



# Removal of platinum (IV) from hydrochloric acid medium with OMImT: Theoretical and experimental evidences for a neutral complexing mechanism

Qi Wang<sup>a</sup>, Xiaolu Yin<sup>a</sup>, Wenjuan Lu<sup>b</sup>, Cheng Lv<sup>a</sup>, Xu Sun<sup>a</sup>, Yudong Wang<sup>a</sup>, Ning Wang<sup>a</sup>, Yanzhao Yang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory for Special Functional Aggregate Materials of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

<sup>b</sup> Institute of Materia Medica, Shandong Academy of Medical Sciences, Key Laboratory for Biotech-Drugs Ministry of Health, Key Laboratory for Rare & Uncommon Diseases of Shandong Province, Jinan 250062, Shandong, China

## ARTICLE INFO

### Article history:

Received 8 June 2019

Received in revised form 25 July 2019

Accepted 6 August 2019

Available online 07 August 2019

### Keywords:

Platinum

Imidazole-2-thiones

Extraction mechanism

DFT calculation

Kinetic

## ABSTRACT

As Disperser solvents are commonly toxic and volatile organic solvents in industry, disperser-free strategy enjoys the advantages of environmental benignity and cost control. In this work, 1-octyl-3-methylimidazole-2-thione (OMImT), a neutral sulfur-bearing extractant with low melting point and negligible vapor pressure, was synthesized and first utilized for the removal of Pt(IV) from hydrochloric acid medium by disperser-free precipitation owing to its excellent hydrophobicity and low viscosity. Estimation for the removal performance of Pt(IV) by disperser-free precipitation, in comparison with that by liquid-liquid extraction (LLE) with disperser cyclohexane, was conducted on the effects of the dosage of OMImT and vibration time. Subsequently, variable influence factors on the removal of Pt(IV) (e.g. phase ratio, HCl concentration,  $H^+$  concentration and  $Cl^-$  concentration) were also explored. Afterwards, the removal mechanism of Pt(IV) with OMImT was first proposed and evidenced to be a special neutral complexing mechanism via a combination of quantum-chemical calculations and experimental measurements. At last, kinetic data were analyzed by kinetics fitting methods. In brief, OMImT is a highly effective, environmentally benign and cost efficient candidate for the Pt(IV) removal.

© 2019 Elsevier B.V. All rights reserved.

## 1. Introduction

As an extremely valuable and strategic metal of platinum-group elements, platinum (Pt) is extensively employed in jewellery, catalysts, electronic devices, pharmaceutical, fuel cells, and so on [1,2]. Owing to its scarcity and industrial significance, recovering platinum from secondary sources (spent catalysts, chemical wastes, and electronic devices) is environmentally and economically crucial. The recovery of Pt is usually performed by leaching processes into an aqueous phase containing substantial amounts of acids, normally above 1 M HCl [3–6], where most platinum is oxidized as Pt(IV) and forms stable  $PtCl_6^{2-}$  [7].

For recovering or refining platinum, liquid-liquid extraction (LLE) is among the oldest techniques and still widespread up to now [6,8–10]. Nonetheless, LLE, which demands a substantial amount of toxic and volatile organic solvent as disperser solvent, is expensive, labor-intensive and environmentally unfriendly. To overcome the shortcomings mentioned above, extractants with bad water solubility and low viscosity are necessary for dispersing utterly in the absence of disperser solvent.

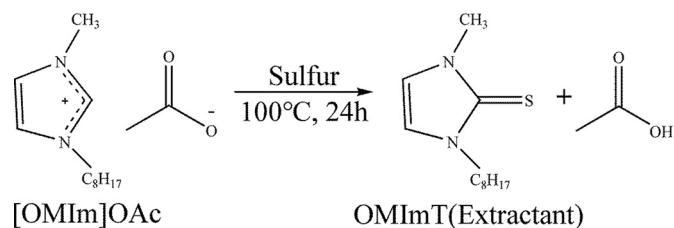
Imidazole-2-thiones have attracted considerable attention due to its wide applications in vulcanization accelerators, complexing agents,

rubber antioxidants, and high-speed photothermographic materials, etc. [11–15]. However, few researches on the removal of metals from aqueous solutions have been reported by 1, 3-disubstituted imidazole-2-thiones [16–18], which are a kind of versatile catalysts [19]. 1-octyl-3-methylimidazole-2-thione (OMImT) is a promising neutral sulfur-bearing extractant for noble metal due to its bad solubility in water (0.0057%), low melting point and negligible vapor pressure. Moreover, our attention was arrested by its low-viscosity (12.2 cP, 298 K), which makes it a potential candidate for dispersing completely in the absence of disperser.

In this work, OMImT was synthesized and first employed for the removal of Pt(IV) from hydrochloric acid medium by disperser-free precipitation and by LLE with low toxic disperser cyclohexane. For comparison purposes on the removal performance of Pt(IV), the effects of the dosage of OMImT and vibration time on the removal percentage of Pt(IV) by disperser-free precipitation and by LLE were investigated. Furthermore, variable influence factors on the removal of Pt(IV) (e.g. phase ratio, HCl concentration,  $H^+$  concentration and  $Cl^-$  concentration) by disperser-free precipitation and by LLE were explored. Afterwards, a special neutral complexing mechanism between OMImT and Pt(IV) was first put forward and confirmed by experimental evidences given by maximum metal loading experiments, FT-IR spectra,  $^1H$  NMR spectra, UV-vis spectra and elemental analysis. To support the

\* Corresponding author.

E-mail address: [yzhyang@sdu.edu.cn](mailto:yzhyang@sdu.edu.cn) (Y. Yang).



mechanism from a theoretical insight, quantum chemical calculations based on density functional theory (DFT) were performed. The electrostatic potential (ESP) maps and average local ionization energy (ALIE) maps of OMImT were calculated to verify the coordination of sulfur atom with Pt(IV) theoretically. Then kinetics studies of the Pt(IV) removal process were performed. At last, hydrazine hydrate was first tested to reduce the OMImT-Pt complexes into platinum powders.

