]
	Dca^-	Pt(732)			
N_{6666}^+	Tf_2N^-	Pt(0.1)			
	SCN^-	Pt(1000)			
	Dca^-	Pt(319)			
	Br^-	Pt(1000)			

D: distribution ratio

Giridhar et al. investigated the potential of $N_{8881}Cl$ and $N_{8881}NO_3$ for extraction of Pd from nitric acid media [64]. The extraction efficiency of $N_{8881}NO_3$ increased with increasing HNO_3 concentration. The opposite trend was observed for $N_{8881}Cl$. The distribution ratio of Pd (D_{Pd}) values of $N_{8881}Cl$ were very high (~20) in the lower acid region owing to the strong complexation ability of the chloride ions present in $N_{8881}Cl$ [64]. Even though the efficiency was still low, ammonium-based ILs exhibited interesting behavior in extraction of Rh. The Rh extraction efficiency of $N_{8881}Cl$ increased with increasing HCl concentration from 1 to 10 mol L⁻¹. Protic ammonium-based ILs have also been reported to be extraction reagents for PGMs. Katsuta et al. investigated the potential of a mixture of trioctylammonium bis(trifluoromethanesulfonyl)imide ($N_{888H}Tf_2N$) and trioctylammonium nitrate ($N_{888H}NO_3$) for extraction of Pt and Pd [65]. The mixture was able to selectively extract Pt and Pd in the presence of other metals. The mixture performed better than $N_{8881}Cl$ and $C_{4mim}Tf_2N$. Addition of $N_{888H}NO_3$ greatly enhanced the extraction efficiency owing to its role as an anion exchanger. $N_{888H}NO_3$ itself is a potential extractant. $N_{888H}NO_3$ can effectively extract Pt and Pd at any HCl concentration. Among the quaternary ammonium-based ILs, extraction of Pd follows the order $N_{888H}NO_3 > N_{8881}NO_3 > N_{888H}Cl > N_{888H}Tf_2N > N_{8881}Tf_2N > C_{4mim}Tf_2N$, and extraction of Pt follows the order $N_{8881}NO_3 > N_{888H}NO_3 > N_{888H}Cl > N_{888H}Tf_2N > N_{8881}Tf_2N > C_{4mim}Tf_2N$ [66]. Wei et al. showed that the metal concentration plays an important role in Pt and Pd extraction [67]. $N_{8881}Cl$ tends to exhibit high efficiency at low metal concentration. The Pt and Pd efficiencies are lower than the Au efficiency, which can be extracted at low IL concentration and has high loading capacity. Extraction of Pt and Pd occurs by the anion-exchange mechanism. Thus, extraction of Pt and Pd with $N_{8881}Cl$ from 0.1 M HCl can be expressed as follows:

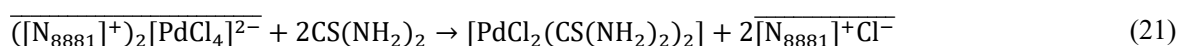
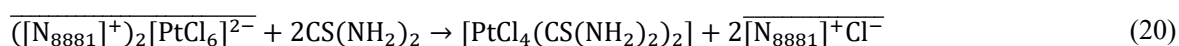


Because the trend for the metal-chloro complexes of PGMs by anion exchangers in the liquid phase is $[MCl_4]^- > [MCl_6]^{2-} > [MCl_4]^{2-} > [MCl_6]^{3-}$, gold complexes have less charge density than those of Pt and Pd. A complex with a lower charge density attracts less water molecules to form a smaller hydration shell, which is beneficial for complex formation by anion-exchange reactions [34,67]. Thus, the extraction efficiency follows the trend Au(III) > Pt(IV) > Pd(II).

