Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates via Inner or Outer Sphere Binding

Citation for published version:
Wilson, AM, Grant, RA, Gordon, RJ, Love, JB, Morrison, CA, Macruary, KJ, Nichol, GS & Tasker, PA 2023, 'Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates via Inner or Outer Sphere Binding', *Solvent extraction and ion exchange*. https://doi.org/10.1080/07366299.2023.2197969

Digital Object Identifier (DOI):
10.1080/07366299.2023.2197969

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Solvent extraction and ion exchange

Solvent Extraction and Ion Exchange

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsei20

Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates *via* Inner or Outer Sphere Binding

A. Matthew Wilson, Richard A. Grant, Ross J. Gordon, Jason B. Love, Carole A. Morrison, Kirstian J. Macruary, Gary S. Nichol & Peter A. Tasker

To cite this article: A. Matthew Wilson, Richard A. Grant, Ross J. Gordon, Jason B. Love, Carole A. Morrison, Kirstian J. Macruary, Gary S. Nichol & Peter A. Tasker (2023) Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates *via* Inner or Outer Sphere Binding, Solvent Extraction and Ion Exchange, 41:4, 401-424, DOI: 10.1080/07366299.2023.2197969

To link to this article: https://doi.org/10.1080/07366299.2023.2197969

SOLVENT EXTRACTION AND ION EXCHANGE
2023, VOL. 41, NO. 4, 401–424
https://doi.org/10.1080/07366299.2023.2197969

Taylor & Francis
Taylor & Francis Group

Ditopic Extractants to Separate Palladium(II) and Platinum(IV) Chloridometalates *via* Inner or Outer Sphere Binding

A. Matthew Wilson[a], Richard A. Grant[b], Ross J. Gordon[b], Jason B. Love[a], Carole A. Morrison[a], Kirstian J. Macruary[a], Gary S. Nichol[a], and Peter A. Tasker[a]

[a]EastCHEM School of Chemistry, Edinburgh, UK; [b]Johnson Matthey Technology Centre, Reading, UK

ABSTRACT

New thioetheramide ligands (L, $PhS(CH_2)_nCONRR'$) co-extract Pd(II) and Pt(IV) from acidic chloride solutions. The Pd is transferred to a water-immiscible phase as a $[Pd(L)_2Cl_2]$ complex with thioether groups in the inner sphere whilst Pt is extracted in an outer-sphere assembly, $[(LH)_2{\cdot}PtCl_6]$, containing protonated reagent molecules LH^+ that charge-balance the chloridoplatinate dianion, $[PtCl_6]^{2-}$. The much higher kinetic and thermodynamic stability of the Pd(II) complex makes it possible to strip the Pt into a weakly acidic aqueous phase before recovering the Pd by back-extraction into aqueous ammonia to form $[Pd(NH_3)_4]Cl_2$, thereby separating the two elements. An alkyl spacer group with two methylene units between the thioether (S) and amide (C) atoms is a stronger extractant for both metals than those with one or three methylene units. The extractants reject trianionic chloridometalates with higher hydration energies such as $[IrCl_6]^{3-}$. X-ray structures of two $[Pd(L)_2Cl_2]$ complexes (L, $PhSCH_2CONH\text{-}n\text{-}C_4H_9$ or $PhS(CH_2)_2CONH\text{-}n\text{-}C_4H_9$) have planar coordination with a *trans*arrangement of the thioether groups and geometries very similar to those predicted by DFT calculations. These calculations show that addition of a proton to the proligands L generates a pseudochelate with the added H^+ located between the S atom and the carbonyl O atom. In contrast to related ether- and amino-amide extractants, this pseudochelate ring is broken in the $[(LH)_2.PtCl_6]$ assemblies formed by the thioetheramides and the OH^+ and NH units make the close contacts to the $PtCl_6{}^{2-}$ ion.

KEYWORDS
Recovery of platinum group metals; separation of Pd and Pt; solvent extraction; ditopic extractants

Introduction

Major technical challenges are associated with the recovery of the platinum group metals (PGMs) from minerals because they are usually present as complex mixtures in such low concentrations that their direct recovery is not practicable. Instead, the minerals undergo comminution followed by froth

CONTACT Peter A. Tasker p.a.tasker@ed.ac.uk EastCHEM School of Chemistry, Edinburgh EH9 3FJ, UK

Supplemental data for this article can be accessed online at https://doi.org/10.1080/07366299.2023.2197969.

flotation then pyrometallurgy and finally leaching to produce a concentrate for refining.[1,3] Recovery from secondary sources such as spent catalysts is also difficult.[2,4,5] Most commonly, separation and purification are performed by multiple hydrometallurgical steps following dissolution in HCl under oxidizing conditions.[6] The resulting pregnant leach solutions contain the PGMs as their chloridometalate anions, $[MCl_x(H_2O)_z]^{y-}$[7] The work in this article focuses on a strategy to co-extract Pd and Pt in a single step, coupled with their subsequent separation by exploiting differences in their coordination chemistry.

Very different flowsheets have been used in commercial operations to recover PGMs from acidic chloride streams, employing a variety of techniques to separate components, for example by crystallization, precipitation, distillation (after conversion of Ru and Os to their tetroxides), ion exchange, and solvent extraction.[8–10] Solvent extraction is a favored option because processes can be operated continuously and the extractants can be recycled.[11] One of the challenges in using solvent extraction to recover PGMs from solutions containing their chloridometalates is that these complexes are generally kinetically inert and it is impractical to use reagents to generate neutral complexes which are soluble in a water-immiscible organic phase by displacement of chloride ions within the timescale of a continuous process, for example as in:

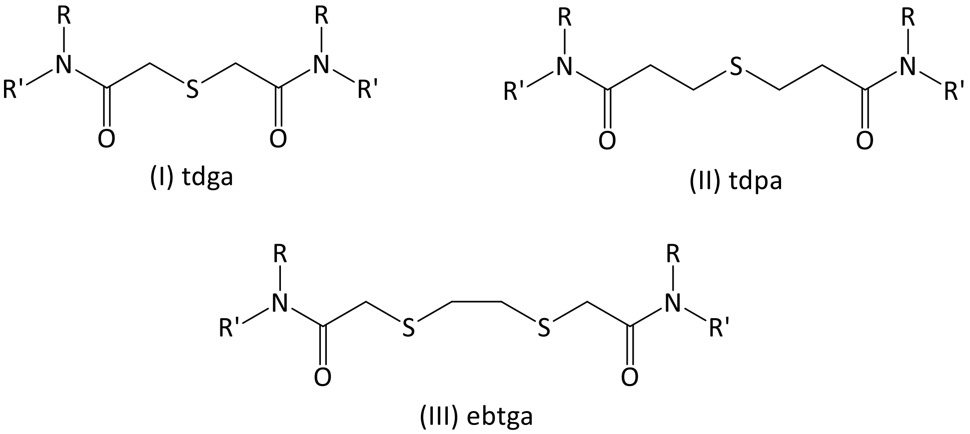
$$[MCl_x]^{y-} + y\,L_{(org)} \rightleftharpoons [L_y MCl_{x-y}]_{(org)} + yCl^- \qquad (1)$$

In this and the following equations, "$_{(org)}$" specifies that the species is present in the water-immiscible phase. Otherwise entities are present in the aqueous phase. Pd(II) is a notable exception. Its classification as a soft metal cation[12–14] ensures that it has a high affinity for sulfur-containing ligands and the higher kinetic lability of $[PdCl_4]^{2-}$ relative to most other PGM chloridometalates, enables selective recovery by di-*n*-hexyl or di-*n*-octylsulfides from oxidative chloride leach solutions as in[15]:

$$[PdCl_4]^{2-} + 2R_2S_{(org)} \rightleftharpoons [PdCl_2(SR_2)_2]_{(org)} + 2Cl^- \qquad (2)$$

An excellent and comprehensive review of thioether and other Pd-extractants has been published recently.[16] Unfortunately, processes involving the thioether extractants are slow and the reagents are relatively easily oxidized under operating conditions. Thiodiglycolamides (I) and related compounds (II – III) (Figure 1) have proved to be effective Pd-extractants from chloride media including streams derived from the leaching of spent catalysts.[4,16–20] Ammonia solutions are commonly used to strip the Pd(II) from the organic phase, regenerating the extractant as in:

$$[PdCl_2(SR_2)_2]_{(org)} + 4NH_3 \rightleftharpoons [Pd(NH_3)_4]^{2+} + 2Cl^- + 2R_2S_{(org)} \qquad (3)$$



(I) tdga

(II) tdpa

(III) ebtga

Figure 1. The structures of thiodiglycolamide-type Pd(II) extractants.[4,17–20] Type **I** extractants frequently carry the abbreviation "tdga" prefaced by a definition of the *N*-alkyl substituents e.g. "*N,N′*-dimethyl-*N,N′*-dicyclohexyl-tdga" and, similarly, abbreviations for **II** and **III** are based on "tdpa" and "ebtga".

As $[PdCl_2(NH_3)_2]$ has a very low solubility in water, Pd is usually stripped using excess ammonia, giving the soluble tetra-ammine complex.

