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In view of the recycling and the preconcentration of palladium(Pd) from aqueous solutions, a sulfur-bearing extractant, 1,3-diethyl-imidazole-2-thione, in ionic liquid organic phase was evaluated for palladium extraction. Extraction conditions were examined followed by mechanism studies. The Pd(II) in bearing extractant, 1,3kdiethylkimidazolek2kthione, in ionic liquid organic phase was evaluated for palladium extraction. Extraction from hydrochloric acid solutions of trihexyl(tetradecyl)phosphonium chloride for palladium extraction. For example, A. Cieszynska et al. probed the use of ionic liquids, which are considered advantageous for their versatility, the traditional solvent extraction is still the most convenient and economical method allow for the large-scale application.

Although solvent extraction has gained long-run development, efficient green extraction systems are still in eagerly needed. Recent studies on the solvent extraction of palladium value the use of ionic liquids, which are considered advantageous for their versatility and "green" credentials, as either the organic phase or the extractants. For example, A. Cieszynska et al. probed the use of trihexyl(tetradecyl)phosphonium chloride for palladium extraction from hydrochloric acid solutions.

Katsuta and Shoichi et al. developed a well founded method to selectively separate palladium and platinum by trietylaminonium-based mixed ionic liquids, which are recyclable, easy to handle, safe, and environmentally. Sasaki, Kotoe et al. used ionic liquid betainium bis(trifluoromethanesulfonyl)imide to extract Pd(II), Rh(III) and Ru(III) from HNO3 aqueous solution, which proceed via the coordination between betaine and metal ions and the cation exchange of the formed complex with proton.

During the above researches, the metal ions are extracted to the organic ionic liquids phase through an ion exchange mechanism, which were shown as follows, where the subscript (aq), (IL) and (or) denote an aqueous phase, ionic liquid phase and the organic phase respectively.

$$2H^+(aq) + PdCl_4^{2−}(aq) + 2R−R′PA(IL) ⇌ (R−R′P)_2PdCl_4(or) + 2HA(aq)$$

$$M^{n+}(aq) + mL(IL) + x[C_{min}][TFSA(IL)] ⇌ [M(L)_m^{n+}](TFSA)^−_m(IL) + x[C_{min}^{−}][aq]$$

$$PtCl_4^{2−}(aq) + 2[C_{min}][PF_6(IL)] ⇌ ([C_{min}]_2⋅PtCl_4^{2−}(or) + 2PF_6^{−}(aq))$$

These mechanisms will certainly lead to the loss of ionic liquids. Therefore in order to facilitate the extraction, the volume of the ionic liquids phase would be relatively large, with volume ratio to aqueous phase about 1:2, which means the higher cost for application. On the other hand, since most of the waste aqueous sources that containing Pd(II) is acidic, and the yields of the extraction with ion exchange will fluctuate with the varying concentration of the aqueous hydrogen ions so an extra procedure is needed to adjust pH. Nevertheless, these disadvantages can be avoided through neutral extraction.

In our work, the sulfur-bearing extractant, 1,3-diethyl imidazole-2-thione (EEImT) was firstly used as the extractant to extract aqueous palladium to the ionic liquid organic phase, i.e., 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([EMIm][NTF2]). Extracted complexes were formed through a neutral coordination rather than ion exchange mechanism therefore avoided the loss of ionic liquid and directly saved the...
volume of the organic phase. The extraction system also provides a new method for the quick preparation of the regularly-shaped metal complexes crystals under certain conditions. Two novel PdCl$_2$-thione crystals were obtained. The X-ray crystallography analysis and computer calculations were conducted to elucidate the construction and configuration of the Pd (II)-EEImT complexes. The extraction is barely dependent on the hydrochloric acid concentration at certain conditions. And the whole system was verified to be effective and stable.

10 Experimental Section
Reagent and materials
1,3-dimethyl imidazole acetate salt and 1-ethyl-3-methyl imidazolium bis (trifluoromethyl) sulfonyl) imide were purchased from Lanzhou Greenchem ILS, LICP, CAS, China. PdCl$_2$ was purchased from Guangfu Institute of Fine Chemical (Tianjin, China). All the reagents (sulfur, sodium bicarbonate, methanol, acetonitrile, methylene dichloride, acetone) were AR and used without additional purification. Distilled water was used to prepare the aqueous solutions in all experiments.