Trioctylmethylammonium hydrogen sulfate ($N_{8881}HSO_4$) has also been reported to be an effective extraction agent for Pt [68]. Optimization of the Pd extraction system using $N_{8881}Cl$ was performed by Mohdee et al. using response surface methodology. The maximum efficiency of Pd extraction (94.68%) was achieved with IL concentration = 0.6 mol L⁻¹, pH = 2, stirring speed = 600 rpm, reaction time = 10 min, and temperature = 45°C [69]. According to the thermodynamic data, the extraction process was an endothermic reaction. A novel tetraalkylammonium halide substituted with various anions, such as Br⁻, DCA⁻, SCN⁻, and Tf₂N⁻, was used for extraction of Pt and Au [70]. Replacement of the bromide ion by these anions on the tetraalkyl bromide salt led to formation of ILs that are suitable for extraction experiments under mild conditions. The extraction mechanisms for Au(III), Pt(II) and Pt(IV) were based on formation of stable ion pairs between the tetraalkylammonium cation and the thiocyanato or halogeno complexes of the noble metals. The extraction efficiency was dependent on the hydrophilicity of the anion, and a more exchangeable anion resulted in a higher extraction yield. The extraction yield of Pt increased in the order DCA⁻ < SCN⁻, while

the Tf_2N^- anion did not extract any Pt owing to the higher charge density of Pt(IV) and the higher standard Gibbs energy than the Au(III) complex [51,69].

$\text{CS}(\text{NH}_2)_2$ has been widely applied as a recovery reagent for PGM-loaded ammonium-based ILs. Katsuta et al. reported almost quantitative stripping of Pt and Pd using 1 mol L^{-1} $\text{CS}(\text{NH}_2)_2$ in 1 mol L^{-1} HNO_3 [65]. A similar result was reported by Lee et al., who obtained 96.7% stripping efficiency for Pd using 0.75 mol L^{-1} $\text{CS}(\text{NH}_2)_2$ in 5 mol L^{-1} HCl [71]. Moreover, quantitative stripping of PGMs can be achieved even with a low concentration of $\text{CS}(\text{NH}_2)_2$. Wei et al. [67] reported that in the separation system, Pt and Pd were almost quantitatively stripped from N_{8881}Cl using 0.05 mol L^{-1} $\text{CS}(\text{NH}_2)_2$ in 0.1 mol L^{-1} HCl . However, in a binary mixture of Pt and Pd, $\text{CS}(\text{NH}_2)_2$ showed excellent selectivity for Pd. This trend with $\text{CS}(\text{NH}_2)_2$ has also been observed for other types of ILs, such as phosphonium-based ILs [37]. $\text{CS}(\text{NH}_2)_2$ possesses excellent stripping performance owing to its high affinity for PGMs. Stripping of Pt and Pd with $\text{CS}(\text{NH}_2)_2$ can be represented by the following reactions:



Katsuta et al. and Lee et al. also found that stripping of Pt from N_{8881}Cl and Pd from protic ammonium-based ILs can be achieved with HNO_3 , albeit in more than one stage [65,71]. Although the stripping efficiency of H_2SO_4 is lower than those of HNO_3 and $\text{CS}(\text{NH}_2)_2$, H_2SO_4 could offer stripping selectivity for Pd.

3.4 Other ILs

Although limited and not greatly investigated, other types of ILs have also been applied to PGM extraction. ILs derived from betainium, pyridinium, pyrrolidinium, piperidinium, and guanidium are some examples. The performance of these ILs is summarized in Table 5.

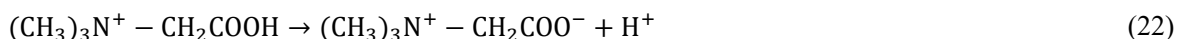
Table 5. Performance of various IL types in PGM extraction.

