Pyridinium-based Task-specific Ionic Liquid with a Monothioether Group for Selective Extraction of Class *b* Metal Ions

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A pyridinium-based task-specific ionic liquid (TSIL) with a monothioether group, [3-TPPy][NTf₂], extracted typical class *b* metal ions, such as Ag(I), Cu(I), Pd(II), and Pt(II), in high selectivity. It was found that the composition ratio of the extracted Ag(I) and Cu(I) species depended on the TSIL concentration, and that TSIL extracted these metal ions through mono-S-coordinated complex formation at low TSIL concentrations. [3-TPPy][NTf₂] can be recycled in the extraction-recovery process, which is of a great advantage for practical use in environmentally benign separation methods.

Keywords Task-specific ionic liquid, extraction, thioether, class *b* metal ion, precious metals, green sustainable chemistry

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A substantial number of task-specific ionic liquids (TSILs), *i.e.*, ionic liquids (ILs) incorporating functional groups in their composite ions, have been explored in the past decade as new environmentally benign multi-functional materials, *e.g.*, extraction media of targeted species,^{1,2} synthetic media for catalyses,^{3,4} *etc.* In general, TSILs for the selective extraction of metal ions have functional group(s) involving donor atom(s) to extract the targeted metal ion through metal complex formation. Among studies on the extraction behaviors of metal ions by TSILs, thioether-functionalized TSILs are rare; (a) an imidazolium-based TSIL having the 3-thiapentyl group,⁵ (b) piperidinium- and pyrrolidinium-based TSILs having 5,6-bis(methylthio)hexyl group,⁶ and (c) a TSIL involving 2-(methylthio)benzoate as an anionic part,⁷ to the best of our knowledge. TSIL (a) having a monothioether group has been reported simply concerning the extraction of Cd(II) and Hg(II).⁵ On the other hand, TSILs (b) and (c) have been reported to extract selectively some heavy metal ions, such as Cu(II), Ag(I), Pd(II), Hg(II), *etc.*^{6,7} According to the HSAB concept, the S-donor atom in thioethers is one of the typical “soft bases” having strong affinity with typical “soft acids”, including precious metal ions, which are classified as Ahrlund’s class *b* metal ions.⁸ Therefore, TSILs having a thioether group would have significant potentials for environmentally-benign selective extraction media of precious metal ions.

On the other hand, it may be important for the practical use of TSILs for the extraction of metal ions that (i) TSIL is simply available for economical preparation, and (ii) the extracted metal ions can be recovered to recycle TSILs. We report here on a highly selective extraction of class *b* metal ions, and their recovery using a simply available TSIL incorporating a monodentate thioether group, 3-thiapentylpyridinium bis(trifluoromethylsulfonyl)imide ([3-TPPy][NTf₂], Fig. 1). Here, a pentyl group in a well-known IL, pentylpyridinium

bis(trifluoromethylsulfonyl)imide ([PPy][NTf₂]),⁹ simply changes into a 3-thiapentyl group.

The introduction of the 3-thiapentyl group to the pyridine nitrogen was achieved simply by heating an equimolar mixture of pyridine and 2-chloroethyl ethyl sulfide under an inert atmosphere. Because pyridine acts as a solvent as well as a reactant, this procedure does not need any other synthetic solvent. After evaporation of the unreacted reagents, the crude product, 3-thiapentylpyridinium chloride ([3-TPPy]Cl), was treated with aqueous Li(NTf₂) to generate [3-TPPy][NTf₂]. Exhaustive washing with water and drying *in vacuo* afforded analytically pure [3-TPPy][NTf₂]. It was a water-insoluble liquid with a density of $\rho = 1.48 \text{ g cm}^{-3}$ at room temperature, whose physical properties are very similar to those of unfunctionalized [PPy][NTf₂] ($\rho = 1.41 \text{ g cm}^{-3}$).

The water/TSIL extraction experiments of metal ions were carried out by shaking a mixture of 1 mL of [3-TPPy][NTf₂] and 2 mL of the aqueous phase containing each metal ion (0.50 mM) as a sulfate salt and pH buffer (200 mM). Table 1 gives the extraction efficiencies (%*E*) of various metal ions, associating with the data of unfunctionalized [PPy][NTf₂]. [3-TPPy][NTf₂] extracted class *b* metals, such as Ag(I), Cu(I), Pd(II), and Pt(II), almost quantitatively. However, this TSIL did not extract any other metal ions classified into class *ab* as well as class *a*. Such extraction selectivity strongly suggests that [3-TPPy][NTf₂] has a significant potential for the selective extraction of class *b* metal ions including precious metal ions. From the fact that unfunctionalized [PPy][NTf₂] did not any

Fig. 1 Structure of [3-TPPy][NTf₂].