The platinum in the acidic chloride leach solutions is present as the kinetically inert anion $[PtCl_6]^{2-}$, and an entirely different class of extractant is used in its recovery.[7] Hydrophobic protonated reagents generate charge neutral assemblies in which the inner sphere remains intact:

$$[PtCl_6]^{2-} + 2H^+ + 2L_{(org)} \rightleftharpoons [(LH)_2{\cdot}PtCl_6]_{(org)} \tag{4}$$

In these assemblies, the charge-diffuse, 'soft', anion $[PtCl_6]^{2-}$ forms secondary bonding interactions with cationic X-H+ or polarized C-$H^{\delta+}$ groups in the extractant.[21–24] If very weakly basic extractants such as amides are used, then the platinum can be readily stripped from the organic phase by contacting with weakly acidic aqueous HCl as in[25]:

$$(LH)_2{\cdot}[PtCl_6]_{(org)} \rightleftharpoons H_2PtCl_{6(aq)} + 2L_{(org)} \tag{5}$$

The aim of the work in this article is to establish whether *a single ditopic extractant* containing a thioether and an amide group can be used to co-extract Pd and Pt and whether their separation can be achieved by selectively stripping the Pt as in Equation 5, followed by the Pd as in Equation 3. This strategy is outlined in Figure 2. It has the advantage of simultaneously removing the two PGMs which are usually present in the highest concentrations, *simplifying the overall flowsheet and requiring the use of one less solvent extractant*. With the exception of **4**, the new extractants (see Figure 3) are *phenyl*thioether analogues of the *alkyl*thioethers which have been reported previously.[26]

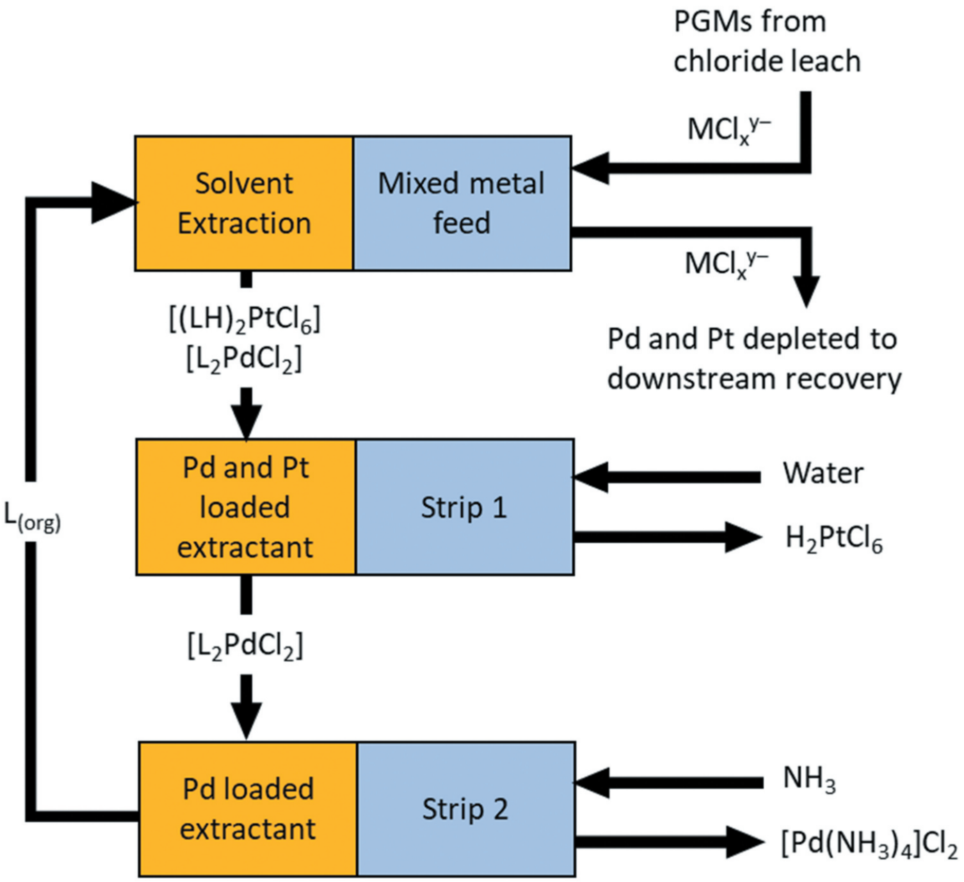
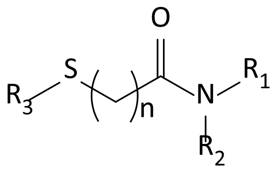


Figure 2. The proposed flowsheet for the recovery of Pt and Pd from acidic chloride leach streams.

Materials and methods

All solvents and reagents were used as received from Sigma-Aldrich, Fisher Scientific UK Ltd., VWR International Ltd. (UK) or Alfa Aesar. Deionised water was obtained from a Milli-Q purification system. Toluene, CH_2Cl_2 and tetrahydrofuran (THF) were dried by passing over activated alumina and stored over activated 4 Å molecular sieves. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35–70 μm) employing the method reported by Still.[27]

Nuclear magnetic resonance (NMR) spectroscopy. ^1H NMR were recorded at 298 K on a Bruker AVA400, Bruker AVA 500 or a Bruker AVA600 spectrometer, at 399.90, 500.12, and 599.85 MHz, respectively, and $^{13}C\{^1H\}$ NMR on Bruker AVA400, Bruker AVA 500 or Bruker AVA600 spectrometers operating at 100.55, 125.76, and 150.83 MHz, respectively. ^1H and $^{13}C\{^1H\}$ NMR were referenced internally to residual solvent signals. Chemical shifts are quoted in δ (ppm).



Extractant/ ligand	n	R_1	R_2	R_3
1	1	2-ethylhexyl	H	phenyl
2	1	*n*-butyl	H	phenyl
3	1	*iso*-tridecyl	H	phenyl
4	1	2-ethylhexyl	2-ethylhexyl	phenyl
5	2	2-ethylhexyl	H	phenyl
6	2	*n*-butyl	H	phenyl
7	2	*iso*-tridecyl	H	phenyl
8	2	2-ethylhexyl	H	2-ethyhexyl
9	3	2-ethylhexyl	H	phenyl
10	3	*n*-butyl	H	phenyl
11	3	*iso*-tridecyl	H	phenyl
12[a]	3	2-ethylhexyl	H	phenyl

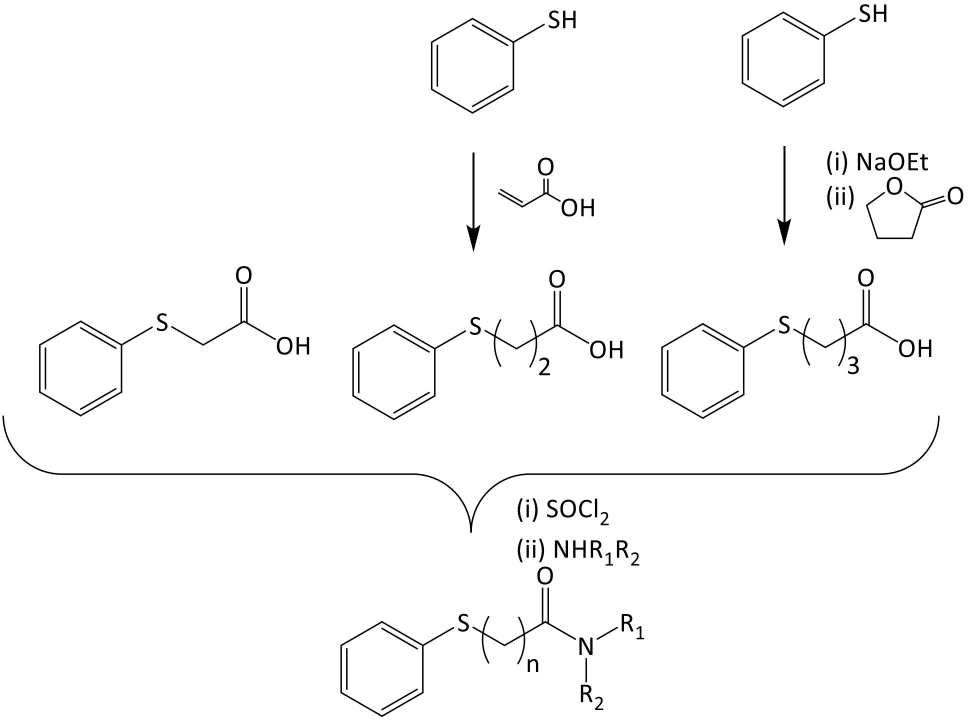


Figure 3. The thioetheramides used in this work and the reactions involved in their syntheses. [a] **12** has the same structure as **9**, but with the S atom of the thioether group replaced by an O atom.

Infrared (IR) spectra were obtained on a Perkin Elmer Spectrum85 FT/IR spectrometer either as a thin film on sodium chloride plates or sampled directly on a Pike MIRacle Single Reflection ATR with a diamond/ZnSe crystal. Absorption peaks are reported in wavenumbers (cm^{-1}). Elemental analyses were determined by Mr. Stephen Boyer at London Metropolitan University, School of Human Sciences, London, N7 7DD. Mass spectra were recorded on a MAT 900×P electron impact (EI) spectrometer or a Thermo-Fisher LCQ Classic spectrometer.

ICP-OES analysis was carried out using a Perkin Elmer Optima 5300DV or an Agilent Technologies 725 Spectrometer. Aqueous sample solutions were taken up using a peristaltic pump into a Gem Tip cross-flow nebulizer and a Scotts spray chamber at a rate of $1.5\,mL\ min^{-1}$. Samples were analyzed employing a radio frequency (RF) forward power of 1400 W and argon gas flows of 15, 0.2, and $0.75\,L\ min^{-1}$ for plasma, auxiliary, and nebulizer flows. Organic sample solutions in butan-1-ol or 1-methoxy-2-propanol were taken up into a Gem Tip cross-flow nebulizer and a Glass Cyclonic spray chamber at a rate of $2.0\,mL\ min^{-1}$. Samples were analyzed employing a RF forward power of 1500 W and argon gas flows of 20, 1.4, and $0.45\,L\ min^{-1}$ for plasma, auxiliary, and nebulizer flows. ICP-OES data were processed using WinLab32 for ICP-OES, version 3.0.0.0103. ICP-OES calibration standards for platinum, palladium, iridium, and ruthenium in 10% hydrochloric acid were obtained from VWR International Ltd. (UK).

Single crystal X-ray data sets were collected on a Rigaku Oxford Diffraction SuperNova diffractometer with Mo-Kα for (*trans*-$[Pd(\mathbf{2})_2Cl_2]$) and Cu-Kα for (*trans*-$[Pd(\mathbf{6})_2Cl_2]$) radiation. An Oxford Cryostream 700+ Cooler at either 170 K (*trans*-$[Pd(\mathbf{2})_2Cl_2]$) or 200 K (*trans*-$[Pd(\mathbf{6})_2Cl_2]$) was used to maintain a constant crystal temperature throughout data collection. Complete data have been deposited in the Cambridge Structural Database (CDS): *trans*-$[Pd(\mathbf{2})_2Cl_2]$) and *trans*-$[Pd(\mathbf{6})_2Cl_2]$ with Deposition Numbers 2,173,061 and 2,173,062, respectively.