Cation	Anion	D	E(%)	Author and year	Ref.
1-butyronitrile-4-methyl pyridinium		Pd(50.3)			
1-methyl-2-pentene pyrrolidinium		Pd(1002)			
1-methyl-1-[4,5- bis(methylsulfide)]pentyl piperidinium	Tf_2N^-	Pd(10000)		Lee et al., 2012	[76]
1-methyl-2-pentene piperidinium		Pd(1017)			
1-butyronitrile-1-methyl piperidinium		Pd(148)			
1-octyl-1-methyl pyrrolidinium	Tf_2N^-	Ir(25.3)		Papaiconomou et al., 2014	[53]
1-octyl-3,5-dimethyl	Tf_2N^-	Ir(19)			

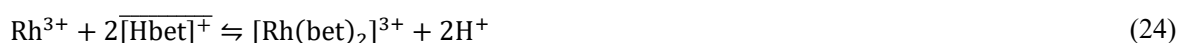
pyridinium					
Hexadecyl pyridinium	Cl ⁻	Pd(450)	Pd(99)	Tong et al., 2014	[78]
Betainium	Tf ₂ N ⁻		Pd(99) Rh(67) Ru(34)	Sasaki et al., 2014	[72]
Betainium	Tf ₂ N ⁻		Pd(83) Ru(97) Rh(91)	Ikeda et al., 2016	[73]
1-hexyl betainium	Br		Pt(99) Ir(75)	Yan et al., 2017	[75]
Betainium	Tf ₂ N		Ru(99) Rh(97)	Kono et al., 2018	[74]
2,2-diheptyl-1,1,3,3-tetramethylguanidinium	Br ⁻	Pt(72)	Pt(91)	Wang et al., 2019	[79]

D: distribution ratio

Takao's group investigated the potential of betainium-based ILs for PGM extraction [72-74]. In their initial study, they found that betainium bis-(trifluoromethanesulfonyl)imide (HbetTf₂N) showed good performance for Pd, Rh, and Ru extraction. At that time, HbetTf₂N achieved fairly high extraction efficiency for Rh compared with other studies [72]. PGM extraction decreased with increasing HNO₃ concentration. Deprotonation occurred through the extraction process, resulting in the zwitterionic betaine species ((CH₃)₃N⁺CH₂COO⁻, bet) [74]:



Deprotonated betainium has high affinity for PGMs, resulting in formation of coordination species, such as [M(bet)_m]^{m+}. It should be noted that the charge of the complex depends on the charge of the metal because betainium is a zwitterionic ligand and thus non-charged [73]. Extraction of the PGMs followed the cation-exchange process, in which H⁺ was released from [Hbet]⁺. A similar trend was also found in Rh extraction with HbetTf₂N. HbetTf₂N showed a clear dependency on the HNO₃ concentration. The dependency on the HNO₃ concentration indicates that Rh extraction proceeds by coordination of bet to Rh³⁺, followed by cation exchange. Thus, the extraction mechanisms of Pd and Rh with HbetTf₂N are as follows [74]:



Microwave irradiation efficiently assists extraction of substitution-inert PGMs like Ru and Rh using HbetTf₂N to give nearly quantitative yields within 101–102 s [74]. Rapid microwave heating also facilitates homogeneous mixing of the aqueous/IL biphasic system without vigorous shaking because of its thermomorphic behavior. In contrast to the efficient extraction of Mⁿ⁺, their separation seems to not be very simple from the similar *D* values and stripping efficiencies by HNO₃. The Pd/Rh separation factor was ≤1.04. However, the kinetic aspect of microwave-assisted extraction could be a solution to individually isolate each Mⁿ⁺. The thermomorphic behavior of HbetTf₂N can also significantly enhance extraction of Ru and Rh by increasing the temperature of extraction from 25 to 55°C [75]. Initial extraction of Ru and Rh took 3.5 and 113 days, respectively. However, at 55°C, extraction occurred in only 1 and 3 h to reach extraction efficiencies

of 99.2% and 96.6% for Ru and Rh, respectively.