20 Synthesis of 1,3-dimethyl-imidazole-2-thione
The synthesis of thione was designed according to literature procedure to give 1,3-diethyl imidazole-2-thione in 63 % yield. 1H NMR (300MHz, DMSO) : δ=7.378 (s, 1 H), 4.051 (t, 4 H), 1.247 (trip, 6H). The 1,3-diethyl imidazolium acetate (2.0 g) was stirred with sulfur (0.1 g) in an round-bottom flask at 50 °C. After several minutes, the mixture turned yellow to dark brown. Then 10 mL acetonitrile was added after 24 h. The mixture was leached with filter to eradicate sulfur. Then the acetonitrile was distilled under vacuum. The product was dissolved in 15 mL methylene dichloride. Deionized water and sodium bicarbonate solution (5%) were used to wash the oil to remove 1, 3-diethyl imidazole acetate salt and acetic acid. Then the methylene dichloride was distilled under vacuum. The product was recrystallized at room temperature to give the almost colorless crystal. This procedure was shown as the following scheme.

![Scheme 1. Synthesis of 1,3-dimethyl-imidazole-2-thione](image)

25 Extraction procedure
Extraction was conducted with using 0.01 - 0.05 mM of EEImT in 0.5 mL [EMIm][NTf$_2$] as the organic phase. Feed solutions contained 0.001 mM of palladium(II) chloride in 0.1 mM - 5 M HCl. The two phases with volume ratio of aqueous phase to organic phase ($R_{AO}$) of 10, were mechanically shook in an orbital shaker for 0.5 - 20 min and separated with centrifuge at 2000 rpm for 5 min. Atomic absorption spectrophotometer (3150, Precision & Scientific Instrument Shanghai Co., Ltd., Shanghai, China) was used to determine Pd(II) concentrations in the aqueous solutions before and after extraction. High Performance Liquid Chromatography (LC2000, TianMei, Shanghai, China) was used to analyze the consumed extractant after the extraction.

Each experiment was carried out 3 times and the standard deviations did not exceed 5%. Extraction percentage E (%) and distribution coefficient (D) of Pd(II) were calculated from the equations below.

\[
E_{25} = \frac{[\text{Pd}]_{\text{aq}} - [\text{Pd}]_{\text{aq}}}{[\text{Pd}]_{\text{aq}}} \times 100\% \\
D_{25} = \frac{[\text{Pd}]_{\text{aq}}}{[\text{Pd}]_{\text{aq}}} \times R_{AO}
\]

Crystal growth and analyzation
Single crystals suitable for the X-ray diffraction study were grown by slow solvent evaporation. Ethanol water solutions (10 mL) containing 0.0282 mM PdCl$_2$ and one or two equivalent of EEImT were stirred and filtered with a funnel, then volatilized in serum bottle at 298 K for two weeks. Reddish brown needle-like crystals were obtained.

It was worth mentioning that at high complexes concentration (0.282 mol/L), the organic phase become rather viscous. The Adding of 2 mL ethanol will easily wash out the Pd-EEImT complexes, which also can form regularly-shaped needle like crystal. This procedure was not shown by earlier literature reports, and it may represent a novel method to prepare the metal complexes crystals.

Single crystal X-ray diffraction data collection was conducted on an area detecting system (Bruker-Nonius SMART APEX II CCD) and graphite monochromated Mo-Kα radiation (λ = 0.71000 Å). A hemisphere of data was measured using a strategy of omega scans of 0.5° per frame. Empirical absorption corrections were applied. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions riding on the parent carbon atoms. The unit cell parameters were obtained by full-matrix least-squares refinement. Data collection, integration, and absorption corrections were performed using the APEX222 software suite (Bruker). Computing structure solution and refinement was carried out using the SHELXL-97 software package (Bruker).

Crystal data and details of the structure determination are summarized in Table 1. CCDC 994393 and 994500 contain the supplementary crystallographic data for the structures described in this paper.