Details of the syntheses and characterization of new thioetheramide extractants **1–11** listed in Figure 3 are provided in the Supporting Information, section A. The etheramide extractant **12** was prepared as described previously.[22,25]

Density functional theory calculations were performed using the Gaussian16 software package, utilizing the 6-31 G* basis set, coupled to the B3LYP level of theory.[28]

For extraction experiments, stock solutions of **1–12** (ca. $1.0\,mol\ L^{-1}$) were made up in Multisolve 150 or in analytical grade toluene. Varying volumes of these stock solutions were transferred to glass screw top vials and diluted to 5 mL with the appropriate water-immiscible solvent to give extractant concentrations ranging from 0.01 to $1.00\,mol\ L^{-1}$. Metal stock solutions containing Pd(II) ($0.01\,mol\ L^{-1}$), Pt(IV) ($0.01\,mol\ L^{-1}$) or Ir(III) ($0.005\,mol\ L^{-1}$) were prepared by dissolving the appropriate metal chloride in 6 M HCl. Aliquots of

5 mL were added to the vials containing the extractant solutions and the mixtures were stirred at 1000 r.p.m. at room temperature for 24 h. The phases were allowed to separate. A 0.5 mL sample of the aqueous phase was diluted to 10 mL with deionised water or with 1-methoxy-2-propanol. Samples of 0.5 mL of the water-immiscible phase were diluted to 10 mL with 1-methoxy-2-propanol and the metal content of these was determined by ICP-OES.

Results and discussion

Synthesis of new thioamide proligands and extractants

The thioetheramide reagents selected to establish proof of concept for the flowsheet in Figure 2 are shown in Figure 3. The secondary amide unit CO.NHR in these is known to be capable of protonation by strong acid (6 M HCl was used in this work),[22] allowing the transport of $[PtCl_6]^{2-}$ into a water-immiscible phase as shown in Equation 4. The influence of the disposition of the thioether group relative to the amide should be revealed by varying the linking group from one to three methylene units ($n = 1$ to 3, Figure 3).

The new extractants were prepared as outlined in Figure 3. An excess of amine was used in the final stage of thioamide ligand syntheses to enhance yields by neutralizing the liberated HCl. However, it was necessary to remove the excess of unreacted free amine because amines are known to form complexes with PGM in the organic phase when protonated, as in $(\text{amineH})_2{\cdot}PtCl_6$.[29,30] The presence of such amine complexes could lead to inaccurate reporting of PGM extraction if not removed before solvent extraction studies. The different methods used to remove the excess amine are described in the supplementary material (section A). Solutions of the extractants in glacial acetic acid were titrated with 0.1 M perchloric acid to determine the residual amine concentrations in the purified extractants.

PGM uptake into toluene by the ditopic thioetheramides

An initial screening of the extraction properties of the new reagents was undertaken to probe the influence of the spacer group between the thioether group and the amide, was undertaken using the 2-ethylhexyl-substituted reagents **1**, **5** and **9**. The loading of Pd(II) from a 0.01 M solution in 6 M HCl is shown in Figure 4. These compounds are all good extractants, showing > 90% uptake of Pd(II) at concentrations > 0.2 mol L^{-1}. At lower concentrations **5**, is the strongest extractant.

The thioamide reagents are much weaker extractants for Pt(IV) than for Pd(II) (Figure 5). Only at extractant concentrations > 0.4 M do loadings exceed 90%. The variant of **9**, in which the sulfur atom of the thioether group has been replaced by an oxygen atom (**12**) has a very similar loading

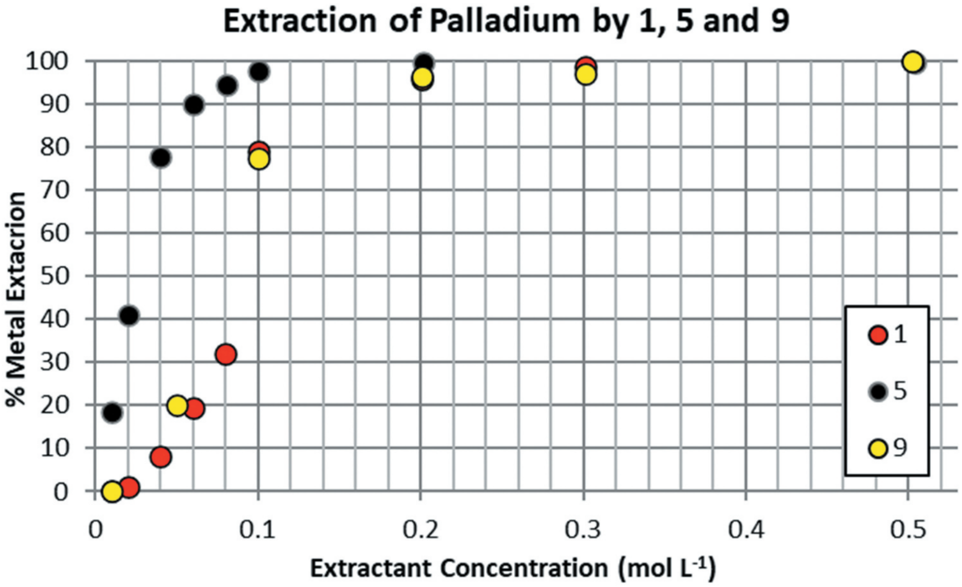


Figure 4. Extraction of Pd(II) from aqueous solutions (0.01 M Pd in 6 M HCl) into toluene solutions of extractants **1**, **5**, or **9** as a function of extractant concentration. **1**, **5**, and **9** have have one, two, or three methylene groups separating the thioether and the amide functionalities.

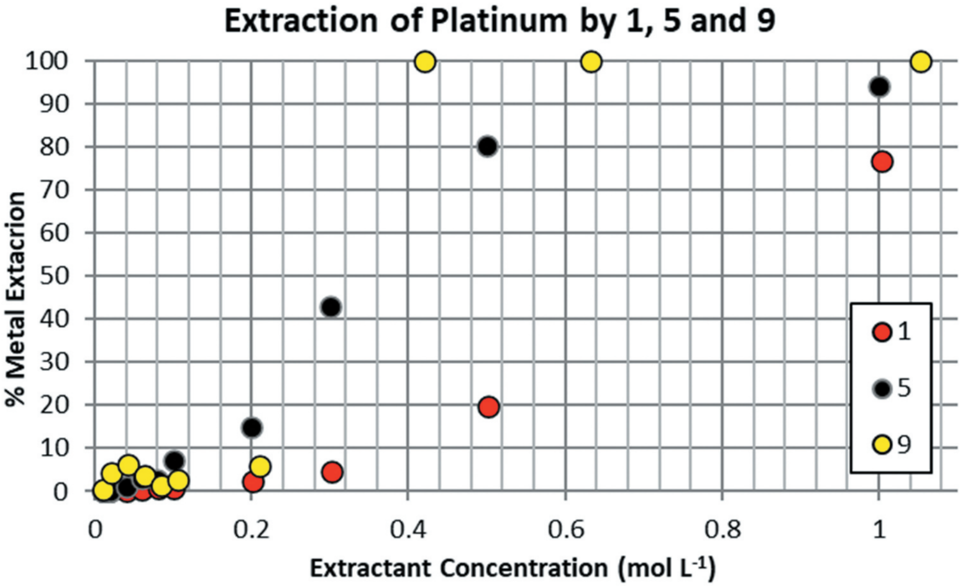


Figure 5. The dependence of uptake of Pt(IV) from aqueous solutions (0.01 M in 6 M HCl) into toluene solutions of extractants **1**, **5** and **9** as a function of extractant concentration.

capacity. This implies that the thioether unit does not form an *inner-sphere* complex with the Pt(IV) ion and supports the proposition that it is the protonated amide functionality which is involved in binding to the $[PtCl_6]^{2-}$ anion in its *outer* sphere. Such assemblies are formed by extractants containing only an amide functionality.[25] This outer-sphere transport mechanism is consistent with the observation that the trianionic chloridometallates $[MCl_6]^{3-}$ are much more weakly extracted (see section **Selectivity of PGM extraction** below). The higher hydration energy of the trianionic species such as $[IrCl_6]$[2] disfavors their transport from the aqueous phase as in Equation 6. The influence of hydration energy of charged species on the ability to form charge-neutral species with extractant molecules has been known for some time in the solvent extraction community.[11,31] More recently, it has been referred to as the "Hofmeister bias"[32] based on a study in 1888 of the influence different salts had on the of coagulation of proteins.[33]

$$[IrCl_6]^{3-}+3H^{+}+3R_{(org)} \rightleftharpoons (RH)_3{\cdot}[IrCl_6]_{(org)} \tag{6}$$

These preliminary results were encouraging as they show that the extractant concentration, or extent of extractant protonation by the acid, could be used to enable selectivity of recovery of Pd over Pt. The results also suggest that the separation of Pd(II) and Pt(IV) from acidic chloride streams would be feasible using a ditopic thioetheramide extractant provided that selective stripping can be achieved as outlined in Figure 2. After equilibration, an inner sphere complex would be formed with Pd(II) and an outer-sphere assembly with Pt(IV).

Unfortunately, when extractions were performed using the 2-ethylhexyl functionalized extractants **1**, **5** and **9** on mixed-metal {Pd(II), Pt(IV) and Ir(III)} feed solutions, there was a tendency for a third phase to form, particularly at lower extractant concentrations (0.10 M, see Figure 6) and the majority of the Pd and Pt is located in this phase (very little Ir was found in the organic or in the third phase). The tendency to form a third phase was minimized using the *iso*-tridecyl functionalized extractants **3**, **7** and **11** and consequently these were selected to demonstrate the feasibility of the flowsheet in Figure 2 (see section **Extraction using commercial diluents**, below).

