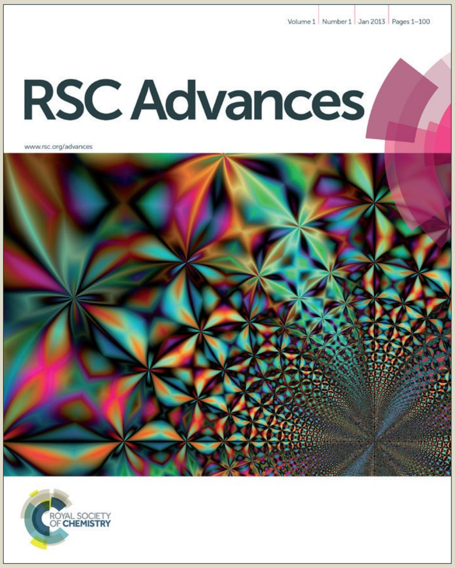
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name RSCPublishing

ARTICLE

# Selone behavior towards palladium(II) extraction with hydrophobic ionic liquids and mechanism studies

wwCite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chen Wang,[a] Yu Tong,[a] Yixian Huang[a] , Hong Zhang and Yanzhao Yang[a*]

The selenium-bearing extractant was evaluated for palladium extraction for the first time. The 1-butyl-3-methylimidazole-2-selone was synthesized, and dissolved in hydrophobic ionic liquids to extract palladium from aqueous solutions. Based on the studies of influencing factors, the first elaboration of the selone extraction mechanism was offered. One of the Pd-selone complexes was analyzed with single crystal X-ray diffraction, in explaining the elevation of extractability relative to thiones from molecular level. A novel combination of UV-vis spectra, HPLC and $^{77}Se\{^1H\}$ NMR was first used to characterize the extraction system and determine the complexing number. It is confirmed that various kinds of complexes were extracted to the organic phase at different selone concentration, thus the apparent complexing number was proposed to describe the extraction system. Both the extractability and the selectivity of the selone for Pd(II) extraction over other metal ions were evaluated to be high.

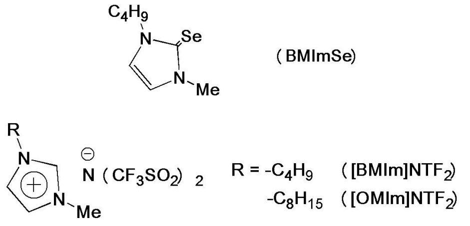
## Introduction

Among different separation methods, solvent extraction was characterized by simplicity, efficiency and selectivity, making it be frequently carried out.[1-2] In recent years, the ionic liquids[3] have been employed as alternatives to either extractants or diluents in the conventional solvent extraction systems,[4] to separate or concentrate metals like the platinum group metals (PGMs). One of the PGMs, palladium， is increasingly important because of its continuous application in diverse areas such as chemical catalyst, electrochemiluminescence materials and alloy membranes.[5-6] Considering the environmental stress and economic benefits, the use of ionic liquids in palladium recovery or recycling process is rapidly expanding because of their green credentials like non-inflammability, wide electrochemical window, high stability and non-volatility.[7] K. Sasaki et al. demonstrated the extraction of Pd(II), Rh(III) and Ru(III) from aqueous $HNO_3$ to $[Hbet][NTF_2]$ (ionic liquid) via the cation exchange mechanism.[8] Q. Yang et al. reported the long chain phosphonium ionic liquids, which showed satisfying solvent extraction performance towards metal recovery and water treatment.[9] Generally, the use of ionic liquids as either extractants or organic phases could notably reduce the emulsion and enhance the mass transfer.

However, the advantages of ionic liquids in extracting metals are usually limited. For example, since most extraction mechanisms are the ion exchange between ionic liquids and aqueous metals, the equilibration with the aqueous phase will bring loss to ionic liquids, and contaminate the aqueous phase in return. Besides, most of the extractions are dramatically affected by the $H^+$ concentration, which calls for an extra pH adjustment procedure before extraction.[10] What is more, the volume ratio of organic phase to aqueous phase is usually large to attain better extraction percentage.[11] Nevertheless, the adding of neutral extractants could not only avoid or reduce the ion exchange to tolerate the variation of hydrogen ion concentration, but also maintain the advantages of ionic liquids. What is more, the coordination reaction is faster and more thorough than the ion exchange reactions. In this case, based on the Hard-Soft-Acid-Base theory, the neutral extractants containing S or N as donor atoms have been extensively discussed for PGMs.[12-18]

In our previous studies, it was found that the neutral ionic liquid based imidazole-2-thione extractant 1,3-diethylimidazole-2-thione (sulfur-bearing) owns good Pd(II) extractability and high hydrogen ions tolerance.[19] Then its selenium analogues, aroused our interest in the imidazole-2-selone extractant. Generally, selenium compounds have only been exploited for their application ranging from organic synthesis[20] to pharmaceutical industry[21] and biochemistry[22]. According to the records of the Cambridge Crystallographic Data Centre (CCDC), there are more than 4,000 entries related to the palladium complexes with sulfur-containing ligands. While only about 250 single crystal data of selenium-palladium organometallics. The selenium-bearing ligands have barely gained investigations for their behavior towards metal extractions. The extraction mechanisms and related coordination chemistry are far from complete.

Herein we report the Pd(II) extraction behavior and mechanism of the novel ionic liquid based selone extractant, 1-butyl-3-methyl imidazole-2-selone (BMImSe). To facilitate the mass transfer, it was dissolved in its structurally similar ionic liquids including 1-n-butyl-3-methyl imidazolium bis((trifluoromethyl)sulfonyl) imide ([BMIm]NTF$_2$) and 1-n-octyl-3-methyl imidazolium bis((trifluoromethyl)sulfonyl) imide ([OMIm]NTF$_2$) **(Scheme 1)**. By far, the present work is the first to elaborate the use and mechanism of selenium compound for metal extraction, especially with ionic liquids being the diluents. According to the results, it is satisfying that the imidazoleselone extractant, BMImSe, exhibits good extractability and selectivity for palladium.