<table>
<thead>
<tr>
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<th>Pd$_2$(EEImT)$_2$Cl$_4$</th>
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<tbody>
<tr>
<td>CCDC number</td>
<td>994393</td>
<td>994500</td>
</tr>
<tr>
<td>Formula</td>
<td>Cl$_2$H$_2$Cl$_2$N$_2$Pd$_2$S$_2$</td>
<td>Cl$_2$H$_2$Cl$_2$N$_2$Pd$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>667.09 g/mol</td>
<td>489.79 g/mol</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-421c</td>
<td>C2/c</td>
</tr>
<tr>
<td>Temperature(K)</td>
<td>298</td>
<td>293</td>
</tr>
<tr>
<td>a(Å)</td>
<td>10.954(3)</td>
<td>18.078(19)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>10.954(3)</td>
<td>9.268(1)</td>
</tr>
</tbody>
</table>
X-ray powder diffraction was carried out by using a D8 Advance X-ray diffractometer with a graphite monochromater and Cu-K radiation ($\lambda=0.15418$nm).

## Calculation Methods

All calculations were performed with gaussian-09 21. Optimization for the geometrical structures in this investigation was conducted firstly by Hartree Fock method using STO-3G basis set 22. Symmetric and internal coordinate constraints were applied during optimizations. Harmonic frequency calculations were carried out at the same level to determine the sum of electronic and thermal Free Energies. None of the imaginary frequencies showed in all cases. The single point energies of optimized structures were determined by employing the density functional hybrid model Becke3LYP at 6-31+G(d,p) basis set for hydrogen, carbon, nitrogen, sulfur, chlorine atoms, and palladium was treated by Hay-Wadt effective core potential 23. All energies reported in this paper, unless otherwise noted, are free energies at 298 K and 1 atm.

## Results and discussion

### Extraction of Pd(II) with EEImT/[EMIm]NTF$_2$

The influence of mixing time, hydrochloric acid and EEImT concentrations on the extraction of palladium (II) with EEImT/[EMIm]NTF$_2$ were examined to study the optimal conditions.

Establishment of the optimum time to attain equilibrium was conducted with mixing 5 ml aqueous phase (0.1 mM PdCl$_2$ in 0.1 mM HCl) and 0.5 ml organic phase (2 mM EEImT in [EMIm]NTF$_2$ and [EMIm]NTF$_2$ alone) from 0.5 to 30 min. The ionic liquid [EMIm]NTF$_2$ itself can extract only 8% of Pd(II) after 15 min of contact, while the adding of EEImT results in the percentage extraction of Pd(II) maintaining about 98% within 3 min of contact. This indicates a fast and stable equilibrium for the Pd(II) extraction with EEImT/[EMIm]NTF$_2$. In addition, through the whole extraction process, there was no observable change in the volumes of the two phases. And there was no emulsion between the interphase, which further represents the easily separation for the two phases.

The effect of EEImT concentration on the palladium percentage extraction(E) was investigated. The results were shown in Figure 1. The $E_{Pd}$ attains maximum (about 98%) when molar ratio of EEImT : Pd is 4.

#### Figure 1. The effect of EEImT concentration ($C_{EEImT}$) on the Pd(II) extraction rate ($E_{Pd}$). Aqueous and organic phase were in the volume ratio of 10. Aqueous Pd(II) concentration is 0.1 mM.

Then the influence of hydrochloric acid concentration was studied under the optimized conditions. The adding of HCl is obviously against neutral extraction of Pd(II), since it can lower the $E_{Pd}$ from 97.8% to 88.1%, as illustrated in Figure 2.

#### Figure 2. Influence of the hydrochloric acid concentration on Pd(II) extraction rate. Aqueous phase: 5 ml, 0.1 mM PdCl$_2$, Organic phase: 4 mM and 5 mM EEImT in 0.5 mL [EMIm]NTF$_2$.

This was previously explained that the Pd(II) exists in the form of PdCl$_4^{2-}$ at higher level of Cl$^-$ thus the coordination of the Pd(II) and EEImT was intervened 24. It is note worthy that the adding of $25\%$ extra extractant will dramatically shrink this decline, as the red line in Figure 2 shows. According to many previous reports, the extraction rate will be fluctuated about $\pm 10\%$ with the varying of HCl concentration 25,26,27. Nevertheless, in the case of the neutral extraction with EEImT/[EMIm]NTF$_2$, the extraction rate become less dependent on the H$^+$ concentration at appropriate extractant concentration, with only $-2\%$ fluctuation in...
the tested range, which is more preferable for the practical application, since many waste effluent that containing Pd(II) is at various concentration of H⁺.