Structures of Pd(II) complexes

Solid forms of the Pd(II) complexes of the *n*-butyl-substituted ligands **2** and **6** were isolated from toluene solutions after contacting with an aqueous solution of $PdCl_2$ in 6 M HCl. Crystals of *trans*-[Pd(**2**)$_2$Cl$_2$] suitable for X-ray structure determination were obtained directly from such a toluene solution, whilst those of *trans*-[Pd(**6**)$_2$Cl$_2$] were grown by diffusion of hexane into a toluene solution. Their structures are shown in Figure 7. In both cases, the Pd atoms lie on crystallographic inversion centers and, as inferred from the extraction data

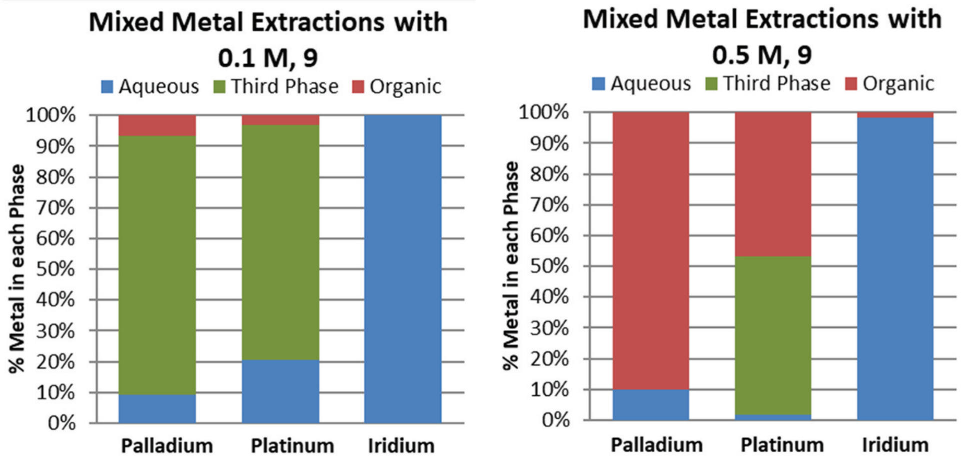


Figure 6. Distribution of Pd, Pt, and Ir between the organic, aqueous, and third phases after contacting 0.10 and 0.5 M solutions of **9** in toluene with the mixed metal feed solution containing 0.1 M of each metal in 6 M HCl (left and right).

above, the thioamide ligands are bonded in the inner sphere through the sulfur atoms of the thioether groups with the palladium centers adopting *trans*-square planar geometries.

The amide groups do not interact with the Pd atoms and instead form strong intermolecular N-H···O=C hydrogen bonds which generate well-defined sheets in the extended structure (Figure 8). Formation of these H-bonded networks lowers solubility and for this reason the *iso*-tridecyl functionalized were selected for much of the solvent extraction work performed in hydrocarbons. Low solubility and third phase formation are, as expected, even more problematic with the extraction of Pt via formation of the “ionic” assemblies, $[(\mathbf{L}H)_2 \cdot PtCl_6]$. In this case, reverse micelles can readily form which are organophobic and can associate into third (liquid or solid) phases.[34–38]

The formation of *inner sphere* complexes $[Pd\mathbf{L}_2Cl_2]$ within the time of mixing by the reagents in Figure 3 is worthy of note. Normally extractions to yield such Pd(II) complexes are slow.[16] Possibly, the much faster processes involving **1** – **12** arise because the initial rapid formation of *outer sphere* assemblies, $[(\mathbf{L}H)_2 \cdot [PdCl_4]$, allows an intramolecular mechanism (“approximation catalysis”) to occur for substitution of coordinated chloride.

Whilst these X-ray structures demonstrate that inner sphere attachment of the thioetheramides is favorable in the crystalline state, they do not prove that it is present in solution. Nevertheless, the crystalline samples of *trans*-$[Pd(\mathbf{2})_2Cl_2]$ and *trans*-$[Pd(\mathbf{6})_2Cl_2]$ were isolated from toluene, the same diluent that was used in solvent extraction experiments, and the structure/activity correlations in these experiments discussed above are all consistent with this presumption. A comparison of the ^{1}H NMR spectrum of a d_6-benzene solution of the 2-ethylhexyl substituted extractant **5** with those obtained after

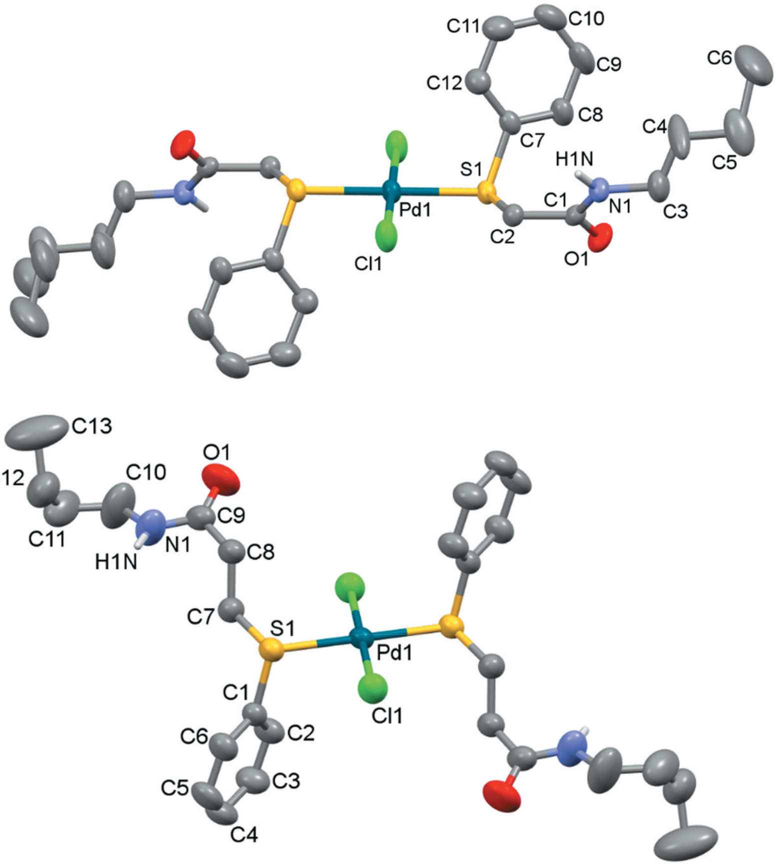
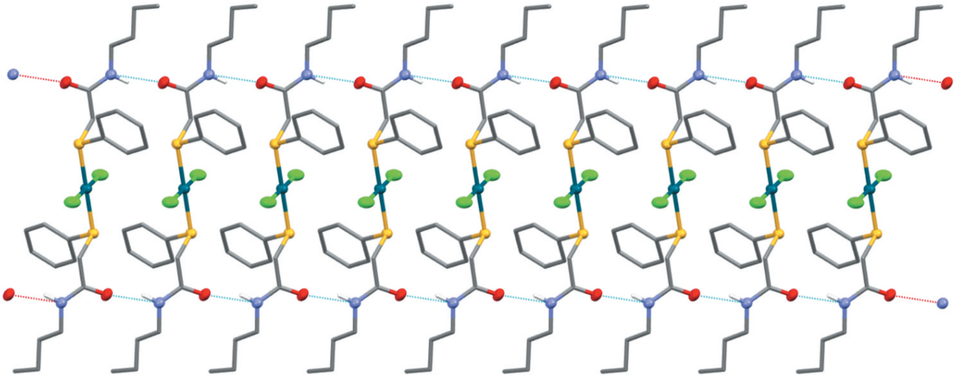


Figure 7. The X-ray crystal structures of *trans*-[Pd(**2**)$_2$Cl$_2$] (top) and *trans*-[Pd(**6**)$_2$Cl$_2$] (bottom). For clarity, disordered components in the ^{n}Bu groups and all hydrogen atoms except those involved in hydrogen bonding are omitted (displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (°): *trans*-[Pd(**2**)$_2$Cl$_2$] Pd1-Cl1 2.2952(7), Pd1-S1 2.3251(6), Cl1-Pd1-S1 94.45(2); *trans*-[Pd(**6**)$_2$Cl$_2$] Pd1-Cl1 2.2994(5), Pd1-S1 2.3164(5), Cl1-Pd1-S1 96.07(2).

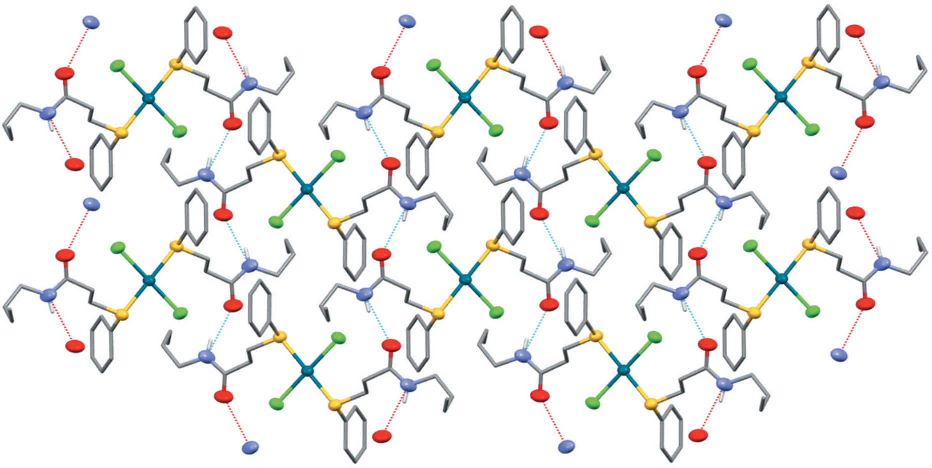
contacting with a 6 M aqueous HCl and with a 6 M aqueous HCl containing PdCl$_2$ (see Figures B1-B3 in the Supporting Information) is consistent with the formation of the inner sphere complex *trans*-[Pd(**5**)$_2$Cl$_2$].

Structures of assemblies containing Pt(IV) complexes

All evidence from earlier work on the modes of action of the amino- and ether-containing analogues, **V** and **VI** Figure 9, of the extractants listed in Figure 3 is consistent with two molecules of a protonated form associating with the chloridoplatinate anion, PtCl$_6^{2-}$, to generate a charge neutral, hydrocarbon-soluble assembly (Equation 4).[21,23] A common feature of the extraction by the amino- and ether-containing reagents **V** and **VI** is that the added proton forms a strong intra-ligand H-bond with the amide



trans-[Pd(**2**)$_2$Cl$_2$]



trans-[Pd(**6**)$_2$Cl$_2$]

Figure 8. The intermolecular N-H···O=C hydrogen bonding networks in the X-ray crystal structures of *trans*-[Pd(**2**)$_2$Cl$_2$] [N1-O1′ 2.808(3) Å] and *trans*-[Pd(**6**)$_2$Cl$_2$] [N1-O1′ 2.929(6) Å].

carbonyl oxygen atom (see Figure 9). This "chelation" of the proton makes it unfavorable for the$^+$X-H bond to interact with chloridometalate anions. The templating of the amide N-H and the polarized C-H$^{\delta+}$ bonds has important consequences in ensuring that the extractant binds more strongly to the charge diffuse $[PtCl_6]^{2-}$ ion than to the charge dense Cl^- ion.[21]

The concentration dependence of the uptake of Pt by the thioetheramide extractant **7** is also consistent with formation of a 2:1 assembly, $[(7H)_2{\cdot}PtCl_6]$ as the plot of logD against log[7] shown in Figure 10 has a slope of 0.50.

