



# Ionic liquids containing cationic SNS-pincer palladium(II) complexes: Effects of ancillary ligands on thermal properties and solvent polarities

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## ABSTRACT

Ionic liquids comprising cationic Pd<sup>II</sup> complexes with SNS-pincer ligands ([Pd(L<sup>SNS</sup>)Me]<sup>+</sup> (**1**)<sup>+</sup> and [Pd(L<sup>SNS</sup>)Cl]<sup>+</sup> (**2**)<sup>+</sup>; L<sup>SNS</sup> = 2,6-bis(*n*-butylthiomethyl)pyridine) and bis(trifluoromethanesulfonyl)amide (Tf<sub>2</sub>N) or tetrafluoroborate (BF<sub>4</sub>) anions were prepared, and the effect of ancillary ligands on their thermal properties and solvent polarities were investigated. **1**]Tf<sub>2</sub>N and **2**]Tf<sub>2</sub>N were liquids and exhibited glass transitions at −47 °C and −23 °C, and their solvent polarity parameters (*E*<sup>N</sup><sub>T</sub>) were 0.51 and 0.46, respectively. **1**]BF<sub>4</sub> and **2**]BF<sub>4</sub> were solids with melting points of 73.2 °C and 141.5 °C, respectively. X-ray structure determination of **2**]BF<sub>4</sub> revealed a structure with alternating ionic and non-polar alkyl chain layers.

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## 1. Introduction

Ionic liquids, defined as salts with melting points below 100 °C, exhibit distinct physical properties such as low volatility, wide liquid state temperature range, and high ionic conductivity [1]. Recently, metal-containing ionic liquids have attracted much attention because of their magnetic properties [2], catalytic activities [3], and redox activities [4]. We have also developed ionic liquids containing cationic sandwich complexes [5] or metal-chelate complexes [6] that exhibit interesting electronic properties and chemical reactivities. From our interest in Pd complex chemistry, we previously prepared ionic liquids from Pd<sup>II</sup> complexes with diamine-diketonato mixed ligands, [Pd(diamine)(diketonato)]Tf<sub>2</sub>N (Tf<sub>2</sub>N = bis(trifluoromethanesulfonyl)amide) [7]. However, these salts exhibited high melting points (62–85 °C) because of the formation of a head-to-tail dimer-like arrangement in the solid state, which probably originates from the large polarity of the cation. Indeed, the use of molecules with high polarity, or a large dipole moment, is disadvantageous in designing ionic liquids

with low melting points and viscosities. In the present study, to elucidate the effects of the polarity of cationic metal complexes on their thermal properties and solvent polarities, we focused on Pd<sup>II</sup> complexes with SNS-pincer ligands. Pd<sup>II</sup> complexes with halogen or alkyl ancillary ligands have been reported previously [8]; hence, their comparison may allow investigation of the polarity effects while maintaining the cation framework. Although substituent effects in ionic liquids have been extensively investigated, the understanding of the effects of only polarity is comparatively poor.

In this paper, we report on the preparation, thermal properties, and solvent polarities of salts containing cationic Pd<sup>II</sup> complexes, [Pd(L<sup>SNS</sup>)Me]<sup>+</sup> (**1**)<sup>+</sup> and [Pd(L<sup>SNS</sup>)Cl]<sup>+</sup> (**2**)<sup>+</sup>, bearing SNS-pincer ligands (Fig. 1; L<sup>SNS</sup> = 2,6-bis(*n*-butylthiomethyl)pyridine). The chloride complex **2**)<sup>+</sup> has a larger polarity than the methyl complex **1**)<sup>+</sup>, while their molecular volumes are comparable. Tf<sub>2</sub>N<sup>−</sup> and BF<sub>4</sub><sup>−</sup> anions were used as the counteranions. The crystal structure of **2**]BF<sub>4</sub> was determined to investigate the molecular structure and cation–anion arrangements. Given the rich chemistry of pincer-type complexes [9,10], the development of their ionic liquids may lead to various functional fluids in the future. Several ionic liquids containing the Pd ion have been developed to date, but only a few of them are liquids at room temperature [7,11].