**Scheme 1**. The ionic liquids and selone extractant used in the present work.

## Experimental Section

### Reagents and materials

1-butyl-3-methy imidazole acetate salt ([BMIm]OAc), 1-butyl-3-methyl imidazolium bis ( (trifluoromethyl) sulfonyl) imide ([BMIm]NTF$_2$) and 1-octyl-3-methyl imidazolium bis ( (trifluoromethyl) sulfonyl) imide ([OMIm]NTF$_2$) were purchased from Lanzhou Greenchem ILS, LICP, CAS, China. PdCl$_2$ were purchased from Guangfu Institute of Fine Chemical (Tianjin, China). All the other reagents (hydrochloric acid, selenium, sodium bicarbonate, methanol, acetonitrile, methylene dichloride, acetone, chloroform, and chloride of diverse metals, etc.) were AR and used without additional purification. Distilled water was used to prepare the aqueous solutions in all experiments.

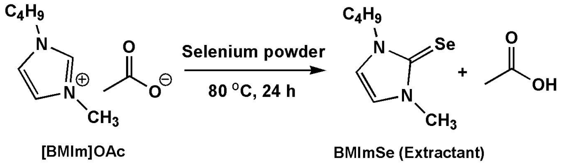
### Analytical techniques

The Pd(II) concentrations in aqueous phase before and after extraction were determined with a flame atomic absorption spectrometer (3150, Precision & Scientific Instrument Shanghai Co., Ltd., Shanghai, China). The concentrations of multi-metal ions (Pd(II), Mn(II), Zn(II), Cd(II), Ni(II), Al(III) and Sn(IV)) in solutions were determined with an ICP-AES (IRIS Intrepid II XSP, Thermo electron corporation, Boston, US).

High performance liquid chromatogram was conducted with a chromatographer (LC2000, TianMei, Shanghai, China) equipped with a Kromasil C18 column. Samples were determined at 279 nm, with methanol as mobile phase, 1 mL min$^{-1}$. $^1$H NMR and $^{77}$Se{$^1$H} NMR were carried out on a Bruker AV300 spectrometer. UV-vis spectra were determined by UV spectrophotometer (UV-9000, Shanghai Metash Instruments Co., Ltd., Shanghai, China). FT-IR was performed by pressing the obtained samples to a tablet with dry KBr powders, and analyzed with infrared spectrometer (Tensor27, Bruker corporation, Karlsruhe, Germany), with the scanning regions ranged from 400 to 4000 cm$^{-1}$.

### Synthesis of BMImSe extractant

The synthesis of selone was designed according to literature procedure[23-24] to afford 1-butyl-3-methyl imidazole-2-selone in 85.7% yield. 1-n-butyl-3-methyl-imidazolium acetate (5.0 g) was stirred with selenium powder (2.5 g) in an round-bottom flask at 80 °C. After 24 hours, 20 mL acetonitrile was added. The mixture was leached with a filter to eradicate selenium and the acetonitrile was distilled under vacuum. The product was dissolved in 20 mL methylene dichloride. Deionized water and sodium bicarbonate solution (5%, 15 ml each time) were used to wash the oil to remove the 1-n-butyl-3-methyl-imidazolium acetate salt and acetic acid. Then, methylene dichloride was distilled under vacuum. The product was red brown viscous liquid. $^1$H NMR (300 MHz, DMSO-d$_6$) δ (ppm) = 7.331 (s, 2 H), 4.022 (t, 2 H), 3.556 (s, 3 H), 1.676 (m, 2 H), 1.279 (m, 2 H), 0.898 (t, 3 H). FT-IR (KBr, cm$^{-1}$) 3464 (w), 3089 (s), 2959 (m), 2868 (s), 1671 (m), 1568 (s), 1459 (s), 1400 (s), 1238 (m), 1141 (s), 1077 (s), 940 (s), 721 (m), 663 (s). This procedure was shown as following (**Scheme 2**.)



**Scheme 2**. Synthesis of 1-butyl-3-methyl imidazole-2-selone (BMImSe extractant)

### Extraction

Extraction was conducted with BMImSe in [EMIm]NTF$_2$ or [OMIm]NTF$_2$ as organic phase. Feed solutions contained 0.2 mM palladium(II) chloride in 0.8 mM hydrochloric acid unless otherwise noted. The two phases were mechanically shaken, with 10 of $R_{A/O}$ (volume ratio of aqueous phase to organic phase) in orbital shaker and separated with a centrifuge at 2000 rpm for 5 min. Each experiment was carried out 3 times and the relative standard deviation did not exceed 5%. Extraction percentage E (%) were calculated based on mass balances.[25]

### Crystal growth and analysis

Single crystals suitable for the X-ray diffraction study were grown by solvent evaporation. Ethanol-water solutions (10 mL) containing 0.0282 mM PdCl$_2$ and one equivalent of BMImSe were stirred and filtered with a funnel and then volatilized in a serum bottle at 298 K for two weeks. Single crystal X-ray diffraction was conducted using an area detecting system (Bruker-Nonius SMART APEX II CCD) and graphite monochromated Mo-Ka radiation (λ = 0.71073 Å). Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[26] Data reduction was performed with the SAINT software; the data were also corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[27] The CCD data were integrated and scaled using the Bruker SAINT software package, and the structure was solved and refined using SHEXTL V6.12.2.[28] Atoms were located from iterative examination of difference F-maps following least squares refinements of earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times $U_{eq}$ of attached C atoms. Crystal data for $Pd_2(BMImSe)_2Cl_4$: $M_r$ = 788.94, monoclinic, space group P21/c, a = 12.6713(4), b = 15.2764(4), c = 13.6503(4)Å, T=100 K, $\alpha = 90^o$ $\beta = 103.285(2)^o$ $\gamma = 90^o$; V = 2571.60(13) Å$^3$, Z = 4, $R_1$ = 0.0794(1944), $wR_2$ = 0.1815(5856) ($I > 2\sigma(I)$). CCDC 1057131 contains the ESI† for the structures described in this paper.

## Results and discussion

### Effect of BMImSe concentration and ionic liquids

The kinetics study was carried out before subsequent studies. The extraction percentage was determined with varying vibrating time ranging from 0.5 min to 1 h, and the extraction equilibrium could attain within 5 min (not shown), which indicates a fast and steady extraction procedure. When the ionic liquids are used without adding neutral complexes, the extractions are generally ionic exchange mechanism [29], but the selone extracts Pd via coordination reaction. Usually the coordination reaction is faster and much more thorough than the ionic exchange reaction.