Structures of Pt(IV) complexes predicted by DFT calculations

In the current work, it proved impossible to isolate crystals of the Pt(IV) assemblies suitable for X-ray structure determinations. Consequently, a series

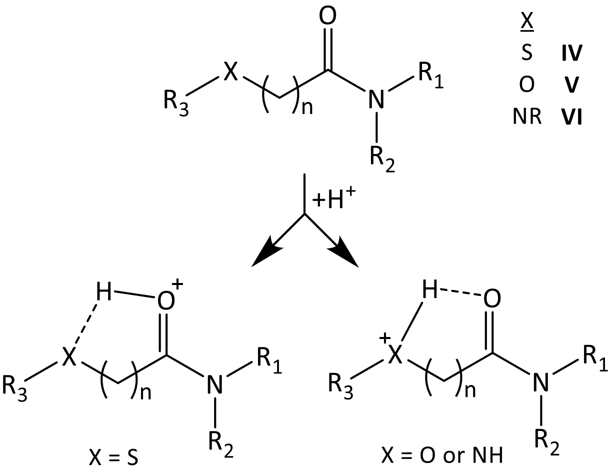


Figure 9. Etheramide (**V**) and aminoamide (**VI**) analogues of the thioetheramide extractants (**IV**) used in this work.

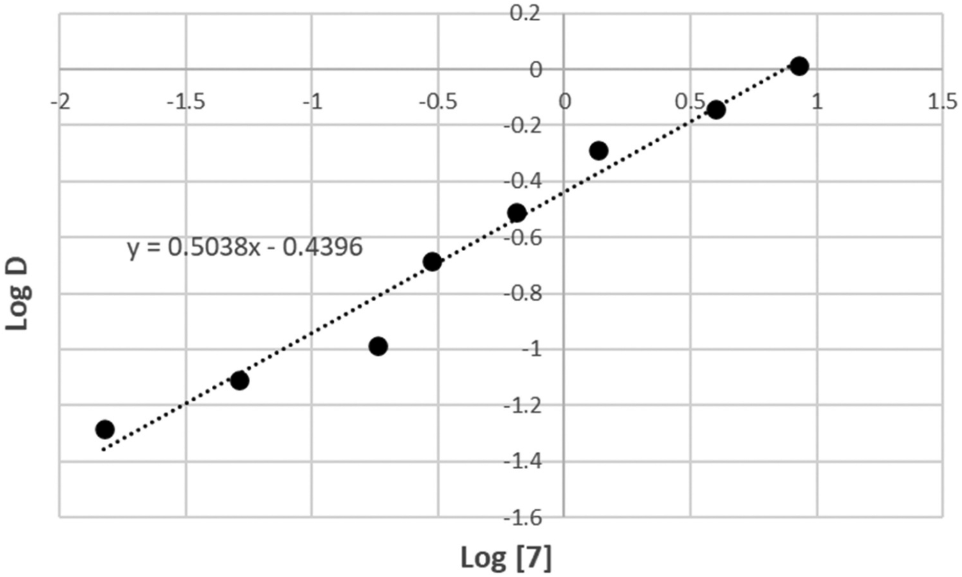
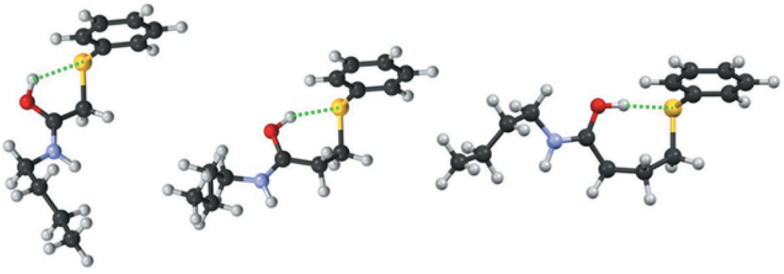


Figure 10. Plot of $\log D_{[Pt(org)]/[Pt(aq)]}$ against log[**7**] (slope of 0.50).

of density functional theory (DFT) calculations was carried out to probe the influence that increasing the number of methylene groups in the linkage between the ether and amide groups has on the structures of the complexes formed. Calculations were carried out on the *n*-butyl-containing proligands **2**, **6**, and **10** to reduce the number of possible conformers and thus simplify computations.

The lowest energy forms of the protonated extractants **2**, **6**, and **10** have the added proton bound to the carbonyl oxygen atom in each case. The formation

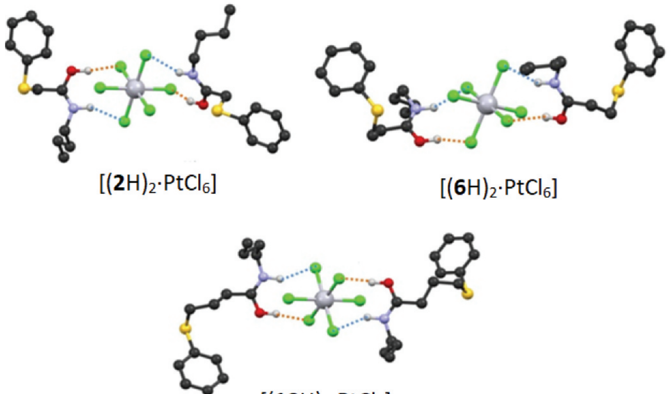


2H^+ **6**H^+ **10**H^+

Figure 11. The energy-minimized structures of the protonated forms of extractants having *n*-butyl substituents, **2**H^+, **6**H^+ and **10**H^+, calculated using B3LYP/6-31g).[28] These have 5-, 6- and 7-membered rings defined by the OH···S hydrogen bond respectively as shown.

of C=O^+-H···S hydrogen bonds in **2**H^+, **6**H^+ and **10**H^+ define 5-, 6- and 7-membered rings as shown in Figure 11.

In marked contrast to the ether- and amine-containing analogues, **V** and **VI**,[21] calculations in which the protonated thioetheramide extractants **2**H^+, **6**H^+ and **10**H^+ are brought into contact with the $[PtCl_6]^{2-}$ anion result in rupture of the proton chelate and the formation of close contacts between the +O-H and N-H bonds and the chlorido ligands in $[PtCl_6]^{2-}$ (Figure 12). The bonding contacts from the former are shorter in every case.



$[(\mathbf{2}H)_2{\cdot}PtCl_6]$ $[(\mathbf{6}H)_2{\cdot}PtCl_6]$

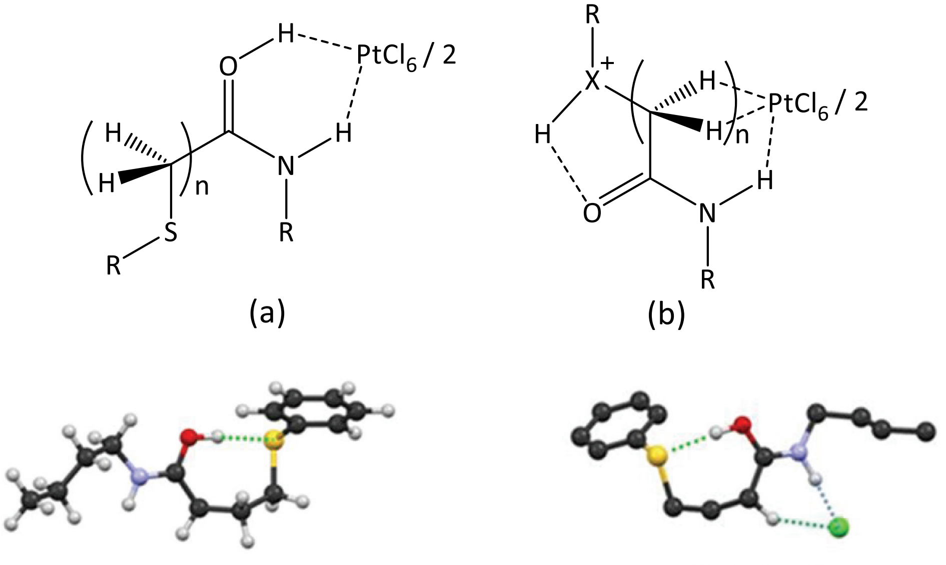
$[(\mathbf{10}H)_2{\cdot}PtCl_6]$

Contact distances/Å:

$[(\mathbf{2}H)_2{\cdot}PtCl_6]$		$[(\mathbf{6}H)_2{\cdot}PtCl_6]$		$[(\mathbf{10}H)_2{\cdot}PtCl_6]$	
N-H···Cl	O-H···Cl	N-H···Cl	O-H···Cl	N-H···Cl	O-H···Cl
2.27 & 2.31	1.99 & 2.01	2.27 & 2.28	2.00 & 2.02	2.27 & 2.30	2.01 & 2.04

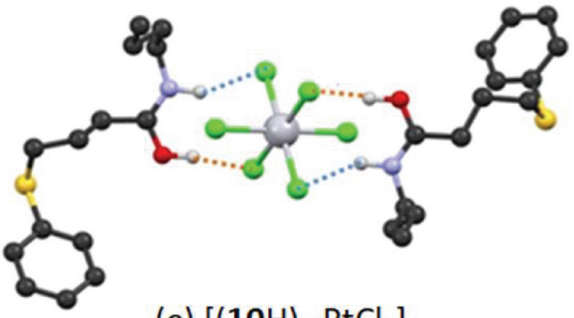
Figure 12. The energy-minimized structures of the $[(\mathbf{L}H)_2{\cdot}PtCl_6]$ assemblies formed by **2**H^+, **6**H^+ and **10**H^+ showing the two N-H···cl (blue) and two O-H···cl (red) H-bonding contacts. These are made to chlorido ligands which are mutually *cis* in the coordination spheres of the assemblies $[(\mathbf{2}H)_2{\cdot}PtCl_6]$ and $[(\mathbf{6}H)_2{\cdot}PtCl_6]$, but in $[(\mathbf{10}H)_2{\cdot}PtCl_6]$ they are formed to chlorido ligands which are mutually *trans*..