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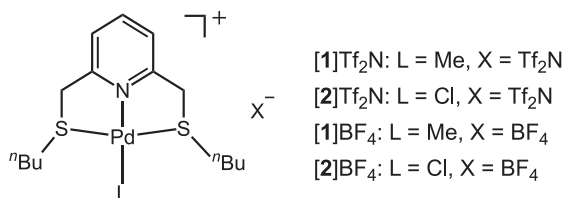


Fig. 1. Structural formulae of the ionic liquids investigated in this study.

## 2. Results and discussion

### 2.1. Preparation and properties

Tf<sub>2</sub>N and BF<sub>4</sub> salts were prepared in 41%–95% yields by anion exchange from the corresponding chloride salts that were obtained by reacting L<sup>SNS</sup> and [(1,5-cyclooctadiene)Pd(L)(Cl)] (L = Me, Cl). The Tf<sub>2</sub>N salts were liquids at room temperature, and although the BF<sub>4</sub> salts were solids at room temperature, [1]BF<sub>4</sub> melted below 100 °C (*vide infra*) and thus can be regarded as an ionic liquid. All the four salts were stable in air. These salts were soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, acetone, and MeCN, less soluble in alcohols, and insoluble in diethyl ether, hexane, and water.

### 2.2. Thermal properties

Thermal properties of the Tf<sub>2</sub>N and BF<sub>4</sub> salts were investigated by differential scanning calorimetry (DSC). The DSC traces are shown in Fig. S1. The glass transition temperatures (*T<sub>g</sub>*), melting points (*T<sub>m</sub>*), melting enthalpies ( $\Delta H_m$ ), and melting entropies ( $\Delta S_m$ ) of these salts are listed in Table 1. [1]Tf<sub>2</sub>N and [2]Tf<sub>2</sub>N were liquids with *T<sub>g</sub>* values of –47 °C and –23 °C, respectively. [1]BF<sub>4</sub> and [2]BF<sub>4</sub> were solids with *T<sub>m</sub>* values of 73.2 °C and 141.5 °C, and  $\Delta S_m$  values of 58.5 J K<sup>–1</sup> mol<sup>–1</sup> and 48.3 J K<sup>–1</sup> mol<sup>–1</sup>, respectively. On cooling the respective melts, [1]BF<sub>4</sub> and [2]BF<sub>4</sub> underwent glass transitions at around –24 °C and 3 °C, respectively. The melt of [2]BF<sub>4</sub> underwent partial crystallization at around 88 °C and 61 °C on cooling and heating, respectively. Both *T<sub>m</sub>* and *T<sub>g</sub>* of the salts with [2]<sup>+</sup> were higher than those of [1]<sup>+</sup>, as the cation with the chloride ligand ([2]<sup>+</sup>) has greater polarity than that with the methyl ligand ([1]<sup>+</sup>). The dipole moments of [1]<sup>+</sup> and [2]<sup>+</sup> estimated from density functional theory (DFT) calculations were 5.0 D and 10.9 D, respectively, thus confirming the above statement.

The *T<sub>g</sub>*/*T<sub>m</sub>* values of [1]BF<sub>4</sub> and [2]BF<sub>4</sub> were 0.72 and 0.67, respectively, consistent with the values generally observed in molecular and ionic liquids [12]. The crystal of [2]BF<sub>4</sub> exhibited a phase transition at 56.3 °C ( $\Delta H = 6.3$  kJ mol<sup>–1</sup>,  $\Delta S = 18.9$  J K<sup>–1</sup> mol<sup>–1</sup>), whereas the crystal of [1]BF<sub>4</sub> exhibited no phase transitions. The sum of the phase transition entropy and the melting entropy of [2]BF<sub>4</sub> is 62.2 J K<sup>–1</sup> mol<sup>–1</sup>, which is comparable to the melting entropy of [1]BF<sub>4</sub> (58.5 J K<sup>–1</sup> mol<sup>–1</sup>). This result is reasonable due to their similar molecular structures, and demonstrates the fact that the difference in their melting points originates purely from their enthalpy difference because

Table 1  
*T<sub>g</sub>*, *T<sub>m</sub>*,  $\Delta H_m$ , and  $\Delta S_m$  values of the Tf<sub>2</sub>N and BF<sub>4</sub> salts.