The influence of extractant concentration was investigated for Pd(II), and results are shown in **Figure 1**, which also represents the impact of the diluents. In the [BMIm]NTf$_2$, the extraction percentage reached 87.98% by using BMImSe twice as much as Pd(II). The maximum of 99.71% was obtained when the amount of extractant quadrupled Pd(II). When a longer chain ionic liquid, [OMIm]NTf$_2$, was used as diluent, the extraction percentage was apparently enhanced (about 40% improved) at lower concentration of extractant ($n_{BMIMSe}$: $n_{Pd}$ =1). Since the two ionic liquids used individually did not make obvious contribution to the extraction percentage, the dissolving capacity for the extracted complexes became the reasonable explanation for this elevation. Besides, comparing to our previous work,[19] where thione extractant (1,3-diethyl-imidazole-2-thione) was used to extract Pd, the extraction ability was largely improved by changing S donor atom to Se.

### Effect of hydrochloric acid and sodium chloride

The effect of hydrochloric acid and sodium chloride was studied (**Figure 2**). At the lower dosage of extractant, the extraction percentage was sharply decreased to about 50% on adding small amount of hydrochloric acid. Then the E% climbs slightly at 4 M hydrochloric acid. Similar change is exhibited by adding NaCl. The E% dramatically decreases as increasing of concentration of NaCl. However there is no trend of rise at higher NaCl concentration. It was indicated that the lifting of E% in **Figure 2** may be attributed to the hydrogen ions. In addition, at higher dosage of extractants, the whole extraction system exhibited high tolerance to the hydrochloric acid, making it be more advantageous than many other systems. [30-32]

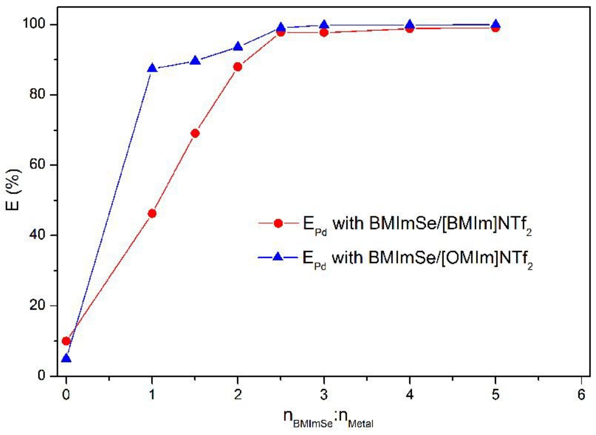


**Figure 1.** Effect of the BMImSe concentration in [BMIm]NTF$_2$ or [OMIm]NTF$_2$ for Pd(II) extraction. Aqueous phase: 0.2 mM Pd(II) in 0.8 mM HCl. Organic phase: BMImSe in [BMIm]NTF$_2$ / [OMIm]NTF$_2$. $R_{A/O}$ = 10.

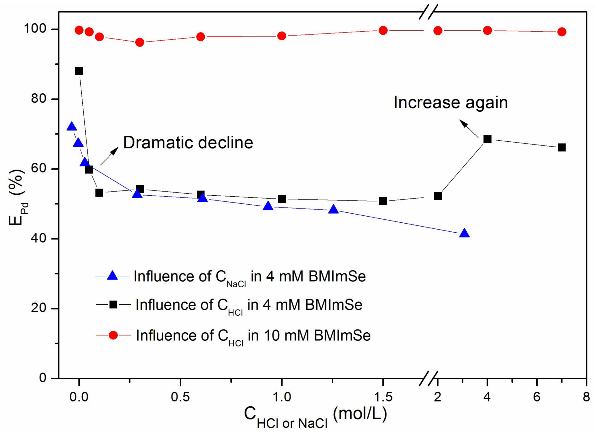


**Figure 2.** Effect of hydrochloric acid and sodium chloride for the Pd(II) extraction under different levels of BMImSe concentration. Aqueous phase 0.2 mM Pd(II). Organic phase: BMImSe in [BMIm]NTF$_2$. $R_{A/O}$ = 10.

### Mechanisms of palladium extraction with selone

Through the above results, it is proposed that the increasing of hydrochloric acid concentration will lead to the transition of extraction mechanism from neutral complexing to acidic ion association.

According to the stability constants of the coordination between $Pd^{2+}$ and $Cl^-$ : $lg\beta_1 = 6.1$, $lg\beta_2 = 10.7$, $lg\beta_3 = 13.1$, $lg\beta_4 = 15.7$,[33] the distributions of palladium chlorocomplexes at different $Cl^-$ concentrations was calculated in **Figure 3.** When the equilibrium concentration of $Cl^-$ is between 0.03 mM and 3 mM, the $Pd^{2+}$ predominantly exists as the complex anion [$PdCl_2$]. Further increase of $Cl^-$ concentration will lead to the sharp increase of [$PdCl_4$]$^{2-}$ distribution fraction, the [$PdCl_3$]$^-$

only occupies a small portion. Thus the increase of hydrochloric acid concentration will result in the higher chloro coordination number on palladium. Therefore extra Pd-Cl bond cleavage energy is needed for the coordination of selone to Pd, which is expressed in the lower extraction percentage. At this stage, the extraction mechanism is the neutral complexing, which means that neutral complexes were formed and extracted to the organic phases (**eq.** 1 to 3). It is similar to the case of sulfoxides extractant.[34]

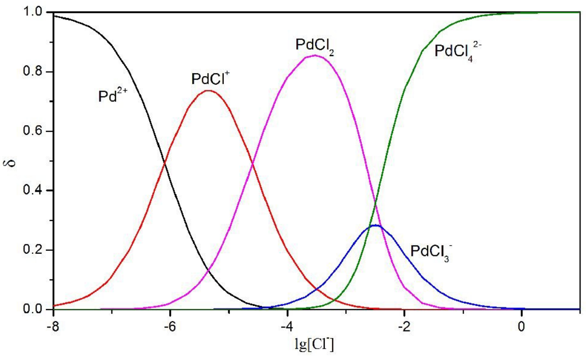
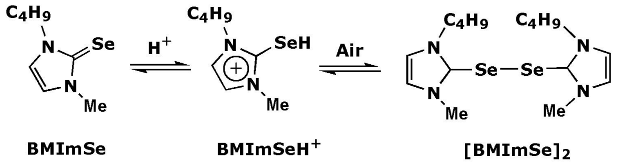


**Figure 3**. Distributions of palladium chlorocomplexes in HCl solutions with different concentrations

However, the continuous increased hydrochloric acid concentration could acidize part of the BMImSe to the BMImSeH$^+$,[35] as shown in **Scheme 3.** The electronegative Se atom have stronger interaction with Pd than neutral Se, which is account for the increased extraction percentage.