Back-extraction was carried out by mixing the loaded organic phase with four times the volume of stripping reagent solutions, among which the 0.5 M thiourea / 1.0 M HCl and 4.0 M NH₄SCN / 1.5 M NH₄OH were tested to be the most efficient. Both of the two stripping reagent led to the color fading of the loaded ionic liquid phase from reddish brown to white transparent, and above 96% Pd(II) was stripped to aqueous phase through ICP-AES determination.

Since very high extractability was shown by prior experiments, the traditional slope method and Job’s method become unsatisfying to determine the stoichiometry of Pd-EEImT complex. What is more, the HPLC analysis for the concentration of EEImT before and after extraction indicated that the consumed EEImT was less than two times but more than one times of the extracted Pd(II), which means that there may be more than one structure existed in the extracted complexes (not shown). Therefore X-ray single crystal diffraction combining with X-ray powder diffraction were alternatively used to figure out the extracted complex.

X-ray crystallographicanalysis

Since traditional methods were not suitable in this case to elucidate the extracted complexes, single X ray diffraction was applied alternatively. Although regularly-shaped needle like crystals can also be obtained quickly by the extraction with high level complexes concentration as mentioned above, there may be remained liquidic on the surface of the crystal which may interfere with the X-ray single crystal diffraction. In addition, the single X ray results may not comprehensively represent all the molecular structure. So the washed crystal was grinded and analyzed with X-ray powder diffraction after dried for 24 h under 80 °C to be compared with the structure-known pattern. Nevertheless, this phenomenon may provide a new clue to synthesize the metal complexes crystals.

According to previous cases related to the neutral metal extraction, we proposed the most probable stoichiometry (1:1 and 1:2) of Pd-EEImT in the extracted complexes, and conducted X-ray single crystal diffraction to verify the speculation.

The Pd₂(EEImT)₂Cl₄ (Figure 3.) adopts a bridging geometry with two Pd atoms connected to two sulfur atoms respectively to form a parallelogram in the space group P -421c. The bond length of Pd-S is 2.311 Å and 2.290 Å, which is comparable to those observed in the related bridging palladium complexes bearing sulfur and chlorine ligands (2.280 Å and 2.271 Å). The angle between the two Pd-S bond distance of 2.324 Å in Pd(EEImT)₂Cl₄ is close to those reported, which is slightly longer than that of Pd₃(EEImT)₂Cl₄ (2.311 Å and 2.290 Å). This indicates that the Pd-S bond is more stronger in Pd(EEImT)₂Cl₄. However, as for the higher degree of chelation of Pd(EEImT)₂Cl₄ (2 of chelation), it can be more favorable in the extraction than Pd(EEImT)₄Cl₄ (1 of chelation).

Back-extraction was carried out by mixing the loaded ionic liquid on the surface of the crystals can also be obtained quickly by the extraction with high level complexes concentration as mentioned above, there may be remained liquidic on the surface of the crystal which may interfere with the X-ray single crystal diffraction. In addition, the single X ray results may not comprehensively represent all the molecular structure. So the washed crystal was grinded and analyzed with X-ray powder diffraction after dried for 24 h under 80 °C to be compared with the structure-known pattern. Nevertheless, this phenomenon may provide a new clue to synthesize the metal complexes crystals.

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However, through the XRD results (Figure 5.) of the extracted complexes, both the 1:1 and 1:2 stoichiometry of the Pd(II)-EEImT complexed were produced during extraction, not simply one structure. This is rather different from previous metal extraction studies, which claimed that the neutral extractant containing S or N atoms would extract the palladium (or other metal ions) in a certain integral ratio (2:1 or 1:1), like sulfoxide and even thione. We speculated that at relatively high

Figure 3. Molecular structure of Pd₂(EEImT)₂Cl₄, ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity.

Figure 4. Molecular structure of cis-Pd(EEImT)₂Cl₂, ORTEP representation on the 50% probability level for all non-carbon atoms. Hydrogen atoms have been deleted for clarity.
Pd(II):EEImT level, about 1:10 to 1:1, the extracted complexes is composed with both 1:1 and 1:2 stoichiometry. While more and more 1:2 stoichiometry would appear with the increasing extractant concentration, as for its higher molecular stability.

