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(Citation)

Dalton Transactions, 43(18):6864-6869

(Issue Date)

2014-05

(Resource Type)

journal article

(Version)

Accepted Manuscript

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<https://hdl.handle.net/20.500.14094/90002537>



Ionic liquids from cationic palladium(II) chelate complexes: Preparation, thermal properties, and crystal structures†

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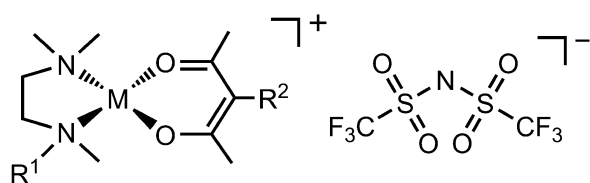
†Electronic supplementary information (ESI) available: DSC traces of **1–3** (Fig. S1) and ORTEP drawings of the molecular structures of **1–3** (Figs. S2–S3). CCDC 975545 (**1**), 975546 (**2**), and 976918 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI:

Metal-containing ionic liquids comprising cationic Pd^{II} chelate complexes and the bis(trifluoromethanesulfonyl)amide (Tf₂N) anion were prepared: [Pd(acac)(Me₄en)]Tf₂N (**1**), [Pd(acac)(BuMe₃en)]Tf₂N (**2**), and [Pd(C₈-acac)(Me₄en)]Tf₂N (**3**) (acac = 2,4-pentanedionate, C₈-acac = 3-octyl-2,4-pentanedionate, Me₄en = *N,N,N',N'*-tetramethylethylenediamine, BuMe₃en = *N*-butyl-*N,N',N'*-trimethylethylenediamine). These salts were yellow solids with melting points of 85.2 °C, 71.1 °C, and 62.3 °C, respectively. During cooling from the liquid state, complex **1** exhibited crystallization, whereas **2** and **3** exhibited only glass transitions at approximately –40 °C. X-ray structure determination revealed that the cations in **1** and **3** form dimer-like arrangements and that there were no direct contacts between the charged moieties of the cations and anions in the solid state.

Introduction

Ionic liquids are salts with melting points below 100 °C, and they exhibit characteristic properties such as low-volatility, non-flammability, and high ion-conductivity.¹ Although ionic liquids are typically derived from onium salts, functional ionic liquids containing metal complexes have been reported recently.^{2,3} We have prepared ionic liquids from metallocenium cations⁴ and cationic chelate complexes,⁵ which exhibit intriguing functionalities such as magnetic properties and chemical reactivities. Among them, the ionic liquids containing cationic Cu^{II}- and Ni^{II}-chelate complexes with diamine and diketonate ligands such as [M(acac)(R₄en)]Tf₂N (Fig. 1; M = Cu^{II}, Ni^{II}, acac = 2,4-pentanedionate, R₄en = *N,N,N',N'*-tetraalkylethylenediamine, Tf₂N = bis(trifluoromethanesulfonyl)amide) exhibit vapochromism.^{5a} These liquids exhibit changes in color and magnetic property in response to vapor molecules that have donor abilities, based on the coordination of the molecules to the metal center.

In this study, we prepared [Pd(acac)(Me₄en)]Tf₂N (**1**), [Pd(acac)(BuMe₃en)]Tf₂N (**2**), and [Pd(C₈-acac)(Me₄en)]Tf₂N (**3**), employing palladium as the metal center (Fig. 1; C₈-acac = 3-octyl-2,4-pentanedionate, Me₄en = *N,N,N',N'*-tetramethylethylenediamine, and BuMe₃en = *N*-butyl-*N,N',N'*-trimethylethylenediamine). Unlike Ni^{II} and Cu^{II} complexes, Pd^{II} complexes exhibit only the square planar coordination geometry and do not respond to molecules having coordination abilities. Therefore, they are suitable for the investigation of the effect of anion coordination. Although the previously reported Cu^{II} and Ni^{II} complexes were liquid at room temperature,^{5a} the Pd^{II} complexes in the current work were solids and thus allowed for crystallographic investigation of the cation–anion interactions. Platinum-group metal complexes are versatile for their reactivity such as oxidative addition and catalytic activities, but only a few ionic liquids containing them have been reported.⁶



- 1: M = Pd, R¹ = Me, R² = H
 2: M = Pd, R¹ = Bu, R² = H
 3: M = Pd, R¹ = Me, R² = C₈H₁₇

Fig. 1 Structural formulae of the ionic liquids prepared in this study (**1–3**). Ionic liquids with M = Cu^{II} and Ni^{II} were reported previously.^{5a}

Experimental

General

N-Butyl-*N,N,N'*-trimethylethylenediamine (BuMe₃en),⁷ 3-octyl-2,4-pentadecionate, (C₈-acacH),⁸ and silver(I) bis(trifluoromethanesulfonyl)amide (AgTf₂N)⁹ were synthesized according to the procedures described in the literature. Other reagents were commercially available. DSC measurements were performed in the temperature range –160 to 100 °C at rate of 10–20 K min^{–1} using a TA Instrument Q100 calorimeter. ¹H NMR spectra were recorded on a JEOL JNM–ECL–400 spectrometer. Infrared spectra were recorded in the range of 550–4000 cm^{–1} on a Nicolet iS5 spectrometer equipped with a diamond ATR attachment. Elemental analyses were performed using a Yanaco CHN MT5 analyzer.