## 2. Experimental

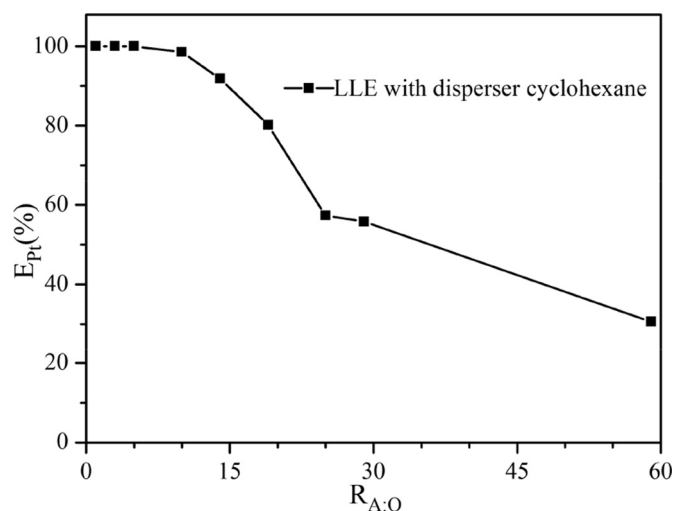
### 2.1. Reagents

All reagents and chemicals were analytical grade and utilized without further purification in this study. 1-octyl-3-methyl-imidazole acetate salt ([OMIm]OAc, > 99%), was purchased from Shanghai Chengjie Chemical Reagent Co., Ltd. (Shanghai, China).  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was dissolved in 1 M HCl, which was diluted for the feed solution. Sulfur and hydrazine hydrate were procured from Tianjin Fuyu Chemical Reagent Co., Ltd. (Tianjin, China). Regents (acetonitrile, sodium chloride, hydrochloric acid, methylene dichloride, sodium bicarbonate) were from Kermel Chemical Reagent Tianjin Co., Ltd. (Tianjin, China). Aqueous solutions were prepared by deionized water in all the experiments.

### 2.2. Experimental procedures

#### 2.2.1. Synthesis of 1-octyl-3-methyl-imidazole-2-thione

The 1-octyl-3-methylimidazole-2-thione (OMImT) was synthesized according to the procedure reported in the literature [16]. The synthesis procedure is displayed in Scheme 1. The mixture of [OMIm]OAc (25.22 mol) and sulfur (28.06 mol) was stirred at 100 °C for 24 h. The unreacted sulfur was filtered out after adding acetonitrile (30 mL), and then acetonitrile was distilled under vacuum. The product was dissolved in methylene dichloride (50 mL). Deionized water and sodium bicarbonate solution (5%) were utilized to wash the product three times to remove unreacted [OMIm]OAc and acetic acid. At last, the red-brown, low-viscosity liquid product was obtained after distilling the methylene dichloride.



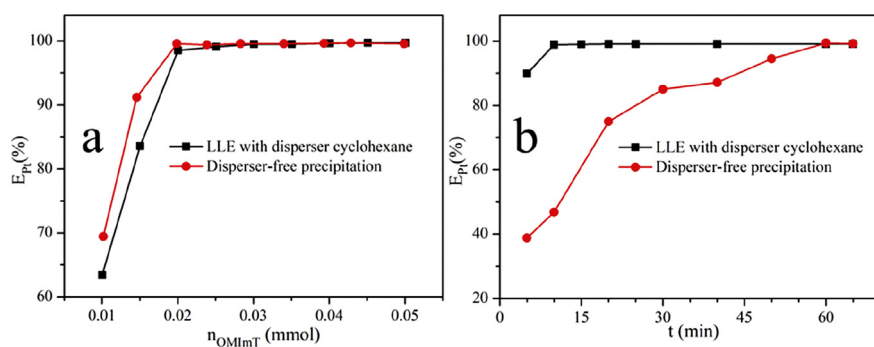
**Fig. 2.** Extraction percentage of Pt(IV) as a function of the phase ratio of aqueous phase to organic phase ( $R_{A:O}$ ). Experimental conditions: 5 mL 1.0 mM Pt(IV) solution, 6.0 M HCl;  $n_{\text{OMImT}} = 0.02$  mmol.

The FT-IR (depicted in Fig. 6) and  $^1\text{H}$  NMR (presented in Fig. 7) of OMImT were obtained. The results proved that OMImT was successfully synthesized without any impurity.  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  (ppm) = 7.18 (dd,  $J = 6.8, 2.3$  Hz, 2H), 4.05–3.91 (m, 2H), 3.51 (s, 3H), 1.78–1.63 (m, 2H), 1.32 (t,  $J = 9.0$  Hz, 10H), 0.91 (t,  $J = 6.9$  Hz, 3H). EI-MS,  $m/z = 227.16$  ( $M^+ + 1$ ).

#### 2.2.2. Disperser-free precipitation or liquid–liquid extraction of Pt(IV)

All experiments were performed with initial Pt(IV) solutions containing 1 mM  $\text{H}_2\text{PtCl}_6$  and 1–10 M HCl at 298 K. A certain amount of extractant OMImT (ranging from 0.01 to 0.05 mmol, dissolved in disperser cyclohexane to constitute the organic phase OMImT/cyclohexane or disperser-free) mixed with 5 mL initial Pt(IV) solutions in a centrifuging tube, then achieved equilibrium after mechanical vibration in an ellipsoid shaker. As shown in Fig. 1b, as the precipitation or extraction efficiency did not increase obviously after 60 min (disperser-free precipitation) or 10 min (LLE with disperser cyclohexane), thus 65 min and 15 min are sufficient for the equilibrium respectively.

For the precipitation experiments, an orange suspension containing fine particles of OMImT-Pt was formed. After a centrifuge at 12000 rpm for 20 min, the particles of OMImT-Pt are sediment in the bottom of the centrifuge tube, and transparent aqueous solutions were acquired for determining the concentration of Pt(IV). After drying, the precipitate would transform to orange powders. As for the LLE experiments, the clear and transparent aqueous phase, which was separated from organic phase with a centrifuge at 12000 rpm for 6 min, was obtained for determining the concentration of Pt(IV).



**Fig. 1.** The comparison of removal percentage of Pt(IV) ( $E_{Pt}(\%)$ ) by disperser-free precipitation and that by LLE versus (a) the dosage of OMImT and (b) vibration time. Experimental conditions: 5 mL 1.0 mM Pt(IV) solution, 4.0 M HCl (disperser-free precipitation) or 6.0 M HCl (LLE);  $R_{A:O} = 10$  (LLE). (b)  $n_{\text{OMImT}} = 0.02$  mmol.

The precipitation or extraction percentage of Pt (IV) ( $E_{Pt}$  (%)) was calculated according to the equation:

$$E_{Pt} \% = \frac{(C_{in,aq} - C_{fi,aq})}{C_{in,aq}} \times 100 \quad (1)$$

where  $C_{in,aq}$  and  $C_{fi,aq}$  (mM) are the initial and final concentration of Pt (IV) in aqueous phase, respectively.

### 2.3. Analytical techniques

The concentration of Pt(IV) in aqueous phase was determined with the help of a flame atomic absorption spectrometer (3150, Precision & Scientific Instrument Shanghai Co., Ltd., Shanghai, China). The moles of Pt(IV) in the disperser-free precipitate or the concentrations of Pt (IV) in organic phase (LLE with disperser cyclohexane) were calculated according to mass balances. Each experiment was performed 3–5 times (relative standard deviation <3%) and the mean was taken.