Yan et al. also reported separation of Pt and Ir using the betainium-based IL C₆betBr, which was synthesized by an alkylation reaction (Figure 10) [75].

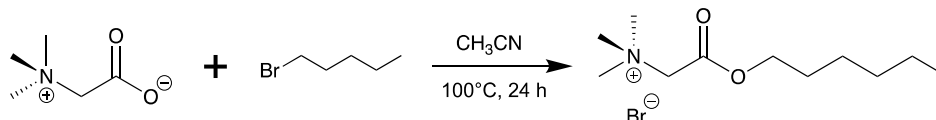
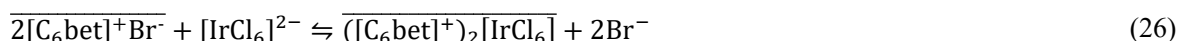
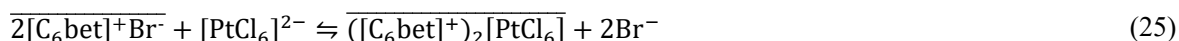


Figure 10. Synthetic pathway of C₆betBr.

C₆betBr was coupled with C₆mimTf₂N in the extraction process. In the absence of C₆betBr, C₆mimTf₂N showed reasonable extraction abilities for Pt and Ir with extraction efficiencies of 49% and 39%, respectively. However, after adding a small amount of C₆betBr to the system, the extraction efficiencies significantly improved, which means that C₆betBr is the key factor for improvement of the extraction efficiency [75]. The ¹H NMR spectrum of C₆bet–Pt was also in agreement with the regular pattern. Combined with the results obtained by UV–Vis spectroscopy, they proposed the anion-exchange mechanism between C₆betBr and Pt/Ir. Thus, the extraction pathways of Pt and Ir are as follows:



Lee et al. reported the use of various types of pyrrolidinium, piperidinium, and pyridinium ILs for extraction of noble metals, such as Pd, Au, and Ag [76]. The ILs included in the study were as follows: 1-methyl-1-[4,5-bis(methylsulfide)]pentylpyrrolidinium ([C₁PS₂pyrro]⁺), 1-methyl-1-[4,5-bis(methylsulfide)]pentylpiperidinium ([C₁PS₂pip]⁺), 1-methyl-2-pentenepyrrolidinium ([C₁C₅pyrro]⁺), 1-methyl-2-pentenepiperidinium ([C₁C₅pip]⁺), 1-butyronitrile-1-methylpiperidinium ([C₁C₄Npip]⁺), 1-butyronitrile-4-methylpyridinium ([C₁C₄Npyr]⁺), 1-methyl-1-octylpyrrolidinium ([C₁C₈pyrro]⁺), 1-methyl-1-octylpiperidinium ([C₁C₈pip]⁺), and 1-butyronitrile-1-methylpyrrolidinium ([C₁C₄Npyrro]⁺). All of the ILs were paired with the [Tf₂N]⁻ anion. However, only five ILs were applied to Pd extraction: C₁PS₂pipTf₂N, C₁C₅pyrroTf₂N, C₁C₅pipTf₂N, C₁C₄NpipTf₂N, and C₁C₄NpyrTf₂N. These five different ILs containing a disulfide and a nitrile group performed excellently. Pd seemed to form stable complexes with these ILs. The molecular structures of tetrachloropalladate ion complexes with nitrile-functionalized pyridinium ILs have been determined by X-ray diffraction [77]. The extraction percentages of these ILs were higher than 99.5%. These results indicate that disulfide, alkenyl, and nitrile groups play important roles as extractants.