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Table 1 Extraction efficiencies (%*E*) of various metal ions^a

Metal ion	Ahrlund's classification	% <i>E</i> ^b	
		[3-TPPy][NTf ₂]	[PPy][NTf ₂]
Ag(I)	class <i>b</i>	> 99	0
Cu(I) ^c	class <i>b</i>	> 99	0
Pd(II) ^d	class <i>b</i>	> 99	0
Pt(II) ^e	class <i>b</i>	> 99	0
Mn(II)	class <i>ab</i>	0	0
Co(II)	class <i>ab</i>	0	0
Ni(II)	class <i>ab</i>	0	0
Zn(II)	class <i>ab</i>	0	0
Sn(II)	class <i>ab</i>	0	0
Li(I)	class <i>a</i>	0	0
Mg(II)	class <i>a</i>	0	0
Ca(II)	class <i>a</i>	0	0
Sr(II)	class <i>a</i>	0	0

a. Initial concentration of metal ion = 0.50 mM (sulfate salt) and pH = 1.0 in aqueous phase.

b. Determined on the basis of the mole ratio of the metal ion between before and after extraction in the aqueous phase.

c. pH = 5.5 in the aqueous phase containing (NH₃OH)₂SO₄ (33 mM) to suppress the oxidation of Cu(I).

d. pH = 0.5 in the aqueous phase.

e. K₂PtCl₄ was used as a Pt(II) salt.

metal ions (Table 1), the extraction by [3-TPPy][NTf₂] was considered to occur through the coordination of the S-donor atom to class *b* metal ions. It is of note that the Pt(II) species in the aqueous phase were also extracted almost quantitatively, though the aqueous phase was prepared by dissolving K₂PtCl₄ in a “chloride-free” acidic buffer. The main Pt(II) species are expected to be [PtCl₃(OH₂)][−] (34%) and [PtCl₂(OH₂)₂] (57%) under the present condition, whose formation ratios were estimated on the basis of reports concerning the equilibria of [PtCl₄]^{2−} in a strongly acidic aqueous solution¹⁰ (detailed estimations are provided in Supporting Information). Therefore, the extraction of Pt(II) may also occur through S-donor coordination to the Pt(II) center, during which neutral H₂O ligand is substituted by an S-donor atom.

Similar extraction selectivity was also observed for the extraction systems using 1-(3-thiapentyl)-3-methylimidazolium TSIL ([3-TPMIM][NTf₂]): the extraction efficiencies were > 99% for class *b* Ag(I), 0% for class *ab* Mn(II) and Zn(II), and 0% for class *a* Mg(II).¹¹ This result predicts that the 3-thiapentyl group in different IL backbones acts similarly to each other. Thus, the extraction selectivity for class *b* metal ions using monothioether-functionalized TSILs is attributed to a significant affinity between the “soft acids” and “soft bases”, as mentioned above.

The dependence of the distribution ratio (log *D*) on the concentration of [3-TPPy][NTf₂] (log [[3-TPPy][NTf₂]]) in the IL phase for the extractions of Ag(I) and Cu(I) is shown in Fig. 2. The concentration of [3-TPPy][NTf₂] was adjusted by diluting with [PPy][NTf₂] as a non-extracting IL (cf. Table 1). Both slopes in Fig. 2 decrease to almost unity at lower TSIL concentrations, indicating that the composition ratio of the extracted species is a metal ion:TSIL = 1:1. On the other hand, both slopes in Fig. 2 increase with an increase of the TSIL concentrations; the composition ratio increased to Ag(I):TSIL = 1:2 (Fig. 2a) and Cu(I):TSIL = 1:4 (Fig. 2b). Since the thioether group of [3-TPPy][NTf₂] can coordinate to the metal center as a monodentate S-donor ligand according to the structure (Fig. 1),

Fig. 2 Dependence of the distribution ratio (log *D*) on the [3-TPPy][NTf₂] concentration (log [[3-TPPy][NTf₂]]) in the [PPy][NTf₂] phase for the extractions of (a) Ag(I) and (b) Cu(I) ions. Conditions of the aqueous phase: initial concentration of metal ion = 0.50 mM; pH = (a) 5.0 and (b) 5.5 using acetate buffer (200 mM). The aqueous phase of Cu(I) contains (NH₃OH)₂SO₄ to suppress the oxidation to Cu(II).