OMImT-Pt complexes, which formed upon the precipitation reaction of OMImT and excess  $H_2PtCl_6$ , were filtrated from the aqueous solution, washed with deionized water for 3 times, and thoroughly evaporated at 323 K and  $2 \times 10^4$  Pa. With DMSO as a solvent, the  $^1H$  NMR spectra (400 MHz) were recorded by a spectrophotometer from Bruker. FT-IR spectra were detected between 200 and 4000  $cm^{-1}$  on a Tensor27 infrared spectrometer from Bruker. The UV-vis spectra dissolved in ethanol were determined by a UV-9000 spectrophotometer from Metash. The viscosity of OMImT was measured by a Brookfield DV-II+ programmable viscometer, and the temperature was set to 298 K via a water bath. The solubility of OMImT in water was obtained via the external standard method by high-performance liquid chromatography, according to the procedure reported in the literature [17], at the wavelength of 253 nm with flow velocity of 1 mL/min. The high-performance liquid chromatography was carried out by a chromatograph (LC2000, TianMei, Shanghai, China) equipped with a Kromasil C18 column. General experiments were conducted in duplicate, unless large differences showed.

### 2.4. Computational details

The geometries of OMImT were in ground state and were fully optimized by density functional theory (DFT) under the M06-2X/6-311++g (d, p) level [20] via Gaussian 09 program package [21]. The optimizations were carried out in the gas phase or with the universal solvation model (SMD) [22] of water and cyclohexane. The wave function analyses here were performed by Multiwfn 3.5 [23,24] to obtain the electrostatic potential (ESP) and average local ionization energy (ALIE) on van der Waals (vdW) surface. During the analyses above, followed by Bader et al. [25], the vdW surface denotes the isosurface of  $\rho = 0.001$  e/bohr<sup>3</sup>. The ESP maps and ALIE maps were generated and rendered by the VMD 1.9.3 program [26].

## 3. Results and discussion

### 3.1. Comparison of disperser-free precipitation and liquid-liquid extraction for Pt (IV) removal

Oriented toward gaining some insight into the performance of disperser-free precipitation for Pt(IV) removal with OMImT, a comparative study on the dosage of OMImT and vibration time was carried out between it and LLE with disperser cyclohexane (Fig. 1). Given that the comparison was conducted for evaluating the removal performance of Pt(IV) through these two methods in industrial applications, the optimum concentrations of HCl (see Fig. 3, 4.0 M HCl for disperser-free precipitation, 6.0 M HCl for LLE) were adopted separately.

As shown in Fig. 1a, the plot of removal percentage of Pt(IV) ( $E_{Pt}$  (%)) versus the dosage of OMImT by disperser-free precipitation almost coincides with that by LLE. For both curves,  $E_{Pt}$  increases dramatically

with increasing amount of OMImT from 0.01 to 0.02 mmol, and subsequently levels off against the amount of OMImT in the range of 0.02–0.05 mmol. It can be concluded that disperser-free precipitation by OMImT is such a thermodynamically high-efficiency approach that could achieve equal maximum of  $E_{Pt}$  (99.6%) with an identically slight amount of OMImT (0.02 mmol,  $n_{OMImT}:n_{Pt} = 4:1$ ) as LLE. It could be attributed to the low viscosity of OMImT and resulting sufficient contact of OMImT and Pt(IV). In addition, 0.02 mmol was chosen as the optimum amount of OMImT for further experiments.

Fig. 1b shows that for LLE, after a rapid rise of  $E_{Pt}$  versus vibration time in the first 10 min, the curve becomes flat with  $E_{Pt}$  remaining about 99.6% thereafter. For disperser-free precipitation, the equilibrium was approached after contacting for 60 min and thus 65 min is sufficient for further experiments. The fact that it took longer to reach equilibrium by disperser-free precipitation could be chalked up to the higher viscosity of OMImT than cyclohexane, which was utilized as a dispersant in LLE to accelerate the removal process kinetically.

On the basis of the above observations, disperser-free precipitation is a superior technique for the removal of Pt(IV) with OMImT than LLE owing to its high efficiency, environmental benignity and cost reduction over acceptable vibration time. Meanwhile, owing to the high efficiency, short vibration time and low toxicity of cyclohexane, LLE with disperser cyclohexane has industrial potential for the removal of Pt(IV) to some extent.

### 3.2. Influence of the phase ratio on the liquid-liquid extraction of Pt(IV)

For LLE with disperser cyclohexane, the effect of the volume ratio of aqueous phase to organic phase ( $R_{A:O}$ ) on  $E_{Pt}$  was studied. As shown in Fig. 2,  $E_{Pt}$  retains about 99.6% when  $R_{A:O}$  ranges from 1 to 10, and decreases rapidly after  $R_{A:O}$  exceeds 10. Therefore, 10 is the optimum value of  $R_{A:O}$  for a balance between high extraction percentage and large aqueous phase volumes.

### 3.3. Influences of HCl, $H^+$ and $Cl^-$ concentrations on the removal of Pt(IV)

The effects of HCl,  $H^+$  and  $Cl^-$  concentrations in the aqueous phase on the removal of Pt(IV) were explored for confirming the optimum acidity and the removal mechanism.

The influence of HCl concentration was researched over the range of 1–10 M HCl, and the results are shown in Fig. 3. For disperser-free precipitation,  $E_{Pt}$  is positively correlated with HCl concentration when the concentration of hydrochloric acid varies from 1 M to 4 M, and levels out at around 99.6% in the range of 4–10 M HCl. For LLE with disperser

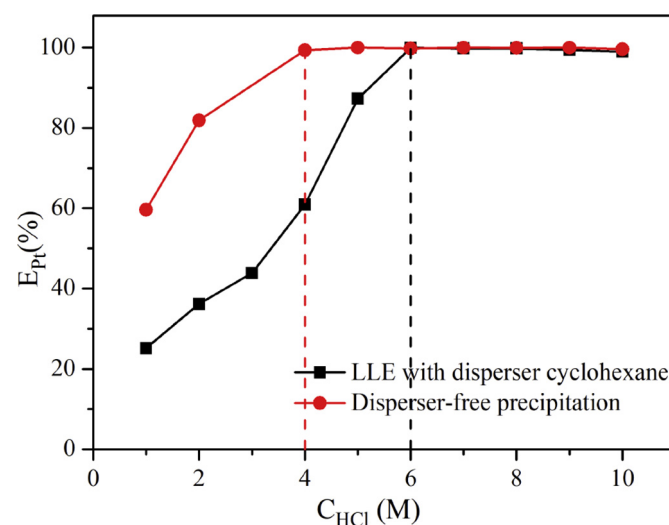


Fig. 3. The effect of HCl concentration on  $E_{Pt}$  (%). Experimental conditions: 5 mL 1.0 mM Pt (IV) solution,  $n_{OMImT} = 0.02$  mmol,  $R_{A:O} = 10$  (LLE).