Preparation of [Pd(acac)(Me₄en)]Tf₂N (**1**)

(a) [{Pd(μ–OH)(Me₄en)}₂](Tf₂N)₂. Aliquots (0.5 mL) of an aqueous solution (2.5 mL) of Na₂PdCl₄·3H₂O (348 mg, 1.0 mmol) were added to an aqueous solution (2.5 mL) of Me₄en (300 mg, 2.6 mmol) under stirring, during which portions of 0.5 M NaOH were added such that the pH was maintained at approximately 12. An acetone solution (5 mL) of AgTf₂N (1.0 g, 2.6 mmol) were added dropwise to the reaction mixture and stirred under dark. The solution was filtered to remove

precipitated AgCl, and evaporation of the filtrate produced $[\{\text{Pd}(\mu\text{-OH})(\text{Me}_4\text{en})\}_2](\text{Tf}_2\text{N})_2$ as a yellow solid (364.7 mg, yield 70%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$, TMS): δ = 2.73 (s, 8H), 2.86 (s, 24H), 2.96 (s, 2H). IR (cm^{-1}) 570 (s), 738 (m), 796 (w), 810 (m), 1050 (s, S=O), 1138 (m), 1175 (s), 1329 (m, S=O), 1345 (s, S=O), 2938 (w), 3462 (w, O-H).

(b) $[\text{Pd}(\text{acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (1**).** The solution of $[\{\text{Pd}(\mu\text{-OH})(\text{Me}_4\text{en})\}_2](\text{Tf}_2\text{N})_2$ (100 mg, 0.19 mmol) and acetylacetone (20 mg, 0.19 mmol) in acetone (10 mL) was refluxed for 30 min, and then the solvent was removed under reduced pressure. The residual oil was dissolved in dichloromethane and washed with water. The organic phase was separated, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow solid of **1** (71 mg, yield 62%). The solid was recrystallized by slow diffusion of ether and hexane into an acetone solution of **1**. Yellow plate crystals were obtained. ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 2.03 (s, 6H), 2.72 (s, 12H), 2.96 (s, 4H), 5.45 (s, 1H). IR (cm^{-1}) 569 (s), 598 (s), 738 (w), 789 (m), 808 (m), 1061 (m, S=O), 1131 (s), 1180 (s), 1324 (s, S=O), 1525 (m), 1573 (m, C=O), 2930 (w), 3026 (w). Anal. Calcd. For $\text{C}_{13}\text{H}_{23}\text{PdF}_6\text{N}_3\text{O}_6\text{S}_2$ (601.88): C, 25.94; H, 3.85; N, 6.98. Found: C, 25.88; H, 3.75; N, 7.15.

Preparation of $[\text{Pd}(\text{acac})(\text{BuMe}_3\text{en})]\text{Tf}_2\text{N}$ (**2**)

(a) $[\{\text{Pd}(\mu\text{-OH})(\text{BuMe}_3\text{en})\}_2](\text{Tf}_2\text{N})_2$. This salt was prepared by the same method as $[\{\text{Pd}(\mu\text{-OH})(\text{Me}_4\text{en})\}_2](\text{Tf}_2\text{N})_2$ using BuMe₃en (205 mg, 1.3 mmol), Na₂PdCl₄·3H₂O (174 mg, 0.5 mmol), 1M NaOH, and AgTf₂N (500 mg, 1.3 mmol). The obtained oil was dissolved in methanol and washed repeatedly with hexane. The product was obtained as a yellow oil (yield 43%). The complex was immediately used for the next step because it decomposed gradually at room temperature. ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$, TMS): δ = -0.31 (m, 2H), 1.01 (s, 6H), 1.41 (m, 4H), 2.65 (t, 4H, J = 7.2 Hz), 2.78 (t, 4H, J = 4.6 Hz), 2.84 (m, 26H). IR (cm^{-1}) 570 (s), 739 (m), 789 (w), 1053 (s, S=O), 1132 (s), 1177 (s), 1345 (m, S=O), 2938 (w), 3478 (w, O-H).