	<i>T<sub>g</sub></i> (°C)	<i>T<sub>m</sub></i> (°C)	$\Delta H_m$ (kJ mol <sup>–1</sup> )	$\Delta S_m$ (J K <sup>–1</sup> mol <sup>–1</sup> )	<i>T<sub>g</sub></i> / <i>T<sub>m</sub></i>
[1]Tf <sub>2</sub> N	–47				
[2]Tf <sub>2</sub> N	–23				
[1]BF <sub>4</sub>	–24	73.2	20.5	58.5	0.72
[2]BF <sub>4</sub>	3	141.5	24.4 <sup>a</sup>	62.2 <sup>a</sup>	0.67

<sup>a</sup> Sum of the phase transition in solid state and melting.

$T_m = \Delta H_m / \Delta S_m$ . Hence, the higher melting point of [2]BF<sub>4</sub> than [1]BF<sub>4</sub> directly reflects stronger intermolecular interactions mainly owing to the larger polarity.

### 2.3. Solvent polarities

The solvent polarity parameters (*E<sub>N</sub><sup>T</sup>*) of the Tf<sub>2</sub>N salts were [1]Tf<sub>2</sub>N and [2]Tf<sub>2</sub>N at 20 °C were 0.51 and 0.46, respectively, as evaluated using Reichardt's dye [13]. This indicates that the solvent polarity of [1]Tf<sub>2</sub>N is slightly larger than that of [2]Tf<sub>2</sub>N; however, the tendency is opposite to the polarity of the corresponding cations. This is probably because a more polarized cation forms stronger ion pairing with the anion, thereby reducing its solvent polarity. A similar tendency has been observed in imidazolium ionic liquids [13]. The value obtained for these liquids are comparable to those of tetraalkylammonium-type ionic liquids (*E<sub>N</sub><sup>T</sup>* ≈ 0.50) [14], but smaller than those of imidazolium ionic liquids (*E<sub>N</sub><sup>T</sup>* ≈ 0.66) [14].

### 2.4. Crystal structure

The crystal structure of [2]BF<sub>4</sub> was determined by X-ray crystallography at –173 °C. This salt crystallized in the space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, and the unit cell contained one crystallographically independent molecule. The packing diagram and Ortep drawing are shown in Fig. 2 and Fig. S2, respectively. The two *n*-butyl groups (linear and bent) in the cation are perpendicular to the coordination plane, oriented in the same direction. The two five-membered Pd–N–C<sub>pyridine</sub>–C<sub>methylene</sub>–S rings adopt envelope conformations with Pd, N, C<sub>pyridine</sub>, and S being coplanar, where C<sub>methylene</sub> lies off by 0.31 Å and 0.38 Å. The coordination distances of Pd–N (2.004(3) Å), Pd–S (2.2940(8) Å and 2.2967(9) Å), and Pd–Cl (2.299(1) Å) are comparable to the typical values of related complexes [8].

In the crystal, cations and anions are alternately located along the *b*-axis. The ionic layers comprising the pincer framework and anions, and the non-polar layers comprising the alkyl chain are alternately arranged perpendicular to the *c*-axis. There are short cation–anion contacts (Fig. 2, dotted lines) between the pyridyl hydrogens and F or B atoms of the anion (CH·····F: 2.28–2.31 Å, CH·····B: 2.79 Å). They are shorter than the sum of van der Waals (vdW) radii for involved atoms by 0.3 Å and are regarded as weak hydrogen bonds. There are no  $\pi$ – $\pi$  interactions or dimer-like arrangements in the crystal, partly because of the bent structure of the cation. In contrast, the cationic Pd<sup>2+</sup> complexes with diamine–diketone mixed ligands exhibit dimer-like arrangements in the solid state [7], despite their smaller dipole moments (~3.8 D, estimated from DFT calculations) than those of [2]<sup>+</sup>, probably due to their planar cation structures, which facilitate  $\pi$ – $\pi$  interactions.

## 3. Conclusions

Ionic liquids containing cationic Pd(II) complexes with SNS-pincer ligands were prepared and their thermal properties were investigated. Comparison with corresponding complexes with chloride and methyl ancillary ligands elucidated the effects of polarity on their thermal properties, without significantly changing the molecular shape. As expected, the salts with the cations containing the chloride ligand possessed the higher polarity, and exhibited higher melting points and higher glass transition temperatures than those with cations containing the methyl ligand. More importantly, however, the total solid-to-liquid phase transition entropies were comparable in the present salts, indicating that the difference in their melting points originates purely from their enthalpy difference. The difference in their intermolecular

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