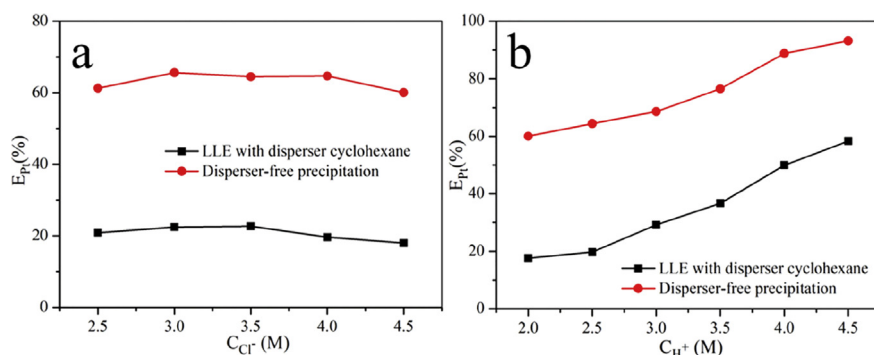


Fig. 4. The plot of  $E_{Pt}$  (%) versus (a) the concentration of  $Cl^-$  and (b) the concentration of  $H^+$ . Experimental conditions: 5 mL 1.0 mM Pt (IV) solution,  $n_{OMImT} = 0.02$  mmol,  $R_{A:O} = 10$  (LLE).

cyclohexane, the plot of  $E_{Pt}$  versus HCl concentration exhibits a similar tendency except for the inflection point at 6 M HCl. Accordingly, the optimum concentration of HCl are 4.0 M and 6.0 M for disperser-free precipitation and LLE with disperser cyclohexane, respectively. Furthermore, as OMImT could retain high removal percentage of Pt (IV) against the influence of HCl in a wide range, it is a superior candidate for removing Pt(IV) industrially [6].

For an in-depth understanding of the removal mechanism of Pt(IV), the effect of  $H^+$  and  $Cl^-$  were investigated separately. The effect of  $Cl^-$  concentration on the removal of Pt(IV) was explored at a fixed 2.0 M HCl concentration, and the  $Cl^-$  concentration varied from 2.5 M to 4.5 M by the adjustment of NaCl. As seen from Fig. 4a,  $E_{Pt}$  is independent of  $Cl^-$  concentration for disperser-free precipitation as well as LLE with disperser cyclohexane. Subsequently, the influence of  $H^+$  concentration was studied over the range of 2.0–4.5 M  $H^+$ , and a fixed 4.5 M  $Cl^-$  concentration was remained by the addition of NaCl. A positive correlation between  $E_{Pt}$  and  $H^+$  concentration, which is suitable for disperser-free precipitation as well as LLE with disperser cyclohexane, was presented in Fig. 4b. As a consequence, it could be concluded that the removal mechanism of Pt(IV) involves the participation of  $H^+$  but the absence of  $Cl^-$  for disperser-free precipitation as well as LLE with disperser cyclohexane.

### 3.4. Removal mechanism of Pt (IV)

To demonstrate the removal mechanism of Pt(IV) with OMImT, considerable efforts were made experimentally and theoretically.

To determine the coordination number of OMImT-Pt complexes in the removal reactions, the maximum metal loading experiments (Fig. 5) were conducted [27]. The concentration of Pt(IV) was maintained at 1 mM against the increasing dosage of OMImT. Given that the removal mechanisms were investigated for the industrial applications, the optimum HCl concentrations (4.0 M HCl for disperser-free precipitation, 6.0 M HCl for LLE) were adopted separately for each approach. The results are shown in Fig. 5. For both disperser-free precipitation and LLE, the molar ratio of OMImT to Pt(IV) removed almost kept constant three, when the molar ratio of OMImT to Pt(IV) added is less than three. It suggests that OMImT-Pt complexes are in the same mole ratio (3:1) at maximum loadings for both approaches. Besides, in combination with the analogous removal behaviors of Pt(IV) discussed in Section 3.3, it could be assumed that the removal of Pt(IV) with OMImT by disperser-free precipitation and by LLE with disperser cyclohexane follows the same mechanism.

To obtain the direct evidence of interactions between OMImT and Pt (IV), FT-IR spectra were determined for OMImT and OMImT-Pt complexes (Fig. 6). The vibration bands of OMImT are as follows: ring alkene C—H stretch, 3095  $cm^{-1}$ ; aliphatic C—H stretch, 2927 and 2857  $cm^{-1}$ ; ring C=C stretch, 1569  $cm^{-1}$ ; —N—C=S group, 1459 and 1230  $cm^{-1}$  [28,29]; C—N stretch, 1408  $cm^{-1}$ . It is quite confusing that no apparent shifts observed between OMImT and OMImT-Pt complexes washed by water, except the negative shift from 1569  $cm^{-1}$  to 1562  $cm^{-1}$  related

to the C=C stretch in the imidazole ring. This unusual phenomenon is against the prediction that nitrogen or sulfur atom of OMImT would be the active site to interact with Pt(IV) on the basis of common sense. However, it is found that many absorption bands related to the imidazole ring changed obviously as long as the OMImT-Pt complexes washed by water and ethanol. In comparison with OMImT, its peaks associated with C=C shifted from 3095  $cm^{-1}$  and 1569  $cm^{-1}$  to 3101  $cm^{-1}$  and 1555  $cm^{-1}$ , respectively; its peaks assigned to the —N—C=S group also shifted from 1459  $cm^{-1}$  and 1230  $cm^{-1}$  to 1472  $cm^{-1}$  and 1224  $cm^{-1}$ , respectively. Nevertheless, the aliphatic C—H peaks barely shifted owing to the weak interaction between Pt (IV) and the alkyl side chains of OMImT. In addition, the absence of peak at 343  $cm^{-1}$  [30], which is assigned to  $PtCl_6^{2-}$ , signifies that Pt (IV) coordinated with the nitrogen atom or sulfur atom of OMImT. Taking steric hindrance into account, it is inferred that the sulfur atom of OMImT would coordinate with Pt(IV) preferentially.