**Scheme 3.** The acidization and dimerization of BMImSe.

The acidization of BMImSe can be proved. After 5 h reaction with 5 M HCl, the selone showed $^1$H NMR nuclei at $\delta = 3.542$ ppm (s, 6H), which was evolved from the original nuclei at $\delta = 3.556$ (s, 3 H). This indicated that selone was partially dimerized. Generally, the dimerization is followed by an acidization step.[36] What is more, the dimerized selone also could coordinate with Pd(II) to form the same neutral complexes. So the whole extraction mechanism is concluded as below (**eq.1** to **eq.4**).

Neutral complexing extraction mechanism:

$[PdCl_2]_{(aq)} + xBMImSe_{(or)} = [PdCl_2{\cdot}BMImSe_x]_{(or)}$ (eq.1)

$[PdCl_3]^-_{(aq)} + xBMImSe_{(or)} = [PdCl_2{\cdot}BMImSe_x]_{(or)} + Cl^-_{(aq)}$ (eq.2)

$[PdCl_4]^{2-}_{(aq)} + xBMImSe_{(or)} = [PdCl_2{\cdot}BMImSe_x]_{(or)} + 2Cl^-_{(aq)}$ (eq.3)

Acidic ion association extraction mechanism:

$[PdCl_4]^{2-}_{(aq)} + x[BMImSeH^+]Cl^-_{(or)} = [PdCl_2{\cdot}BMImSe_x]_{(or)} + xH^+_{(aq)} + (x+2)\ Cl^-_{(aq)}$ (eq.4)

## Selectivity of BMImSe/[BMIm]NTF$_2$ towards diverse metal ions

The selectivity of BMImSe towards diverse metal ions was evaluated(**Figure 4**). The BMImSe/[BMIm]NTF$_2$ phase was used on a mixed solution that included several chlorides of metal ions (Al$^{3+}$, Mn$^{2+}$, Zn$^{2+}$, Mg$^{2+}$, Sn$^{4+}$, Ni$^{2+}$, Cd$^{2+}$, Pd$^{2+}$). The respective extraction percentage was calculated as shown in **Figure 4**. Except for Pd$^{2+}$, all the other metals included were hardly extracted, with extraction percentage generally below 4%. The selectivity is dramatically improved comparing to the corresponding thione extractant, which can extract about 20 - 30% of Sn$^{4+}$, Zn$^{2+}$, Cd$^{2+}$ and 10% of Ni$^{2+}$.

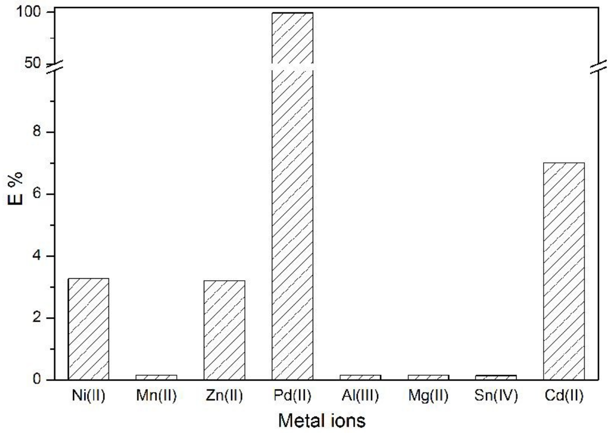


**Figure 4**. Selectivity of BMImSe/[BMIm]NTF$_2$ for the multi-metal ions solutions. Organic phase: 5 mM BMImSe in 0.5 mL [BMIm]NTF$_2$. Aqueous phase: 5 mL, each metal is chloride of 100 ppm, 10 mM HCl .

## Stripping of Pd from loaded organic phases

After equilibration of 1 mL organic phase (0.01M selone in [BMIm]NTF$_2$) with 3 mL 0.2 mM PdCl$_2$ in 8 mM HCl, the loaded organic phase was separated and contacted with stripping reagents. Many reagents used including saturated NaCl solutions, 0.5 M thiourea/1 M HCl, 0.5 M $(NH_4)_2SO_3$, 0.5 M $NaHSO_3$, 0.5 M $(NH_4)_2S_2O_8$, 0.5 M $Na_2S_2O_4$, 4 M $NH_4SCN$/1.5 M $NH_4OH$, only 0.5 M thiourea/1 M HCl and 4 M $NH_4SCN$/1.5 M $NH_4OH$ can faded the organic phase evidently, and ICP-AES results showed 35.4% and 76.8% stripping efficiency for the above two reagents respectively. Two stage back extraction could attain 98% stripping percentage with 4 M $NH_4SCN$/1.5 M $NH_4OH$, while more stages are needed with acid thiourea.

## X-ray crystallographic analysis

The Pd-selone complexes $Pd_2(BMImSe)_2Cl_4$ was prepared and analyzed with single crystal X-ray diffraction. The preparation of complexes crystals at other stoichimetric molar ratio is unsuccessful up to now.

The $Pd_2(BMImSe)_2Cl_4$ (**Figure 5**) adopts a bridging geometry with two Pd atoms connected to two selenium atoms respectively, forming a parallelogram in the monoclinic space group P 21/c. As determined by X-ray diffraction, the C-Se bond lengths in $Pd_2(BMImSe)_2Cl_4$ (1.904 Å) compare well with the value of 1.90 Å calculated for the single C-Se sp$^2$

covalent bond. In contrast, the C-S bond lengths in imidazole-2-thione (1.759 Å)[19] are much shorter than the C-S single bond (1.810 Å) and longer than the C-S double bond (1.610 Å), which indicates that the thione has more double bond character than selone. According to previous reports, owing to the significant polarizability difference between carbon and selenium atoms, the selones predominantly exist in their zwitterionic forms and the selenium center has a larger negative charge than sulfur.[37-38] So the better extractability of selone can be explained by that the Se-Pd bonds are more stronger since the C=Se bond is more polarized.