Hexadecylpyridinium chloride (C₆pyrCl), which is an analogue of pyridinium-based ILs, has been developed as an extractant for Pd [78]. The amphiphilic structure of C₆pyrCl can significantly reduce the interfacial tension between the aqueous and organic phases, which effectively increases the extraction performance. Under the optimum conditions, the C₆pyrCl system showed high extractability for Pd and high selectivity for Pd over base metals (Cu, Co, Ni, Fe, Al and Sn). The extraction mechanism was investigated by UV–Vis spectroscopy. The results indicated formation of the C₆pyrCl–Pd complex, which was supported by Fourier transform infrared (FTIR) spectroscopy and ¹H NMR. The results showed that Pd has a stronger interaction with the C₆pyrCl cationic headgroup than the alkyl side chains.

Wang et al. first reported application of guanidinium-based ILs to PGM extraction [79]. Guanidium ILs have various interesting properties, such as a high degree of cation dispersion, flexibility of the three nitrogen atoms, and high thermal and chemical stability. In this report, a guanidium IL was synthesized following the reaction scheme shown in Figure 11 [79,80]. The final product, 2,2-diheptyl-1,1,3,3-tetramethylguanidium bromide (diHTMGBr), was applied to extraction of Pt.

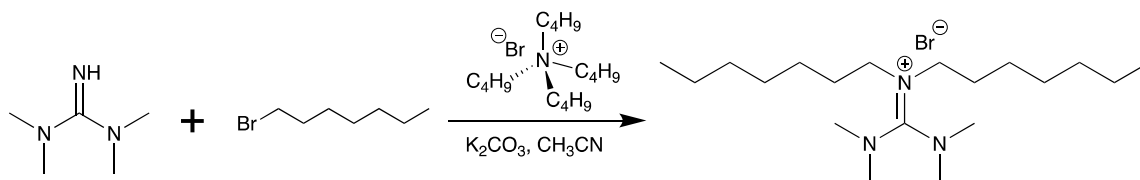


Figure 11. Synthetic pathway of diHTMGBr.

diHTMGBr showed excellent performance in recovery of Pt from aqueous solution. It showed high extractability and facile stripping of Pt. Under the optimum conditions, the extraction and stripping efficiencies reached 99.5% and 99%, respectively. diHTMGBr also showed excellent reusability, with no decrease in performance after reusing four times. The extraction mechanism was suggested to follow the anion-exchange mechanism, which was supported by a Job's plot and UV-vis and FTIR spectra, which showed the presence of the Pt-(diHTMGBr) complex in the organic phase. The point of interaction between PtCl_6^{2-} and diHTMGBr was investigated by an electrostatic potential map. The results showed that PtCl_6^{2-} prefers the three conjugated nitrogen as the point of interaction.

4. Conclusion

ILs are a class of salts that exist in the liquid state at low temperature, usually below 100°C. ILs have various fascinating properties that make them stand out over conventional solvent, such as low vapor pressure, non-flammable nature, and excellent chemical, electrochemical, and thermal stability. ILs have been applied in various fields related to the pharmaceutical, biomedical, environmental, and other industries. They have been used in leaching and solvent extraction processes for extraction of various metals. The physicochemical and electrochemical properties of ILs, such as their melting point, density, viscosity, chemical reactivity, ionic conductivity, and electrochemical window, can be optimized for specific tasks by proper design of the cations and anions. Application of ILs in PGM recovery has boomed in the last few decades. Some ILs work well in PGM extraction, and their performance can be tuned according to the specific needs. The combination of the cation and anion, adding functional groups, and modifying the IL structure have been used to improve the extraction performance. Mixing ILs with a conventional solvent has been attempted to widen the intrinsic limitations of the properties of ILs. Using ILs in extraction systems minimizes the use of organic solvents, and some ILs exhibit excellent regenerability properties, which can reduce operational costs. Because research and development of ILs in this area are steadily increasing, more fundamental approaches will be helpful to achieve real application of ILs in the metal manufacturing industry. ILs have been advertised as green solvents because of their non-volatility. However, the environmental benefits of ILs need to be carefully considered. Not all ILs are safe and non-toxic, especially during their synthesis. Therefore, development of

real green ILs for extraction is still a challenge.

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