It is notable that the OMImT-Pt complexes were prepared by repeated precipitation reaction of OMImT and excess  $H_2PtCl_6$ , thus the residue of unreacted OMImT is impossible, even if the OMImT-Pt complexes washed only by water. It is speculated that the interesting phenomenon mentioned above resulted from the special removal mechanism. Moreover, the absence of peak at 348  $cm^{-1}$  [30] signifies the presence of highly symmetrical trans- $Pt(OMImT)_2Cl_4$ , which retained after washed by ethanol due to its low polarity. Thus, it is inferred that the three OMImT molecules of per OMImT-Pt molecule could be divided into two groups at a coordination/freer state ratio of

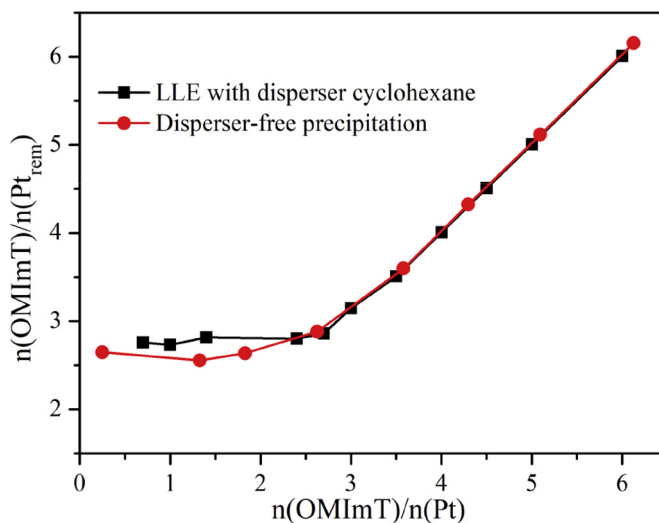


Fig. 5. The mole ratio of OMImT to Pt (IV) removed ( $n(OMImT)/n(Pt_{rem})$ ) versus the mole ratio of OMImT to Pt (IV) added at a constant initial concentration of Pt (IV). Experimental conditions: 5 mL 1.0 mM Pt (IV) solution, 4.0 M HCl (disperser-free precipitation) or 6.0 M HCl (LLE);  $R_{A:O} = 10$  (LLE).



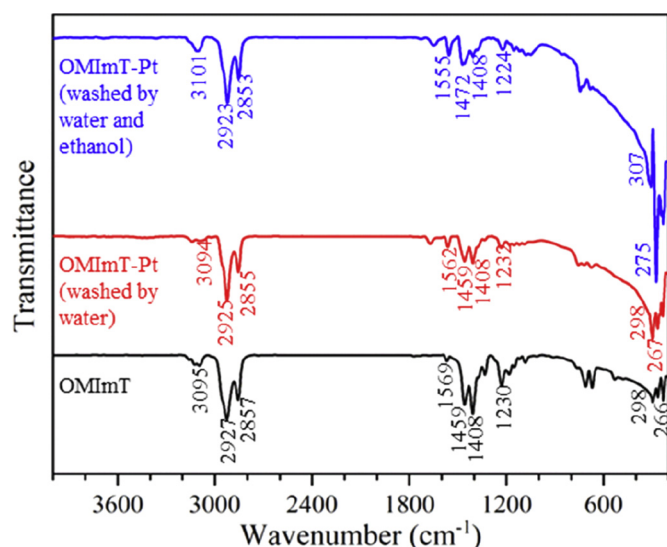


Fig. 6. FT-IR spectra of OMImT and OMImT-Pt complexes.

2:1, and the group with weaker interaction between OMImT and Pt(IV), whose FT-IR resembles that of OMImT owing to its freer state, could mask the shifts from the other group with stronger interaction to a certain extent.

The  $^1\text{H}$  NMR spectra of OMImT and OMImT-Pt complexes by two post-treatment methods further proved the speculation proposed above. As seen in Fig. 7, the chemical shifts of hydrogen nuclei ( $\delta_{\text{H}}$ , ppm) in the aliphatic chain away from imidazole ring hardly changed. For OMImT-Pt complexes washed only by water: A – A' (A''), 0.91 → 0.92; B – B' (B''), 1.32 → 1.32; C – C' (C''), 1.71 → 1.77;  $\Delta\delta_{\text{H}} = 0.00\text{--}0.06$ . For OMImT-Pt complexes washed by water and ethanol: A – A'', 0.91 → 0.85; B – B'', 1.32 → 1.24; C – C'', 1.71 → 1.72;  $\Delta\delta_{\text{H}} = -0.08\text{--}0.01$ . Note, for OMImT-Pt complexes washed only by water, that the  $\delta_{\text{H}}$  related to H nuclei in the aliphatic chain near imidazole ring or in imidazole ring could be divided into two groups with a peak area ratio of 2:1, and the  $\delta_{\text{H}}$  values of the group with larger peak area approximate those of the OMImT-Pt complexes washed by water and ethanol. The most significant changes of  $\delta_{\text{H}}$  attributed to the H nuclei in imidazole ring are as follows: F – F' (G – G'), 7.18 → 7.64; F – F'' (G – G''), 7.18 → 7.74; F – F''' (G – G'''), 7.18 → 7.76;  $\Delta\delta_{\text{H}} = 0.46\text{--}0.58$ . The evident changes of  $\delta_{\text{H}}$  owing to the H nuclei in the aliphatic chain

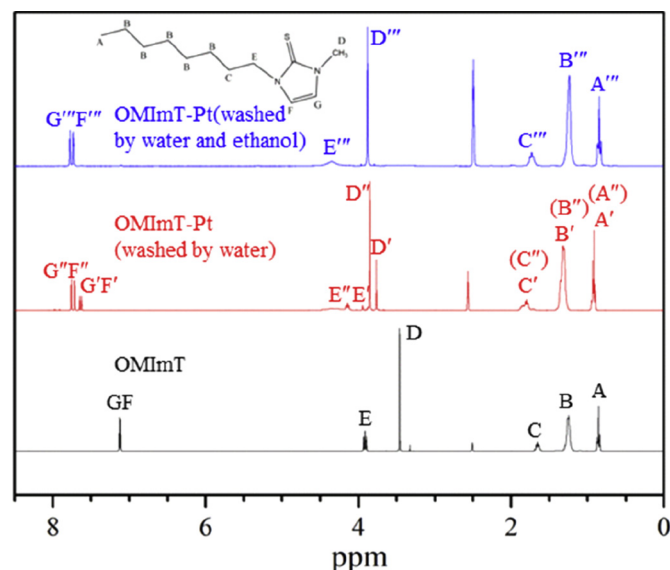


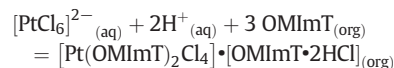
Fig. 7.  $^1\text{H}$  NMR spectra of OMImT and OMImT-Pt complexes.

near imidazole ring are presented as following: D – D', 3.51 → 3.76; D – D'' (D'''), 3.51 → 3.86 (3.88); E – E', 3.98 → 4.05; E – E'' (E'''), 3.98 → 4.24 (4.23);  $\Delta\delta_{\text{H}} = 0.07\text{--}0.37$ . The data above also illustrate that the two OMImT molecules of per OMImT-Pt molecule coordinated with Pt(IV), while the rest one was in a freer state with weaker interaction. It also reveals that Pt(IV) has coordinated with the nitrogen atom or sulfur atom of OMImT in imidazole ring, which coincides with the results of FT-IR analysis.