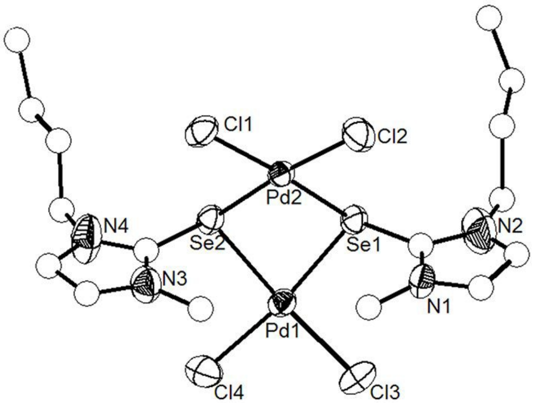


**Figure 5.** Molecular structure of $Pd_2(BMImT)_2Cl_4$, ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity.

**Table 1**. Selected Bond Lengths (Å) and Angles (deg) for $Pd_2(BMImSe)_2Cl_4$.

| A1 | A2 | Bond A1-A2 | A1 | A2 | A3 | Angle A2,A1,A3 |
|---|---|---|---|---|---|---|
| $Pd_1$ | $-Cl_4$ | 2.314(38) | $Pd_1$ | $-Cl_4$ | $-Cl_3$ | 93.919(158) |
|  | $-Cl_3$ | 2.328(48) |  | $-Cl_4$ | $-Se_2$ | 91.262(129) |
|  | $-Se_2$ | 2.400(19) |  | $-Cl_3$ | $-Se_1$ | 93.640(117) |
|  | $-Se_1$ | 2.403(22) |  | $-Se_2$ | $-Se_1$ | 81.381(73) |
| $Pd_2$ | $-Cl_2$ | 2.332(37) | $Pd_2$ | $-Cl_2$ | $-Cl_1$ | 94.523(153) |
|  | $-Cl_1$ | 2.338(47) | $Se_1$ | $-C_2$ | $-Pd_2$ | 104.901(472) |
|  | $-Se_2$ | 2.401(22) |  | $-Pd_2$ | $-Pd_1$ | 87.394(72) |
|  | $-Se_1$ | 2.402(19) |  | $-C_2$ | $-Pd_1$ | 107.747(522) |
| $Se_1$ | $-C_2$ | 1.904(160) | $Se_2$ | $-C_{12}$ | $-Pd_2$ | 104.243(484) |
| $Se_2$ | $-C_{12}$ | 1.904(173) |  | $-Pd_2$ | $-Pd_1$ | 87.325(70) |
| $N_1$ | $-C_2$ | 1.300(232) | $N_2$ | $-C_2$ | $-C_4$ | 110.241(1590) |

The lengths of Pd-Se bonds (about 2.40 Å) correspond to the sum of the covalent radii (2.44 Å). And the Pd-Se-C angle (104.24°) suggests that the Se atom can be deemed to $sp^3$-hybridized. Inspection of short contact interactions specifies that each chlorine atom is involved in two hydrogen bonds with the H-C4 of the imidazole ring. This hydrogen bonds net linking the adjacent molecular units via the chlorine gives stability and compactness to the structure and ascribes for the high crystal density.[39] **Table 1** shows selected bond lengths (Å) and angles (deg) for $Pd_2(BMImSe)_2Cl_4$.

### Analysis of the loading organic phases

With respect to the investigation of the complexing number, traditional methods (Job's method and slope method) were tried, however they did not show clear results. Then the extraction systems for palladium and platinum were analyzed with UV-vis spectrum, HPLC and $^{77}Se\{^1H\}$ NMR.

First, **Figure 6(a)** shows the UV-vis spectra for the loaded organic phase with various concentrations of selone after palladium extraction. **Figure 6(b)** shows the UV-vis spectra of chloroform solutions with direct adding of prepared Pd-Selone complexes (solid) in different molar ratio ($n_{BMImSe}$:$n_{Pd}$) of 1:1, 1:2, 1:3 and 1:4.

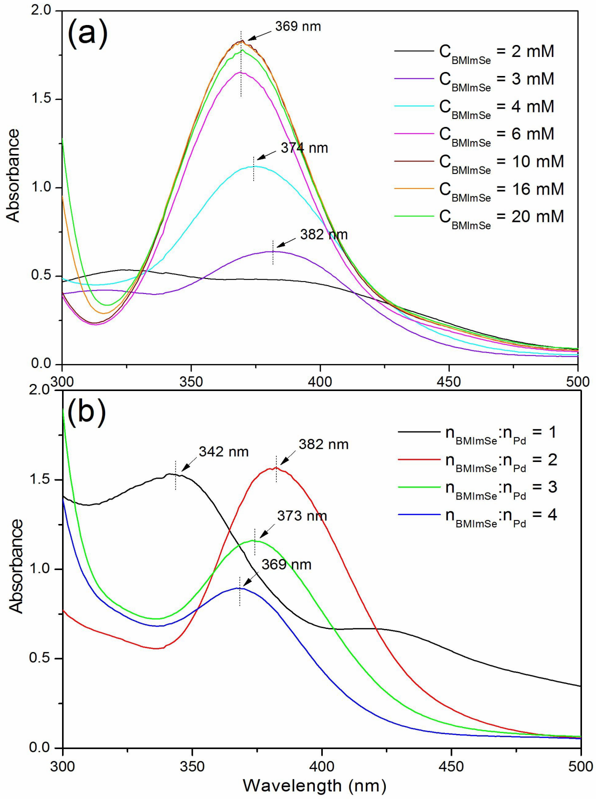


**Figure 6. (a)** UV-vis spectra of the Pd(II) loaded BMImSe/$[BMIm]NTF_2$ with increasing BMImSe concentration. **(b)** UV-vis spectra of Pd-selone complexes in different stoichiometric ratio($n_{BMImSe}$:$n_{Pd}$).