Figure 13 highlights the differences in the structures of the most stable assemblies formed between $PtCl_6^{2-}$ and (**a**) the thioether-amide extractants **2**, **6**, and **10** and (**b**) the ether- and amino-amide extractants **V** and **VI**. It is reasonable to assume that the major factor favoring the structures (**b**) is the formation of the strong X^+-H···O=C hydrogen bond. The proton chelation templates the cation to provide both a strong intramolecular amido H-bond donor and numerous weakly polarized C-$H^{\delta+}$ bonds to interact with the anion.



(c) **10**H⁺

(d) [(**10**H)·Cl]



(e) [(**10**H)₂·PtCl₆]

Figure 13. Contrasting modes of binding of the thioether-amide extractants (**a**) and the ether- and amino-amide extractants (**b**) to $[PtCl_6]^{2-}$ and the energy-minimized structures of the thioether-amide ligand **10**H^+ (**c**) and the assemblies it forms with a chloride ion, [(**10**H)·Cl] (**d**), and with a $[PtCl_6]^{2-}$ dianion, [(**10**H)$_2$·$PtCl_6$] (**e**).

The major differences in the gas phase conformations of the free cation **10**H^+, and assemblies it forms with a chloride ion, [(**10**H)·Cl], and with the $[PtCl_6]^{2-}$ dianion, $[(\mathbf{10}H)_2{\cdot}PtCl_6]$ (see Figure 13) are consistent with the ^1H NMR spectra recorded in solution of the related ligand, (**5**H^+), its hydrochloride salt [(**5**H)·Cl] and its outer sphere complex $[(\mathbf{5}H)_2{\cdot}PtCl_6]$ (see Supporting Information, Section B). These differences in the spectra are a consequence of the very different dispositions of H atoms relative to each other and whether it is the N-H, O-H^+ or polarized C-$H^{\delta+}$ units which make close contacts with a Cl^- or with a $[PtCl_6]^{2-}$ dianion.

DFT calculations were used to define the *gas phase* formation energies of the assemblies $[(\mathbf{L}H)_2{\cdot}PtCl_6]$. Two processes were considered. The gas phase reaction in Equation 7 relates to the strength of extractants and allows a comparison of how the ease of formation of the assemblies $[(\mathbf{L}H)_2{\cdot}PtCl_6]$ varies with number of methylene groups in the spacer between the thioether S and the amido carbonyl group. The reaction in Equation 8 relates to the selectivity of the solvent extraction process in which there is competition between the anions Cl^- and $[PtCl_6]^{2-}$ in binding to the **L**H^+ ligands.

$$(\mathbf{L})_2 + 2H_3O^+ + [PtCl_6]^{2-} \rightleftharpoons (\mathbf{LH})_2{\cdot}[PtCl_6] + 2H_2O \tag{7}$$

$$2(\mathbf{LH}){\cdot}Cl + [PtCl_6]^{2-} \rightleftharpoons (\mathbf{LH})_2{\cdot}[PtCl_6] + 2Cl^- \tag{8}$$

$$(\mathbf{L})_2 + 2H_3O^+ \rightleftharpoons 2\mathbf{LH}^+ + 2H_2O \tag{9}$$

$$2\mathbf{LH}^+ + [PtCl_6]^{2-} \rightleftharpoons [(\mathbf{LH})_2{\cdot}[PtCl_6] \tag{10}$$

The small differences in the ease of formation of the assemblies $[(\mathbf{L}H)_2{\cdot}PtCl_6]$ (column 4 in Table 1) from the dimeric proligands, vary in the order **2** ≈ **6** < **10**, and predict that **10** with three methylene units in the spacer separating the thioether S and the carbonyl group will be the strongest extractant. This agrees with the solvent extraction results presented in Figure 5 for the more hydrophobic reagents with 2-ethylhexyl substituents

Table 1. Gas phase internal energy changes/kJ mol^{-1} for protonation of the dimeric proligands, $(\mathbf{L})_2$, (Equation 9), binding of ligands **L**H^+ to $[PtCl_6]^{2-}$ (Equation 10), formation of outer sphere assemblies of $[(\mathbf{L}H)_2{\cdot}PtCl_6]$ from the dimeric proligands (Equation 7), together with energies of the anion exchange reaction (Equation 8).

Proligand L	ΔU for protonation of L (Equation 9)[a]	ΔU for binding of LH^+ to $PtCl_6^{2-}$ (Equation 10)[a]	ΔU for formation of $[(LH)_2{\cdot}PtCl_6]$ (Equation 7)[a]	ΔU_{Ex} for anion exchange (Equation 8)[a]
2	−419.4	−982.1	−1401.5	−48.2
6	−455.9	−945.0	−1400.9	−49.0
10	−475.7	−932.2	−1408.9	−51.6

[a] The internal energies used to calculate these reaction energies are provided in the Supporting Information, Section E.

(**1**, **5** and **9**). Extractant **9**, with three methylene units in the spacer, is the strongest.

In practice, the amount of Pt transferred is also dependent on the competition between Cl^- and $[PtCl_6]^{2-}$ for the cationic ligands, $\mathbf{LH}^+$, (Equation 8). As the chloride concentration in the extraction experiments in this work is very high (6 M) in comparison with that of the chloridoplatinate (0.01 M), a high selectivity for $[PtCl_6]^{2-}$ over Cl^- is essential for efficient Pt-recovery. The anion exchange energies (calculated by Equation 8, shown in Table 1) suggest that the ease of extraction of Pt as $(\mathbf{LH})_2{\cdot}[PtCl_6]$ will increase in the order $\mathbf{2} \approx \mathbf{6} < \mathbf{10}$. Again, this agrees with the solvent extraction results (Figure 5) which indicate that **9**, with three methylene units in the spacer, is the most efficient extractant from 6 M HCl solutions.

Extractions using commercial diluents

Solvesso 150® (>99% aromatic) and ShellSol D70® (predominantly C_{11}-C_{14} aliphatic) were used to probe solubilities and phase disengagement properties of extractants **3**, **7** and **11** that have an isotridecyl substituent; the results are summarized in section C of the Supporting Information. Only solutions of **7** in Solvesso 150 appeared to show clean phase disengagement in all experiments (see Table C1). The addition of tri-*n*-butylphosphate (TBP), a modifier which is often used to aid phase disengagement and minimize the formation of a third phase,[34,35,37] had minimal effect on phase disengagement. It has been shown previously that very little Pd or Pt are extracted by TBP at the low concentrations used in this article.[39]

As might be expected, increasing the HCl concentration of a mixed PGM feed solution has a greater effect on the uptake of Pt(IV) than Pd(II) (see Figure 14). Pt-loading only exceeds 50% at HCl concentrations>5 M. This is consistent with the very different mechanisms of extraction for Pd and Pt (Equations 11 and 12, respectively).

$$[PdCl_4]^{2-} + 2\mathbf{7}_{(org)} \rightleftharpoons \left[Pd(\mathbf{7})_2Cl_2\right]_{(org)} + 2Cl^- \tag{11}$$

$$[PtCl_6]^{2-} + 2H^+ + 2\mathbf{7}_{(org)} \rightleftharpoons (\mathbf{7}H)_2{\cdot}[PtCl_6]_{(org)} \tag{12}$$

The uptakes recorded in Figure 14 support the proposition that recovery and separation of Pd and Pt could be achieved using the flowsheet in Figure 2, by loading at high HCl concentration and then selectively stripping the Pt at low HCl concentration, followed by ammonia stripping to recover the Pd. The curves confirm that very little Ir, Rh and Ru are loaded from a 6 M HCl solution. For the test described below it was decided to carry out the loading from a 6 M HCl solution, recognizing that this will ensure that most of the Ir, Rh, and

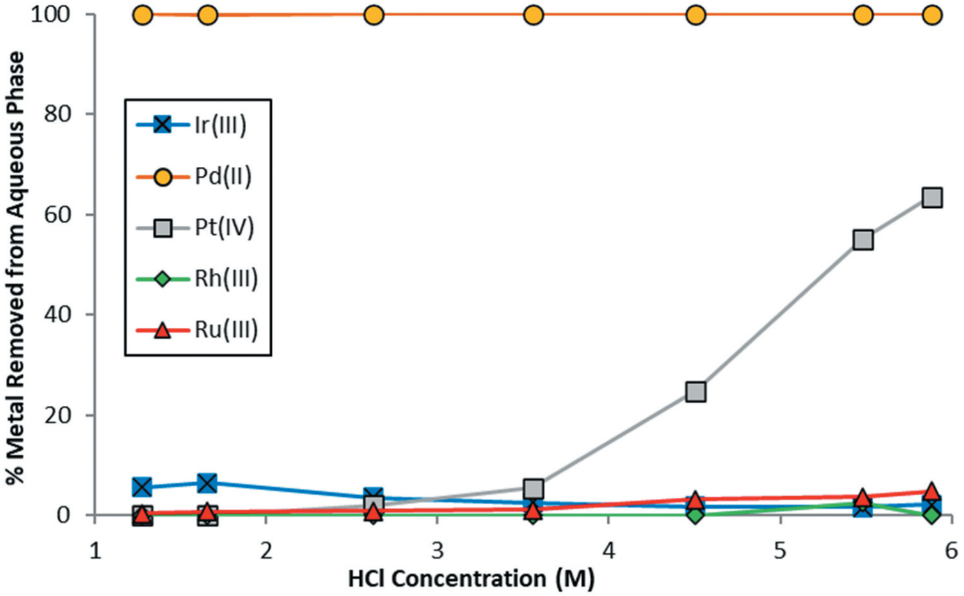


Figure 14. The dependence of uptake of Pt, Pd, Ir, Ru and Rh by **7** (0.6M) in Solvesso 150 on the concentration of HCl in a feed solution containing metal concentrations simulating an industrial stream (Pt; 5.13, Pd; 9.40, Ir; 2.60, Ru; 2.97, and Rh; 0.97 mmol L^{-1}) after mixing for 2 min. Interpolation to aid the eye only.

Ru will be rejected but that multiple contacts would be required to recover most of the Pt.