In order to gain theoretical insight into the extraction mechanism and to identify the coordination sites of OMImT with Pt(IV), the electrostatic potential (ESP) and average local ionization energies (ALIE) on the vdW surface, which are complementary [31], were calculated. ESP on the molecular surface can be utilized to understand and forecast where Pt(IV) would incline to approach from afar, which is dominated by long-range electrostatic interactions. As displayed in Fig. 8a, c and e, the most electron-rich regions as well as the global minima of ESP on the surface (−34.51 kcal/mol, −47.10 kcal/mol and −39.32 kcal/mol for OMImT in the gas phase, in water, and in cyclohexane, respectively) appear around the sulfur atom, thus it is sulfur atom that inclines to coordinate with Pt(IV). In addition, the lowest values of ALIE, which correlate with the locations of the least tightly bound and most reactive electrons, can be employed to predict the preferred coordination positions with Pt(IV). As shown in Fig. 8b, d and f, the fact that the global minima of ALIE on the surface (7.84 eV, 8.02 eV and 7.86 eV for OMImT in the gas phase, in water, and in cyclohexane, respectively) correspond to the sulfur atom, also supports the conclusion that sulfur atom has a higher reactivity toward coordination with Pt(IV). To sum up, the coordination for the sulfur atom of OMImT with Pt(IV) was verified theoretically via a combination of electrostatic potential maps and average local ionization energy maps.

To demonstrate the species difference of OMImT-Pt complexes by two post-treatment methods, UV-vis spectra of  $\text{H}_2\text{PtCl}_6$ , OMImT and OMImT-Pt complexes (Fig. 9) were recorded. The absorption peak of  $\text{H}_2\text{PtCl}_6$  at 262 nm could be assigned to the presence of  $\text{PtCl}_6^{2-}$  anions [32]. We notice that the shape of the absorption peaks for OMImT-Pt complexes washed by water and ethanol is quite different from that washed only by water. Moreover, the wavelength of characteristic absorption peak for OMImT-Pt complexes washed by water is at 321 nm, while that of OMImT-Pt complexes washed by water and ethanol is at 382 nm. It signifies that OMImT-Pt complexes by two post-treatment methods were not the same species indeed and the speculations for their molecular formulas were verified by elemental analysis. As tabulated in Table 1, the elemental analysis data from OMImT-Pt complexes washed by water and that washed by water and ethanol are consistent with the corresponding results calculated for  $[\text{Pt}(\text{OMImT})_2\text{Cl}_4] \cdot [\text{OMImT} \cdot 2\text{HCl}]$  and  $\text{Pt}(\text{OMImT})_2\text{Cl}_4$ , respectively.

Taking the material conservation, charge balance and discussions above into account, the neutral complexing mechanism of OMImT for Pt(IV) removal in this work can be written as:



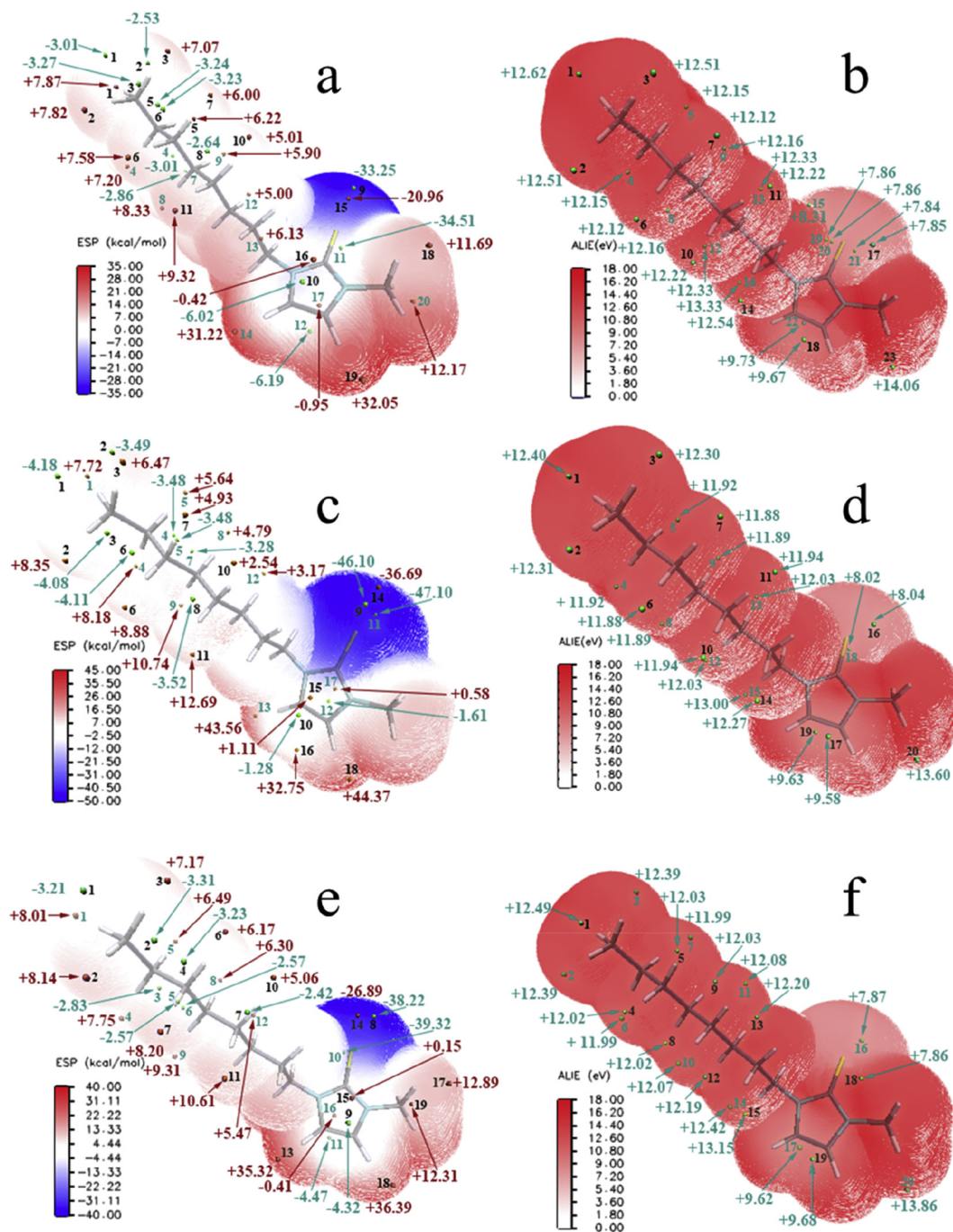
### 3.5. Kinetics of Pt (IV) removal

To gain insight into the removal process of Pt(IV) with OMImT kinetically, the kinetic data were analyzed by kinetics fitting methods with pseudo-first-order rate model and pseudo-second-order rate model [33].