All samples were dissolved in chloroform, which was used as blank as well. Since both the extractant BMImSe and diluent $[BMIm]NTF_2$ have no absorbance in the wavelength range of 300 - 500 nm, the absorbance peaks in both figures represent the corresponding Pd-BMImSe complexes. Comparing **Figure 6(a)** with **6(b)**, a shifting of ultraviolet absorption peaks is found with the increasing selone concentration, i.e., from λ= 382 nm (corresponding to that of the $n_{BMImSe}$:$n_{Pd}$ in 2:1) to 374 nm (corresponding to that of the $n_{BMImSe}$:$n_{Pd}$ in 3:1) then to 369 nm (corresponding to that of the $n_{BMImSe}$:$n_{Pd}$ in 4:1). It was indicated that the extracted species are changing with increasing of extractant concentration at the begining, and finally fixed. From the above results, the only certainty is that no less than two species existed in the loaded organic phase. Detailed elaboration is combined with the subsequent analysis.

Second, to further explore the possible complexes composition, the $^{77}Se\{^1H\}$ NMR was also conducted on the loaded organic phase after Pd extraction with excess extractant (10 times of palladium) (**Figure 7**). The $^{77}Se\{^1H\}$ NMR (vs $SeO_2$) signal for the BMImSe and Pd loaded organic phase is δ (ppm) = 10.23 (s), 62.42 (s) respectively. No other nuclei appears in the scanned range 0 - 1100 ppm (not shown).

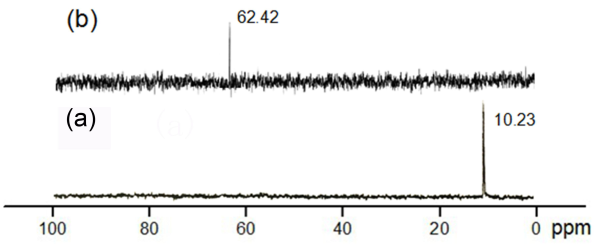


**Figure 7.** $^{77}Se\{^1H\}$ NMR for **(a)** BMImSe/[BMIm]$NTF_2$. **(b)** Pd loaded BMImSe/BMImNTF$_2$. All samples were determined without deuterated reagents. Aqueous phase: 50 mM Pd(II). Organic phase: 0.5 M BMImSe in [BMIm]$NTF_2$. $R_{A/O}$ = 10.

For one thing, the significant down-field shift of the $^{77}Se$ signal from 10.23 to 62.42 ppm indicated that the selenium atom do act as the donor to palladium. For the other thing, since palladium atom usually favors planar four-coordination complexes, more than one signal would appear if odd number of selone (except 1) combine to Pd. Only one signal appeared in the spectrum (b), which strongly suggest that the selone ligands in the Pd-selone complexes adopt chemical symmetrical structure.[40] In other words, the extracted complexes favor even number of selone ligand.

Thirdly, the HPLC was conducted to directly determine the overall arithmetic average of complexing number. Hereby we define it to be the apparent complexing number (ACN). The calculation of ACN is as following. The extractant concentrations were measured at the wavelength of 279 nm, under which the interference from ionic liquid and complexes are minimized. As **Figure 8** shows, the reduced peak area percentage is notably and can be accurately calculated. The reduced peak area percentage after the extraction was regarded as the consumed percentage of free extractant molecules. The HPLC also ensured that the equilibration of water and BMImSe loaded ILs will not lead any loss to the extractant at the experimental conditions. So all the consumed extractant molecules were deemed to be connected to Pd, which can be divided by the extracted Pd molecular number (determined as **Section 2.4**) to afford the ACN. Results are shown in **Figure 9**, which also describes the influence of diluents ([BMIm]$NTF_2$ and [OMIm]$NTF_2$) on the palladium ACN.

It was found that the ACN varies with the adding of extractant. In [BMIm]$NTF_2$, the increase of BMImSe concentration at lower levels will lead to the increase of ACN between 1.5 to 3, which is in good agreement with UV-vis results. Further increase will give rise to higher ACN (about 5). Refering to the $^{77}Se\{^1H\}$ NMR results, the odd number 5 of ACN should be attributed to the coexist of Pd-selone species in both 4 and 6 ratio. ACN in [OMIm]$NTF_2$ is lower than that in [BMIm]$NTF_2$ at lower concentration of extractant, and higher at higher selone concentration. It was speculated that the longer chain on [OMIm]$NTF_2$ will increase its compatibility for Pd-selone complexes, self-adaptively accommodate the complexes in a suitable ACN to attain better extraction percentage.

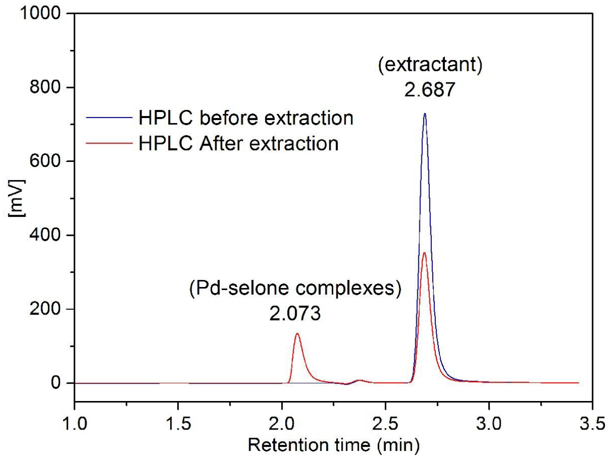


**Figure 8.** The HPLC data for the organic phase before and after extraction. The decrease of peak area for extractant (2.687 min) is notably. Aqueous phase: 0.2 mM Pd(II). Organic phase: 20 mM BMImSe in [BMIm]$NTF_2$. $R_{A/O}$ = 10.

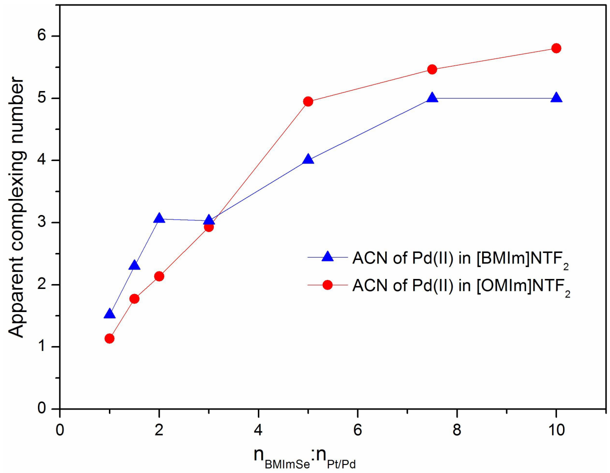


**Figure 9.** The HPLC investigations for the apparent complexing number of Pd(II) extraction with BMImSe extractant in [BMIm]$NTF_2$ or [OMIm]$NTF_2$.