The uptake of both Pd and Pt by **7** is rapid. Equilibrium is achieved within the shortest mixing time recorded in Figure 15. This is to be expected for Pt because transfer to the water-immiscible phase involves only changes in the *outer sphere*. Formation of the *inner sphere* Pd complex, $[Pd(\mathbf{7})_2Cl_2]$, is expected to be slower but could be preceded by rapid phase transfer of the Pd to the organic phase *via* formation of the *outer sphere* complex, $[(\mathbf{7}H)_2{\cdot}PdCl_4]$. This will facilitate rapid conversion to the *inner sphere* complex through approximation catalysis as the effective concentration of the entering thioether groups relative to the Pd atom will be very high (0.6 M **7** *vs.* 9.4 mmol Pd). (Equation 13).[40]

$$[(7H)_2{\cdot}PdCl_4]_{(org)} \rightarrow \left[Pd(7)_2Cl_2\right]_{(org)} + 2HCl \tag{13}$$

The sequence of loading-, washing- and stripping-steps outlined in Figure 16 was undertaken to demonstrate that Pd and Pt could be both recovered and separated from an industrially relevant hydrochloric acid feed solution using a single extractant. No attempt was made to optimize recoveries by either:

- increasing the numbers of stages of extraction, washing and stripping, or
- varying the volume ratios of the aqueous and organic phases used.

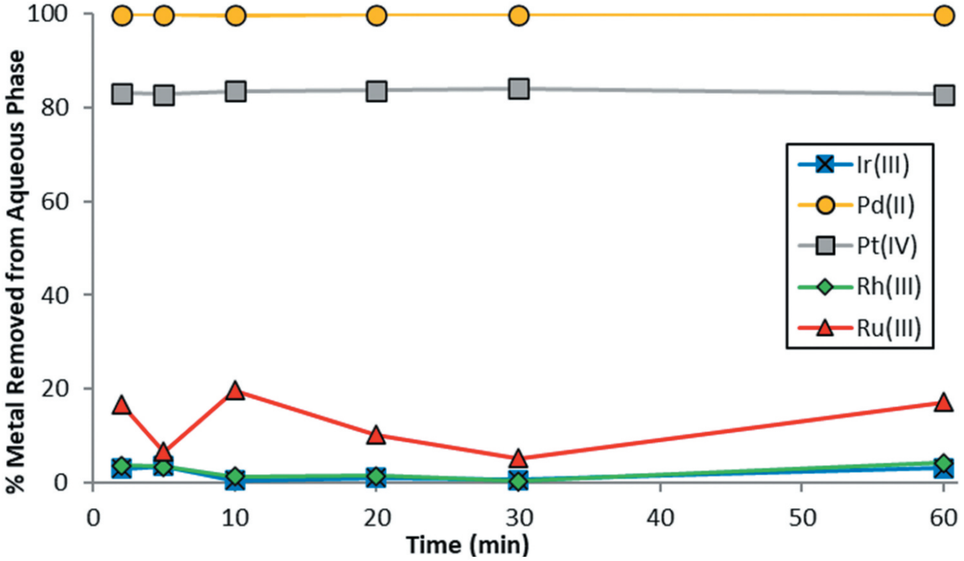


Figure 15. The time dependence of uptake of Ir, Pd, Pt, Rh, and Ru from a 6M HCl solution with metal concentrations as defined in Figure 14 by **7** (0.7M) in Solvesso 150.

A similar preliminary study to define the effects of having Ir, Ru, and Rh in the feed and of adding washing and stripping stages is reported in the Supporting Information, section D. Results are similar to those reported immediately below but more problems were encountered with the formation of third phases and the consequent poor materials balances.

The metal content of the streams in the flowsheet in Figure 16 confirm that **7** is capable of co-extracting Pd and Pt and that these can then be separated using selective stripping based on the differences in the structures of the assemblies formed in the organic phase. Pd is present as an inner sphere complex $[Pd(\mathbf{7})_2Cl_2]$, from which the Pd can be stripped only under forcing conditions by replacing the thioether and chlorido ligands with ammonia. In contrast, the outer sphere complex or "ion pair assembly", $[(\mathbf{7}H)_2{\cdot}PtCl_6]$ releases the chloridometalate, $[PtCl_6]^{2-}$, to the aqueous phase when contacted with water which facilitates loss of the proton from $\mathbf{7}H^+$.

In the sequence of steps shown in Figure 16 the efficiencies of Pt-loading and stripping are low and, as mentioned above, process optimization, requiring several extraction steps, will be needed in a commercially viable process.

Based on the shape of the plot in Figure 14, raising the HCl concentration beyond 6 M would enhance Pt-loading, but as noted for related systems,[38] at very high chloride concentrations, it is likely that metal loading will begin to decrease because the competitive transfer of chloride as in Equation 14 becomes favorable:

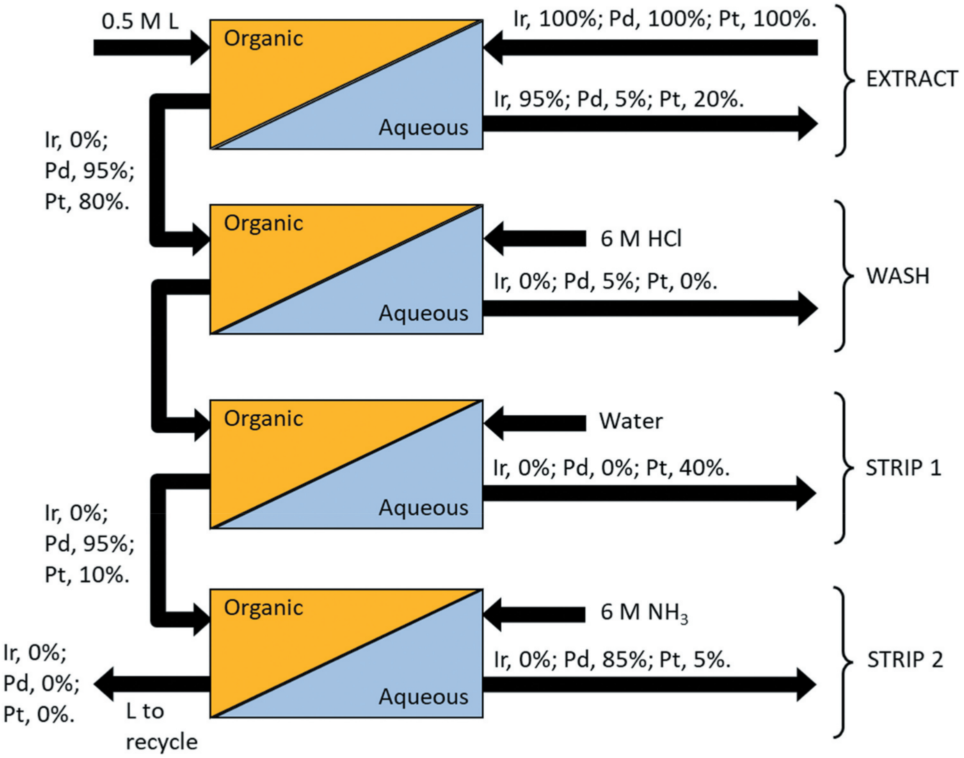


Figure 16. Percentages (to the nearest 5%) of the total metal content in the system residing in: a 0.5 M solution of **7** in Solvesso 150 before and after contact with the aqueous feed {Ir(iii); 2.3, Pd(II); 86.6, Pt(IV); 46.0, Rh(III); 8.5 and Ru(III); 13.6 mmol L^{-1} in 6M HCl}, the 6M HCl wash solution, and in the 0.1 M HCl and 6 M NH_3 strip solutions.

$$[(7H)_2{\cdot}PtCl_6]_{(org)} + 2Cl^- \rightleftharpoons 2[7H \cdot Cl]_{(org)} + [PtCl_6]^{2-} \qquad (14)$$

Conclusions

We have shown that it is feasible to use a *single ditopic extractant* (**L**) to recover and separate Pt and Pd from acidic chloride solutions typical of those involved in both primary and secondary industrial recovery processes, leaving other metals in the process stream. This article demonstrates that this can be achieved by exploiting the differences in the coordination chemistries of Pd(II) and Pt(IV), in particular:

- the dependence of rates of ligand exchange in the inner sphere on the *oxidation state* and *coordination number* of the metal and the nature of the entering ligand favoring the rapid formation of the inner sphere Pd(II) complexes $[Pd(\mathbf{L})_2Cl_2]$,

- the dependence of the formation of outer-sphere complexes/assemblies of chloridometalates, $[MCl_x]^{y-}$, on their *charge/radius ratios*; making it much easier to dehydrate charge-diffuse, “softer”, metalates and transfer them into a water-immiscible solvent, favoring the formation of $[(\mathbf{L}H)_2{\cdot}PtCl_6]$, containing Pt(IV), over $[(\mathbf{L}H)_3{\cdot}IrCl_6]$, containing Ir(III), and
- the marked differences in kinetic stability of the inner sphere complexes $[Pd(\mathbf{L})_2Cl_2]$ of Pd(II) compared with the outer-sphere assemblies $[(\mathbf{L}H)_2{\cdot}PtCl_6]$ of Pt(IV) making it easier to strip the latter rapidly from the loaded organic phase into dilute HCl.

Selectivity of extraction of Pd(II) and Pt(IV) over some other PGMs, e.g. Rh(III) is also favored by them showing a lower tendency to form more hydrophilic aquo complexes such as $[RhCl_5(H_2O)]^{2-}$.

Proof of concept for using the ditopic reagents in Pd/Pt extraction and separation has been established but, as in many solvent extraction processes, a significant amount of development work is needed to ensure that phase separation is sufficiently efficient that reagent losses are minimal and that throughputs are rapid.

Acknowledgments

We thank the University of Edinburgh for support, the EPSRC and Johnson Matthey for the funding of PhD studentships for KJM and AMW and EaStCHEM for access to the Research Computing Facility.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The work was supported by the Engineering and Physical Sciences Research Council UK and Johnson Matthey plc.

References

[1] Renner, H.; Schlamp, G.; Kleinwächter, I.; Drost, E.; Lüschow, H. M.; Tews, P.; Panster, P.; Diehl, M.; Lang, J.; Kreuzer, T. et al, Platinum Group Metals and Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*; Ley, C. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005. DOI: 10.1002/14356007.a21_075.

[2] Bossi, T.; Gediga, J. The Environmental Profile of Platinum Group Metals. *Johnson Matthey Tech. Rev.* 2017, *61*(2), 111–121. DOI: 10.1595/205651317X694713.