Pseudo-first-order rate model and pseudo-second-order rate model could be expressed by Eqs. (2) and (3), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$



**Fig. 8.** Electrostatic potential (ESP) maps on the vdW surface of OMImT (a) in the gas phase, (c) in water, and (e) in cyclohexane. Average local ionization energies (ALIE) maps on the vdW surface of OMImT (b) in the gas phase, (d) in water, and (f) in cyclohexane. (Surface local minima and maxima are characterized as green and orange spheres, respectively. The extrema at backside/front side of the maps are symbolized by transparent/opaque spheres with green/black labels.)

where  $q_t$  (mmol/g) and  $q_e$  (mmol/g) denote the removal capacity of Pt (IV) at time  $t$  (min) and at equilibrium, while  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}/(\text{mmol} \cdot \text{min})$ ) represent the rate constant of the pseudo-first-order model and pseudo-second-order model, respectively.

Due to the pseudo-second-order model was better fit than pseudo-first-order model in terms of higher correlation coefficients ( $R^2$ ), we only show the plot of  $t/q_t$  vs.  $t$  for the pseudo-second-order model rather than the plot of  $\ln(q_e - q_t)$  vs.  $t$  for the pseudo-first-order model in Fig. 10. As pseudo-second-order model is more likely to speculate kinetic behavior of chemical reaction for the rate-controlling step [34], the removal process of Pt(IV) with OMImT can be interpreted with “surface

reaction” model, supposing that the chemical reaction on the surface of OMImT droplets is the slowest step in the whole removal procedure [35]. The values of  $q_e$  and  $k_2$  calculated from the slope and intercept of the fitting plots  $t/q_t$  vs.  $t$  are as follows: for LLE,  $q_e = 1.09$  mmol/g,  $k_2 = 214.6$  g/(mmol·min); for disperser-free precipitation,  $q_e = 1.41$  mmol/g,  $k_2 = 0.049$  g/(mmol·min).

### 3.6. Recovery of Pt (IV)

In order to recover platinum, OMImT-Pt complexes, which were obtained by disperser-free precipitation or through evaporating

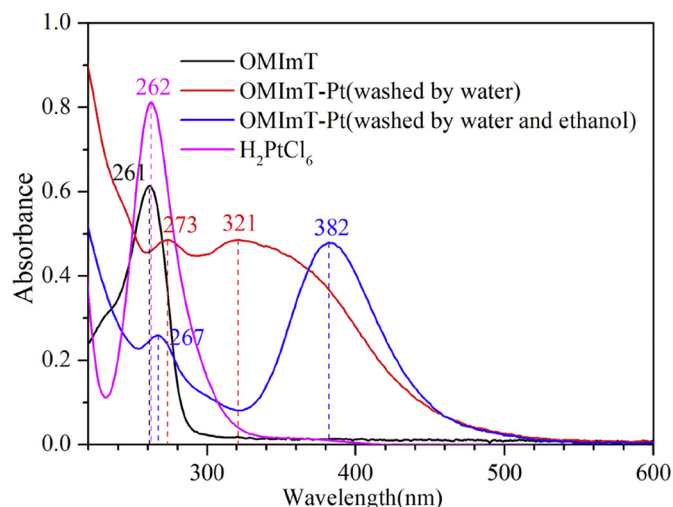


Fig. 9. UV-vis spectra of  $\text{H}_2\text{PtCl}_6$ , OMIImT and OMIImT-Pt complexes.

cyclohexane by LLE, were mixed with 1 mL 3.6 M  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  solutions and maintained at 333 K for 4 h. Black platinum powders and red-brown OMIImT organic phase were formed in this process. After the reduction reaction, the platinum precipitate was filtrated from liquid phases and the two liquid phases (OMIImT phase and aqueous phase) were separated by centrifugation. The stripping percentage of Pt was 95.3%.

#### 4. Conclusions

In this work, OMIImT was synthesized and employed for the removal of Pt(IV) from hydrochloric acid medium for the first time. The performance comparisons for Pt(IV) removal between disperser-free precipitation and LLE with disperser cyclohexane on the dosage of OMIImT and vibration time were carried out, which indicates that disperser-free precipitation was a better approach for Pt(IV) removal than LLE owing to its high efficiency, environmental benignity and cost reduction over viable vibration time. Subsequently, the influences of phase ratio and HCl concentration on Pt(IV) removal were investigated for process optimization, while those of  $\text{H}^+$  concentration and  $\text{Cl}^-$  concentration were explored for removal mechanism, which reveals that the removal mechanism of Pt(IV) with OMIImT involves the participation of  $\text{H}^+$  but the absence of  $\text{Cl}^-$ . Afterwards, a special neutral complexing mechanism between OMIImT and Pt(IV) was first proposed and illustrated by experimental evidences from maximum metal loading experiments, FT-IR spectra,  $^1\text{H}$  NMR spectra, UV-vis spectra and elemental analysis. It was also found to be more robust with the support from ab initio quantum-chemical studies, which validates the coordination of sulfur atom with Pt(IV) theoretically. Moreover, the kinetic data were well fitted by pseudo-second-order rate model, which implies that the chemical reaction on the surface of OMIImT droplets is the slowest step in the whole removal process. At last, the Pt recovery can be achieved by the reduction of hydrazine hydrate. In a word, OMIImT is

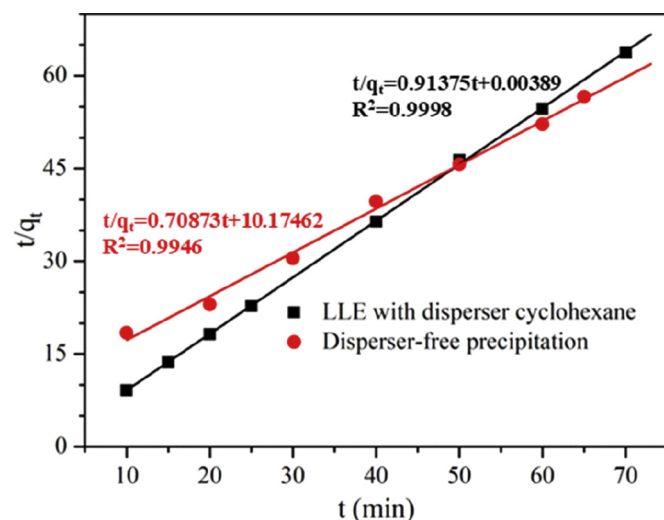


Fig. 10. Pseudo-second-order fitting plot for the removal of Pt (IV) with OMIImT. Experimental conditions:  $n_{\text{OMIImT}} = 0.02$  mmol; 5 mL 1.0 mM Pt (IV) solution, 4.0 M HCl (disperser-free precipitation) or 6.0 M HCl (LLE);  $R_{\text{A.O}} = 10$  (LLE).

an effective, nature-friendly and economical candidate for the removal of Pt(IV).