To summarized, during the extraction, the palladium could form complexes with multiple species, depending on the amount of extractant. The palladium favors even-numbered selone ligands when it was extracted to ionic liquids. Longer-chain ionic liquid has higher compatibility towards complexes, thus is more conducive to the extraction.

## Conclusions

The selone ligand BMImSe in hydrophobic ionic liquids was evaluated for the extraction of palladium. The extraction mechanism was proposed for selone, which includes neutral coordination and acid ions association mechanisms, depending on the acidity. New method for the verification of the extracted complexes covered HPLC analysis, UV-vis spectra and $^{77}$Se{1H} NMR, which demonstrated that Pd could form multiple complexes with varying of the extractant amount. And even-numbered selone coordinated structures were speculated to be more stable in the loaded ionic liquids. Besides, a new conception of 'apparent complexing number' was used to describe the extraction system. Longer-chain ionic liquid has higher compatibility towards complexes, thus is more conducive to the extraction. According to the overall results, it is satisfying that the selone extractant exhibits high extractability and selectivity for palladium, which was also explained by the single crystal X-ray diffraction analysis.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant 21276142 and 21476129)

## Notes and references

[a] Key Laboratory for Special Functional Aggregated Materials of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China. E-mail: yzhyang@sdu.edu.cn

1 A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grantb and J. B. Love. Solvent extraction: the coordination chemistry behind extractive metallurgy, *Chem. Soc. Rev.*, 2014, **43**, 123.

2 P. J. Panak and A. Geist, Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands, *Chem. Rev.*, 2013, **113,** 1199.

3 M. G. Freire, et al., Aqueous biphasic systems: a boost brought about by using ionic liquids, *Chem. Soc. Rev.*, 2012, **41**, 4966.

4 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, Room temperature ionic liquids as novel media for 'clean' liquid–liquid Extraction, *Chem. Commun.*, 1998, 1765.

5 S. Royer, D. Duprez, F. Can, X. Courtois, C. B. Dupeyrat, S. Laassiri, and H. Alamdari, Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality, *Chem. Rev.*, 2014, **114** (20), 10292.

6 X. B. Wang, X.Y. Tan, B. Meng, X.F. Zhang, Q. Liang, H. Pan and S.M. Liu, TS-1 zeolite as an effective diffusion barrier for highly stable Pd membrane supported on macroporous α-$Al_2O_3$ tube, *RSC Adv.*, 2013, **3**, 4821.

7 R. D. Rogers, R. S. Kenneth, Ionic liquids---solvents of the future?. *Science*, 2003, **302**, 792.

8 K. Sasaki, K. Takao, T. Suzuki, T. Mori, T. Araia and Y. Ikeda. Extraction of Pd(II), Rh(III) and Ru(III) from $HNO_3$ aqueous solution to betainium bis-(trifluoromethanesulfonyl)imide ionic liquid, *Dalton Trans.*, 2014, **43**, 5648.

9 Q. Yang, D. Xu, J. Zhang, Y. Zhu, Z. Zhang, C. Qian, Q. Ren and H. Xing, Long-chain fatty acid-based phosphonium ionic liquids with strong hydrogen-bond basicity and good lipophilicity: synthesis, characterization, and application in extraction, ACS Sustainable Chem. Eng., 2015, **3**, 309.

10 P. Giridhar, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, Extraction of fussion palladium by Aliquat 336 and electrochemical studies on direct recovery from ionic liquid phase, *Hydrometallurgy*, 2006, **81**, 30.

11 S. Katsuta, Y. Yoshimoto, M. Okai, Y. Takeda and K. Bessho, Selective Extraction of Palladium and Platinum from Hydrochloric Acid Solutions by Trioctylammonium-Based Mixed Ionic Liquids, *Ind. Eng. Chem. Res.*, 2011, **50,** 12735.

12 M. Y. Mirza, Studies on the extraction of platinum metals with tri-iso-octylamine from hydrochloric and hydrobromic acid: separation and determination of gold, palladium and platinum, *Talanta*, 1980, **27**, 101.

13 A. Zaghbani et al. Selective thiacalix[4]arene bearing three amide groups as ionophore of binary Pd(II) and Au(III) extraction by a supported liquid membrane system. *Sep. Purif. Technol.*, 2007, **57**, 374.

14 M. R. Rosocka et al. Selective extraction of palladium(II) from hydrochloric acid solutions with pyridinecarboxamides and ACORGA®CLX50, *Sep. Purif. Technol.*, 2007, **53**, 337.

15 M. Mojski, Extraction of platinum metals from hydrochloric acid medium with triphenylphosphine solution in 1,2-dichloroethane. *Talanta*, 1980, **27**, 7.

16 M. M. Raj, A. Dharmaraja, K. Panchanatheswaran, K. A. Venkatesan, T. G. Srinivasan, R. Vasudeva, Extraction of fission palladium(II) from nitric acid by benzoylmethylene triphenyl-phosphorane (BMTTP), *Hydrometallurgy*, 2006, **84**, 118.

17 R. Ruhela et al. N,N,N',N'-Tetra(2-Ethylhexyl) Thiodiglycolamide T(2EH)TDGA: A Promising Ligand for Separation and Recovery of Palladium from High Level Liquid Waste (HLLW) Solutions, *Sep. Purif. Technol.*, 2011, **46**, 965.

18 M. Roviraa, J. L. Cortinaa, A. M Sastre, Selective liquid-liquid extraction of palladium(II) from hydrochloric acid media by di-(2-ethylhexyl) thiophosphoric acid (DEHTPA), *Solvent Extr. Ion Exch,* 1999, **17**, 333.

19 C. Wang, W. Lu, Y. Tong, Y. Zheng and Y. Z. Yang, The application of ionic liquid-based system in the extraction of palladium: synthesis, characterization and computer calculation of palladium complexes, *RSC Adv.*,2014, **4**, 57009.

20 D. M. Freudendahl, S. Santoro, S. A. Shahzad, C. Santi, T. Wirth, Angew. *Chem., Int. Ed.*, 2009, **48**, 8409.

21 G. Roy, G. Mugesh, Anti-Thyroid Drugs and Thyroid Hormone Synthesis: Effect of Methimazole Derivatives on Peroxidase-Catalyzed Reactions, *J. Am. Chem. Soc*, 2005, **127**, 15207.