Table 2 Efficiencies of the extraction (%*E*) and recovery (%*R*) of Ag(I) and Cu(I) ions

Extraction-recovery cycle ^a	% <i>E</i> and % <i>R</i> ^b	
	Ag(I) ^c	Cu(I) ^d
1st extraction	52	72
2nd extraction	50	69
3rd extraction	51	72
1st recovery	91	94
2nd recovery	109	91

a. Extraction was carried out from the aqueous phase (1 mL) containing 0.50 mM of metal ion into 50 mM of [3-TPPy][NTf₂] in [PPy][NTf₂] as an IL phase (2 mL). Recovery was carried out from the IL phase containing extracted metal ion into the aqueous phase containing 200 mM of thiourea. The metal ion-recovered IL phase was used for the next extraction after washing with water.

b. The %*E* was determined on the basis of the mole ratio of the metal ion between before and after extraction in the aqueous phase. The %*R* was determined on the basis of the mole ratio of the metal ion between before and after recovery in the IL phase.

c. The pH of the aqueous phase was adjusted to pH = 1.0 using sulfuric acid for the extraction, and pH = 1 using nitric acid for the recovery.

d. The pH of the aqueous phase was adjusted to pH = 5.5 for the extraction and pH = 6 for the recovery using acetate buffer. The aqueous phase for the extraction contains (NH₃OH)₂SO₄ (33 mM) to suppress the oxidation of Cu(I).

it was considered that the number of coordinating S-donor atoms in the extracted metal complexes depends on the TSIL concentration. Therefore, both Ag(I) and Cu(I) are extracted even at low TSIL concentrations through the formation of the mono-S-coordinated metal complexes, whereas at high TSIL concentrations this occurs through the formation of bis- and tetra-S-coordinated complexes for Ag(I) and Cu(I), respectively, both of which are in line with the general coordination numbers

of the corresponding metal ions.¹² The extraction behaviors of Pd(II) and Pt(II) were rather complicated, because the species in the aqueous phase changed depending on the existing anion(s), such as Cl⁻, as mentioned for the Pt(II) system. Thus, the further detailed analyses are needed.

Ag(I) and Cu(I) ions in the IL phase containing [3-TPPy][NTf₂] (50 mM in [PPy][NTf₂]) were recovered almost quantitatively (> 90%) by treating with the acidic aqueous phase containing 200 mM of thiourea, as shown in Table 2. After washing the metal ion-recovered IL phase with water, the resulting IL phase could again extract Ag(I) and Cu(I) ions in comparable %E with the first extraction (Table 2). This result strongly suggests that [3-TPPy][NTf₂] can be recycled in the extraction-recovery processes of class *b* metal ions.

Thus, the present monothioether-functionalized pyridinium TSIL as a good extraction medium of class *b* metal ions would be useful from the points of green sustainability and safety, because (i) ILs are incombustible and nonvolatile,¹⁻⁴ (ii) the pyridinium-based TSILs can be prepared without another synthetic solvent, and (iii) the TSIL can be recycled. Further investigations, such as concerning the detailed extraction behaviors and the preparation of the other effective TSILs, are in progress in our research group.

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Supporting Information

Experimental details such as the preparation of ILs in the present study and the extraction procedures, as well as detailed estimations of Pt(II) species in acidic aqueous solution of

K₂PtCl₄ are given in Supporting Information. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. S. Tang, G. A. Baker, and H. Zhao, *Chem. Soc. Rev.*, **2012**, *41*, 4030.
2. X. Sun, H. Luo, and S. Dai, *Chem. Rev.*, **2012**, *112*, 2100.
3. “*Ionic Liquids in Synthesis*”, ed. P. Wasserscheid and T. Welton, 2nd ed., **2008**, Wiley-VCH, Weinheim.
4. J. P. Hallett and T. Welton, *Chem. Rev.*, **2011**, *111*, 3508.
5. (a) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr., and R. D. Rogers, *Chem. Commun.*, **2001**, 135; (b) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr., and R. D. Rogers, *Environ. Sci. Technol.*, **2002**, *36*, 2523.
6. (a) J.-M. Lee, *Fluid Phase Equilib.*, **2012**, *319*, 30; (b) N. Papaiconomou, J.-M. Lee, J. Salminen, M. von Stosch, and J. M. Prausnitz, *Ind. Eng. Chem. Res.*, **2008**, *47*, 5080.
7. (a) L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler, and S. Hann, *Water Res.*, **2011**, *45*, 4601; (b) A. Stojanovic, D. Kogelnig, L. Fischer, S. Hann, M. Galanski, M. Groessl, R. Krachler, and B. K. Keppler, *Aust. J. Chem.*, **2010**, *63*, 511.
8. S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev. Chem. Soc. [London]*, **1958**, *12*, 265.
9. Q.-S. Liu, M. Yang, P.-F. Yan, X.-M. Liu, Z.-C. Tan, and U. Welz-Biermann, *J. Chem. Eng. Data*, **2010**, *55*, 4928.
10. (a) L. I. Elding, *Acta Chem. Scand.*, **1970**, *24*, 1331; (b) L. I. Elding and I. Leden, *Acta Chem. Scand.*, **1966**, *20*, 706.
11. Unpublished results.
12. F. A. Cotton, G. Wilkinson, and P. L. Gaus, “*Basic Inorganic Chemistry*”, 3rd ed., **1995**, Wiley, New York.