[3] Acres, G. J. K.; Swars, K. *Pt Platinum: Supplement Volume a 1 Technology of Platinum-Group Metals*; Springer: Berlin Heidelberg, 2013.

[4] Paiva, A. P. Recycling of Palladium from Spent Catalysts Using Solvent Extraction—some Critical Points. *Metals* 2017, *7*(11), 505. https://www.mdpi.com/2075-4701/7/11/505

[5] Nicol, G.; Goosey, E.; Yıldız, D. Ş.; Loving, E.; Nguyen, V. T.; Riaño, S.; Yakoumis, I.; Martinez, A. M.; Siriwardana, A.; Unzurrunzaga, A., et al., Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS): Project Overview with a Focus on Processing Spent Autocatalyst: Novel Pgm Recycling Technologies Ready for Demonstration at Next Scale. *Johnson Matthey Tech. Rev.* 2021, *65* (1), 127–147, DOI: 10.1595/205651321X16057842276133.

[6] 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*(3), 205–217. DOI: 10.1016/j.reactfunctpolym.2005.05.011.

[7] Charlesworth, P. Separating the Platinum Group Metals by Liquid-Liquid Extraction. *Platinum Met. Rev.* 1981, *25*(3), 106–112.

[8] Crundwell, F. K.; Moats, M. S.; Ramachandran, V.; Robinson, T. G.; Davenport, W. G. Chapter 37 - Refining of the Platinum-Group Metals. In *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*; Crundwell, F. K., Moats, M. S., Ramachandran, V., Robinson, T. G. Davenport, W. G., Eds.; Elsevier: Oxford, 2011; pp. 489–534.

[9] Grant, R. A.; Gordon, R. J.; Woollam, S. F. The Role of Solvent Extraction in Platinum Group Metal Refining - Past, Present and Future. In *Proceedings of the International Solvent Extraction Conference, ISEC '14*; Würzberg, Germany, Dechema: Wüzberg, Germany; 2014, pp 480–485.

[10] Narita, H.; Kasuya, R.; Suzuki, T.; Motokawa, R.; Tanaka, M. Precious Metal Separations. In *Encyclopaedia of Inorganic and Bioinorganic Chemistry*; Scott, R. Ed.; Wiley Online Library, 2020. DOI: 10.1002/9781119951438.eibc2756.

[11] Marcus, Y. *Principles of Solubility and Solutions. Solvent Extraction Principles and Practice*, Second Edition Revised and Expanded; Rydberg, J., Cox, M., Musikas, C., Choppin, G. Eds.; CRC Press: Boca Raton, 2004; pp. 27–80. DOI: 10.1201/9780203021460.

[12] Housecroft, C. E.; Constable, E. C. *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry*, 3rd; Pearson Education Limited: Harlow, UK, 2006.

[13] Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper & Row: New York, 1983.

[14] Pearson, R. G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* 1963, *85*(22), 3533–3539. DOI: 10.1021/ja00905a001.

[15] Edwards, R. I. Selective Solvent Extractants for the Refining of Platinum Metals. In *Proceedings of the International Solvent Extraction Conference, ISEC '77*; The Canadian Institute of Mining and Metallurgy: Toronto; 1977, p 24.

[16] Wang, J.; Xu, W.; Liu, H.; Yu, F.; Wang, H. Extractant Structures and Their Performance for Palladium Extraction and Separation from Chloride Media: A Review. *Min. Eng.* 2021, *163*, 106708. DOI: 10.1016/j.mineng.2021.106798.

[17] Paiva, A. P.; Carvalho, G. I.; Costa, M. C.; da Costa, A. M. R.; Nogueira, C. Recovery of Platinum and Palladium from Chloride Solutions by a Thiodiglycolamide Derivative. *Solvent. Extr. Ion Exch.* 2014, *32*(1), 78–94. DOI: 10.1080/07366299.2013.810969.

[18] 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*(4), 2303–2315. DOI: 10.3390/met5042303.

[19] Ortet, O.; Santos, M. S. C. S.; Paiva, A. P. Palladium(ii) and NN′-Dimethyl-N,N′-Dicyclohexylthiodiglycolamide – the Extracted Species from Concentrated Chloride Solutions. *Sep. Purif. Technol.* 2016, *170*, 1–9. DOI: 10.1016/j.seppur.2016.06.021.

[20] Narita, H.; Morisaku, K.; Tanaka, M. Structural Effect of Sulfide-Containing Diamides on the Extraction of Palladium(ii) from HCl. *Solvent. Extr. Ion Exch.* 2021, *39*(5–6), 533–544. DOI: 10.1080/07366299.2021.1876372.

[21] Bell, K. J.; Westra, A. N.; Warr, R. J.; Chartres, J.; Ellis, R.; Tong, C. C.; Blake, A. J.; Tasker, P. A.; Schröder, M. Outer-Sphere Coordination Chemistry: Selective Extraction and Transport of the [PtCl6]2− Anion. *Angew. Chem. Int. Ed.* 2008, *47*(9), 1745–1748. DOI: 10.1002/anie.200703272.

[22] Carson, I.; MacRuary, K. J.; Doidge, E. D.; Ellis, R. J.; Grant, R. A.; Gordon, R. J.; Love, J. B.; Morrison, C. A.; Nichol, G. S.; Tasker, P. A., et al. Anion Receptor Design: Exploiting Outer-Sphere Coordination Chemistry to Obtain High Selectivity for Chloridometalates Over Chloride. *Inorg. Chem.* 2015, *54*(17), 8685–8692. DOI: 10.1021/acs.inorgchem.5b01317.

[23] Turkington, J. R.; Bailey, P. J.; Love, J. B.; Wilson, A. M.; Tasker, P. A. Exploiting Outer-Sphere Interactions to Enhance Metal Recovery by Solvent Extraction. *Chem. Commun.* 2013, *49*(19), 1891–1899. DOI: 10.1039/C2CC37874D.

[24] Warr, R. J.; Westra, A. N.; Bell, K. J.; Chartres, J.; Ellis, R.; Tong, C.; Simmance, T. G.; Gadzhieva, A.; Blake, A. J.; Tasker, P. A., et al. Selective Extraction and Transport of the [PtCl6]2− Anion Through Outer-Sphere Coordination Chemistry. *Chem. Eur. J.* 2009, *15*(19), 4836–4850. DOI: 10.1002/chem.200802377.

[25] Grant, R. A.; Murrer, B. A. Extraction of Metals. US 4726841, 1988.

[26] 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. DOI: 10.1021/ie404363b.

[27] Still, W. C.; Kahn, M.; Mitra, A. Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution. *J. Org. Chem.* 1978, *43*(14), 2923–2925. DOI: 10.1021/jo00408a041.

[28] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H., et al., Inc., Wallingford CT, 2016.

[29] Peng, C. -Y.; Tsai, T. -H. Recovery of Palladium(ii) from Acidic Chloride Solution Using Kerosene Containing Tri-*N*-Octyl/decyl Amine (Alamine 336). *Desalinat. Water Treat.* 2012, *47*(1–3), 105–111. DOI: 10.1080/19443994.2012.696803.

[30] Grant, R. A.; Woollam, S. F. Development of a Computer Simulation of the Platinum Solvent Extraction at Precious Metal Refiners. In *18th International Solvent Extraction Conference*; Canadian Institute of Mining, Metallurgy and Petroleum: Tucson, Arizona, USA, 2008; pp 425–420.

[31] Marcus, Y. Thermodynamics of Solvation of Ions. Part 5.—gibbs Free Energy of Hydration at 298.15 K. *J. Chem. Soc. Faraday Trans.* 1991, *87*(18), 2995–2999. DOI: 10.1039/FT9918702995.

[32] Moyer, B. A.; Bonnesen, P. V.; Custelcean, R.; Delmau, L. H.; Hay, B. P. Strategies for Using Host-Guest Chemistry in the Extractive Separations of Ionic Guests. *Kem. Ind.* 2005, *54*(2), 65–87. DOI: 10.1002/chin.200531276.

[33] Hofmeister, F. Zur Lehre von der Wirkung der Salze. *Archiv. Exptl. Pathol. Pharmakol.* 1888, *24*(4–5), 247–260. DOI: 10.1007/bf01918191.

[34] Kedari, C. S.; Coll, T.; Fortuny, A.; Sastre, A. Third Phase Formation in the Solvent Extraction System Ir(iv)—cyanex 923. *Solvent. Extr. Ion Exch.* 2005, *23*(4), 545–559. DOI: 10.1081/SEI-200068505.

[35] Osseo-Asare, K. Aggregation, Reversed Micelles, and Microemulsions in Liquid-Liquid Extraction: The Tri-*N*-Butyl Phosphate-Diluent-Water-Electrolyte System. *Adv. Coll. Interf. Sci.* 1991, *37*(1), 123–173. DOI: 10.1016/0001-8686(91)80041-H.

[36] Tasker, P. A.; Doidge, E. D.; Parkin, G.; Que, L. The Coordination Chemistry of Extractive Metallurgy. In *Comprehensive Coordination Chemistry III*; Constable, E., Ed.; Elsevier Ltd: Oxford, 2021; pp. 494–557.

[37] Ueda, Y.; Morisada, S.; Kawakita, H.; Ohto, K. Selective Extraction of Platinum(iv) from the Simulated Secondary Resources Using Simple Secondary Amide and Urea Extractants. *Separations*. 2021, *8*(9), 139. DOI: 10.3390/separations8090139.

[38] Wilson, A. M.; Bailey, P. J.; Tasker, P. A.; Turkington, J. R.; Grant, R. A.; Love, J. B. Solvent Extraction: The Coordination Chemistry Behind Extractive Metallurgy. *Chem. Soc. Rev*. 2014, *43*(1), 123–134. DOI: 10.1039/C3CS60275C.

[39] Macruary, K. J.; Gordon, R. J.; Grant, R. A.; Woollam, S.; Ellis, R. J.; Tasker, P. A.; Love, J. B.; Morrison, C. A. On the Extraction of HCl and H2ptcl6 by Tributyl Phosphate: A Mode of Action Study. *Solvent. Extr. Ion Exch.* 2017, *35*(7), 531–548. DOI: 10.1080/07366299.2017.1379724.

[40] Berg, J. M.; Tymoczko, J. L.; Stryer, L. *Biochemistry*, 5th ed, Chapter 9; W. H. Freeman: New York, 2002.