#### Acknowledgements

We acknowledge Natural Science Foundation of Shandong Province, China (ZR2019MB060). We also appreciate the National Natural Science Foundation of China (21476129 and 21606147) for the financial support. The scientific calculations in this paper have been done on the HPC Cloud Platform of Shandong University.

#### References

- [1] R.J. Seymore, J.I. O'Farrelly, L.C. Potter, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York, 1998.
- [2] Platinum 2012 Interim Review, Johnson Matthey PLC, Hertfordshire, England, 2012.
- [3] S. Génand-Pinaz, N. Papaiconomou, J.-M. Leveque, Removal of platinum from water by precipitation or liquid-liquid extraction and separation from gold using ionic liquids, *Green Chem.* 15 (2013) 2493–2501.
- [4] B. Green, D. Smit, H. Maumela, G. Coetzer, Leaching and recovery of platinum group metals from UG-2 concentrates, *J. South. Afr. Inst. Min. Metall.* 104 (2004) 323–331.
- [5] J.M. Mwase, J. Petersen, J.J. Eksteen, A conceptual flowsheet for heap leaching of platinum group metals (PGMs) from a low-grade ore concentrate, *Hydrometallurgy* 111–112 (2012) 129–135.
- [6] R.S. Marinho, J.C. Afonso, J.W.S.D. da Cunha, Recovery of platinum from spent catalysts by liquid-liquid extraction in chloride medium, *J. Hazard. Mater.* 179 (2010) 488–494.
- [7] S.A. Cotton, Chemistry of Precious Metals, Chapman & Hall, London, 1997.
- [8] M.K. Jha, D. Gupta, J.C. Lee, V. Kumar, J. Jeong, Solvent extraction of platinum using amine based extractants in different solutions: a review, *Hydrometallurgy* 142 (2014) 60–69.
- [9] D. Parajuli, K. Hirota, K. Inoue, Trimethylamine-modified lignophenol for the recovery of precious metals, *Ind. Eng. Chem. Res.* 48 (2009) 10163–10168.
- [10] D. Parajuli, H. Kawakita, K. Inoue, M. Funaoka, Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives, *Ind. Eng. Chem. Res.* 45 (2006) 6405–6412.
- [11] Chem. Abstr. 120 (1988), 136824.

Table 1  
Elemental analysis of OMIImT-Pt complexes.

Species	C (%)		H (%)		N (%)		S (%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
[Pt(OMIImT) <sub>2</sub> Cl <sub>4</sub> ] $\cdot$ [OMIImT $\cdot$ 2HCl]	39.7	39.6	6.29	6.07	7.72	7.36	8.83	8.73
Pt(OMIImT) <sub>2</sub> Cl <sub>4</sub>	36.5	36.6	5.62	5.43	7.10	7.12	8.12	8.09



- [12] X. Tao, M. Lei, Y. Wang, Unexpected microwave reaction of 1,3-disubstituted imidazolium salts: a novel synthesis of 1,3-disubstituted imidazole-2-thiones, *Synth. Commun.* 37 (2007) 399–408.
- [13] Chem. Abstr. 108 (1988) 113624.
- [14] Chem. Abstr. 136 (2002), 270656.
- [15] M. Feroci, M. Orsini, A. Inesi, An efficient combined electrochemical and ultrasound assisted synthesis of imidazole-2-thiones, *Adv. Synth. Catal.* 351 (2009) 2067–2070.
- [16] W. Lu, P.S. Barber, S.P. Kelley, R.D. Rogers, Coordination and extraction of mercury (II) with an ionic liquid-based thione extractant, *Dalton Trans.* 42 (2013) 12908–12916.
- [17] X. Yin, Q. Wang, S. Wang, H. Zhang, J. Guo, Y. Yang, Behavior, mechanism, and equilibrium studies of rhodium(I) extraction from hydrochloric acid with HMLmT, *New J. Chem.* 41 (2017) 10054–10061.
- [18] X. Yin, H. Yi, Q. Wang, Y. Wang, X. Sun, C. Lv, J. Guo, Y. Yang, Extraction and separation of multiple platinum group metals from hydrochloric acid solution with sole 1-hexyl-3-methylimidazole-2-thione using microextraction method, *Hydrometallurgy* 174 (2017) 167–174.
- [19] Chem. Abstr. 117 (1992) 50846.
- [20] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Accounts* 120 (2008) 215–241.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, A.F. Izmaylov, G. Zheng, J.L. Sonnenberg, J.V. Ortiz, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2010.
- [22] A.V. Marenich, C.J. Cramer, D.G. Truhlar, Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, *J. Phys. Chem. B* 113 (2009) 6378–6396.
- [23] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, *J. Comput. Chem.* 33 (2012) 580–592.
- [24] T. Lu, F. Chen, Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm, *J. Mol. Graph. Model.* 38 (2012) 314–323.
- [25] R.F.W. Bader, M.T. Carroll, J.R. Cheeseman, C. Chang, Properties of atoms in molecules: atomic volumes, *J. Am. Chem. Soc.* 109 (1987) 7968–7979.
- [26] W. Humphrey, A. Dalke, K. Schulten, VMD: visual molecular dynamics, *J. Mol. Graph.* 14 (1996) 33–38.
- [27] S. Riaño, K. Binnemans, Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets, *Green Chem.* 17 (2015) 2931–2942.
- [28] E. Lieber, C.N.R. Rao, C.N. Pillai, J. Ramachandran, R.D. Hites, The infrared spectra of 4-substituted-thiosemicarbazides and diazotization products, *Can. J. Chem.* 36 (1958) 801–809.
- [29] E.S. Raper, P.H. Crackett, Complexes of imidazoline (1,3H)-2-thione with Co(II) and Zn(II) salts, *Inorg. Chim. Acta* 50 (1981) 159–165.
- [30] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Handbook of Vibrational Spectroscopy, John Wiley & Sons, 2006.
- [31] F.A. Bulat, A. Toro-Labbé, T. Brinck, J.S. Murray, P. Politzer, Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies, *J. Mol. Model.* 16 (2010) 1679–1691.
- [32] P.-H. van Wyk, W.J. Gerber, K.R. Koch, A robust method for speciation, separation and photometric characterization of all  $[\text{PtCl}_{6-n}\text{Br}_n]^{2-}$  ( $n=0-6$ ) and  $[\text{PtCl}_{4-n}\text{Br}_n]^{2-}$  ( $n=0-4$ ) complex anions by means of ion-pairing RP-HPLC coupled to ICP-MS/OES, validated by high resolution  $^{195}\text{Pt}$  NMR spectroscopy, *Anal. Chim. Acta* 704 (2011) 154–161.
- [33] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [34] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.
- [35] W. Plazinski, J. Dziuba, W. Rudzinski, Modeling of sorption kinetics: the pseudo-second order equation and the sorbate intraparticle diffusivity, *Adsorption* 19 (2013) 1055–1064.