22 A. J. Mukherjee, S. S. Zade, H. B. Singh and R. B. Sunoj, Organoselenium Chemistry: Role of Intramolecular Interactions, *Chem. Rev.*, 2010, **110**, 4357.

23 H. Rodriguez, G. Gurau, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, 2011, **47**, 3222.

24 W. J. Lu, et al. Coordination and extraction of mercury(ii) with an ionic liquid-based thione extractant, *Dalton Trans.*, 2013, **42**, 12908.

25 Y. Tong, C. Wang, J. Li, Y. Y. Yang, Extraction mechanism, behavior and stripping of Pd(II) by pyridinium-based ionic liquid from hydrochloric acid medium. *Hydrometallurgy*, 2014, **147–148**, 164.

26 Bruker, *SMART, SAINT and SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

27 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

28 *SHELXTL/PC, Version 6.12 for Windows XP*, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.

29 D. Parmentier, S. J. Metza and M. C. Kroon, Tetraalkylammonium oleate and linoleate based ionic liquids: promising extractants for metal salts, *Green Chem*., 2013, **15**, 205-209

30 A. T. Mohammad, et al. Simultaneous extraction and preconcentration of copper, silver and palladium with modified alumina and their determination by electrothermal atomic absorption spectrometry, *Chin.Chem. Lett*., 2014, **25**, 649.

31 T. Juliane, et al. Development of a solvent extraction system with 1,2-bis(2-methoxyethylthio)benzene for the selective separation of palladium(ii) from secondary raw materials, *Hydrometallurgy*, 2012, **127–128**, 30.

32 M. M. Raja, A. Dharmarajaa and K. Panchanatheswarana, et al. Extraction of fission palladium(ii) from nitric acid by benzoylmethylenetriphenylphosphorane (BMTPP), *Hydrometallurgy*, 2006, **84**, 118.

33 Ju. Lurie, Handbook of Analytical Chemistry, Mir, Moscow, 1978.

34 Y. W. Li, G. B. Gu 1, H. Y. Liu, Herman H. Y. Sung, I. D. Williams and C. K. Chang, A new iso-amyl benzothiazolyl sulfoxide as an extractant for palladium and the crystal structure of its palladium (II) complex, *Molecules*, 2005, **10**, 912.

35 G. Roy, D. Das, G. Mugesh, Bioinorganic chemistry aspects of the inhibition of thyroid hormone biosynthesis by anti-hyperthyroid drugs, *Inorg. Chim. Acta*, 2007, **360**, 303.

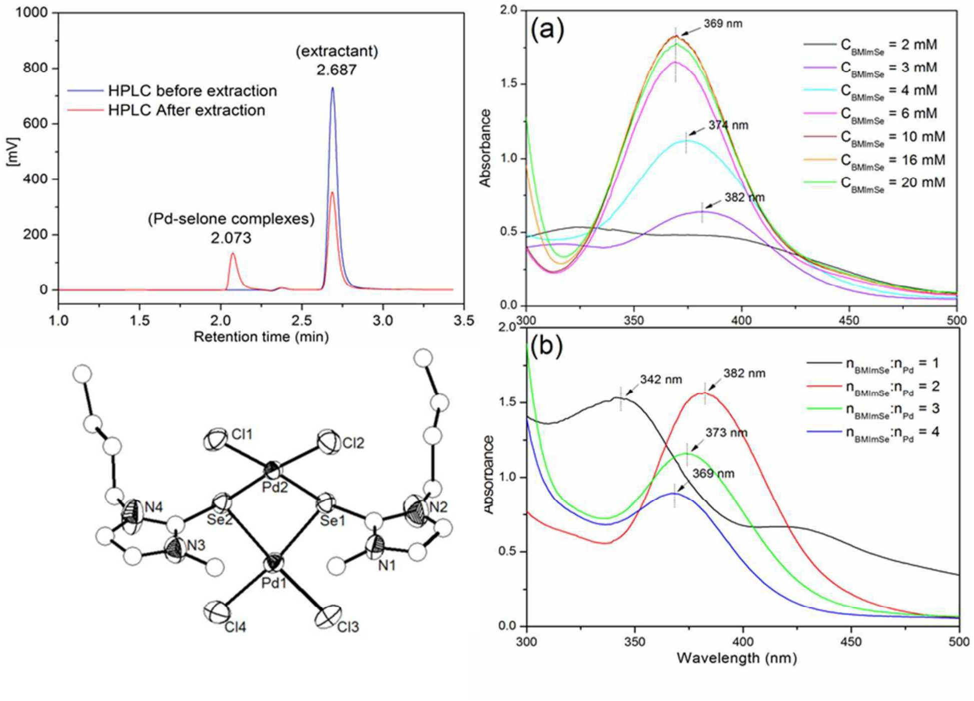
36 J. Choi, J. H. Ko et al., Reaction of Imidazoline-2-Selone with Acids and Its Use for Selective Coordination of Platinum Ions on Silica Surface, *Chem. Mater*., 2009, **21**, 2571.

37 D. Fregona, R. Graziani and G. Fraglia, Palladium and platinum complexes with N,N-dimethyselenourea, *Polyhedron,* 1996, **15**, 2523.

38 D. Manna, G. Roy, and G. Mugesh, Antithyroid Drugs and Their Analogues: Synthesis, Structure, and Mechanism of Action, *Acc. Chem. Res*, 2013, **46**, 2706.

39 M. M. Kimani, C. A. Bayse and J. L. Brumaghim, Synthesis, characterization, and DFT studies of thione and selone Cu(I) complexes with variable coordination geometries, *Dalton Trans.*, 2011, **40**, 3711.

40 D. Das, G. K. Rao, and A. K. Singh, Palladium(II) Complexes of the First Pincer(Se,N,Se) Ligand, 2,6-Bis((phenylseleno)methyl)pyridine (L): Solvent-Dependent Formation of [PdCl(L)]Cl and Na[PdCl(L)][$PdCl_4$] and High Catalytic Activity for the Heck Reaction, *Organometallics*, 2009, **28**, 6054.



The first evaluation and mechanism studies of selone for palladium extraction
254x190mm (96 x 96 DPI)