There is the possibility of two structures for the configuration of Pd(EEImT)Cl₂ which involve the ligation of palladium with sulfur and chlorine atoms on diagonally opposite sides (trans, Figure 6.) and a symmetrical (cis) configuration.

Figure 5. Experimental powder X-ray diffraction pattern of (A) complexes washed from loaded ionic liquid and simulated powder patterns for B) Pd₄(EEImT)₂Cl₄ and A) cis-Pd(EEImT)₂Cl₂

Figure 6. Optimized geometry of the trans-Pd(EEImT)₂Cl₂

Trans configurations of palladium are in the majority as reported 32,43,44 and are more energetically stable in view of the smaller steric hindrance 45, nevertheless the cis configuration was obtained according to the results of x-ray crystallography. However, the powder pattern does not fully matched with XRD result of the sediment washed out of the [EMIm][NTF₂], which indicates that the trans configuration may also exists in the extracted complexes.

Calculation Results

Quantum chemical calculations were performed to get the thermodynamic parameters for the optimized geometries of the two possible structures. Selected Bond Lengths (Å) and Angles (deg) for Pd-EEImT complexes are presented in Table 2. The trans form was not given directly by crystal growth, therefore the optimized structure parameters was used for comparison. The DFT (B3LYP) structure of the cis-Pd(EEImT)Cl₂ is in good agreement with X-ray crystallographic data. The bond distances and angels are generally within 0.0854 Å and 2.938°. According to the parameters of the optimized trans-Pd(EEImT)Cl₂, the Pd-S bond length is 2.378 Å, the angle of 0(S-Pd-Cl) is 93.065°. Further energy calculations revealed that the structure involves the ligation of similar donor atoms in a cis configuration has a lower molecular energy of ~8285.910 a.u., and is more energetically feasible than that with similar donor atoms in a trans configuration (with molecular energy about ~8281.184 a.u.). What is more, the cis configuration has a larger dipole moment, which will lead to a higher solubility in the polar solvent phase. This may account for the crystal growth result.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Pd-EEImT complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Pd–Cl</th>
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<th>Pd–S</th>
<th>Cl–Pd–S</th>
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<td>Cis-Pd(EEImT)₂Cl₂</td>
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<td>90.53(5)</td>
<td>2.3240(11)</td>
<td>92.52(3)</td>
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<tr>
<td>Trans-Pd(EEImT)₂Cl₂</td>
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<td>2.4094</td>
<td>91.59</td>
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<tr>
<td>C–S</td>
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<td>84.56(5)</td>
<td>1.7207</td>
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<td>C–S–Pd</td>
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<td>102.7</td>
<td>108.5</td>
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Conclusions

The extraction of Pd(II) with EEImT in the ionic liquid system was studied with detail mechanism clarification. During extraction experiments for the Pd(II) with EEImT, the extraction rate of Pd(II) can attained 97.8% with 10 of aqueous: organic
phase volume ratio and 4 of EEImT:Pd(II) molar ratio. At appropriate extractant concentrations, the extraction rate become barely dependent on the hydrochloric acid concentration. Which represent that the EEImT is an efficient extractant for palladium.

What is more, the ionic liquid-based extraction system also provides a quick and convenient method to prepare metal complexes crystals, however detailed conditions are still waiting for the further exploration. Single X ray diffraction results illustrated the Pd(II)-EEImT complex with 1:2 and 1:1 stoichiometry in detail. At the experimental conditions, both the two structures existed in the extracted complexes dissolved in the ionic liquid. And the percentage of the former one will increase as the adding of extractant amount. The computer calculations further illustrated that the cis configuration of Pd(EEImT)Cl₂ owns a lower molecular energy than the trans one. The larger dipole moment also promotes its stability in the polar solvent. Which may explain why the crystal growth result in the cis form.

Acknowledgements

Thanks go to Professor Xiaoxia He and Di Sun in helping with computer calculations and X-ray crystallographic analysis.

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Notes and references

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The extraction is less $\text{H}^+$ dependent with less ionic liquid loss and can also quickly prepare palladium complexes crystals.