(b) $[\text{Pd}(\text{acac})(\text{BuMe}_3\text{en})]\text{Tf}_2\text{N}$ (2**).** The solution of $[\{\text{Pd}(\mu\text{-OH})(\text{BuMe}_3\text{en})\}_2](\text{Tf}_2\text{N})_2$ (120 mg,

0.18 mmol) and acetylacetone (30 mg, 0.30 mmol) in acetone (10 mL) was stirred overnight at room temperature. The solution was filtered to remove white precipitates, and the filtrate was evaporated. The residue was dissolved in dichloromethane, washed repeatedly with water, and dried over magnesium sulfate. Removal of solvent under reduced pressure produced a yellow solid of **2** (55 mg, yield 40%). The solid was recrystallized by slow cooling of an ethanol–hexane (1:10) solution of **2**. Yellow plate crystals were obtained, which was dried under vacuum. ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.99 (t, 3H, J = 7.2 Hz), 1.41 (m, 2H), 1.93 (m, 1H), 2.02, 2.04 (each s, 6H), 2.18 (m, 1H), 2.40 (m, 1H), 2.67, 2.73, 2.82 (m, 12H), 3.23 (m, 2H), 5.45 (s, 1H). IR (cm^{-1}) 570 (s), 740 (m), 795 (m), 1047 (s, S=O), 1135 (s), 1177 (s), 1329 (s, S=O), 1520 (m), 1567 (m, C=O), 2930 (w), 3022 (w). Anal. Calcd. For $\text{C}_{16}\text{H}_{29}\text{PdF}_6\text{N}_3\text{O}_6\text{S}_2$ (643.96): C, 29.84; H, 4.54; N, 6.53. Found: C, 29.86; H, 4.54; N, 6.54.

Preparation of $[\text{Pd}(\text{C}_8\text{-acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (**3**)

A solution of $[\{\text{Pd}(\mu\text{-OH})(\text{Me}_4\text{en})\}_2](\text{Tf}_2\text{N})_2$ (105 mg, 0.1 mmol) and $\text{C}_8\text{-acacH}$ (55 mg, 0.26 mmol) in acetone (10 mL) was stirred overnight at room temperature under a nitrogen atmosphere. The solution was filtered to remove white precipitates, and the filtrate was evaporated. The residue was dissolved in dichloromethane and washed repeatedly with water, dried over magnesium sulfate, and solvent removed under reduced pressure. The residue was dissolved in methanol and washed repeatedly with hexane, and evaporated. The residue was dissolved in ether and washed repeatedly with water, dried over magnesium sulfate, and concentrated under pressure to give a yellow solid of **3** (40 mg, yield 27%). ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.89 (t, 3H, J = 6.7 Hz), 1.28 (m, 10H), 2.15–2.22 (m, 8H), 2.72 (s, 12H), 2.96 (s, 4H). IR (cm^{-1}) 568 (s), 739 (m), 809 (m), 1051 (s, S=O), 1138 (s), 1179 (s), 1348 (s, S=O), 1563 (m, C=O), 2853 (w), 2923 (w). Anal. Calcd. For $\text{C}_{21}\text{H}_{39}\text{PdF}_6\text{N}_3\text{O}_6\text{S}_2$ (714.09): C, 35.32; H, 5.50; N, 5.88. Found: C, 35.40; H, 5.56; N, 6.07.

X-ray crystal structure determination

X-ray diffraction (XRD) data were collected on a Bruker APEX II Ultra CCD diffractometer at $-173\text{ }^{\circ}\text{C}$ using Mo K_{α} radiation ($\lambda = 0.71073\text{ \AA}$). All calculations were performed using SHELXL 97.¹⁰ The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted at calculated positions. The packing diagrams were drawn using Ortep 3 for Windows.¹¹ Crystal data, data collection parameters, and analysis statistics for these compounds are listed in Table 1. The crystal structure of **1** determined at $25\text{ }^{\circ}\text{C}$ was isostructural to that determined at $-173\text{ }^{\circ}\text{C}$. Structure determination of **3** at $-10\text{ }^{\circ}\text{C}$ did not give satisfactory results as extensive disorder was observed. Crystallographic parameters at $-10\text{ }^{\circ}\text{C}$: space group $P\bar{1}$, $a = 8.8800(17)\text{ \AA}$, $b = 12.007(2)\text{ \AA}$, $c = 15.850(3)\text{ \AA}$, $\alpha = 76.048(3)^{\circ}$, $\beta = 76.177(3)^{\circ}$, $\gamma = 88.044(3)^{\circ}$, $V = 1592.1(5)\text{ \AA}^3$, $Z = 2$.

Table 1. Crystallographic parameters of **1–3**.

	1	2	3
Empirical formula	$\text{C}_{13}\text{H}_{23}\text{F}_6\text{N}_3\text{O}_6\text{PdS}_2$	$\text{C}_{16}\text{H}_{29}\text{F}_6\text{N}_3\text{O}_6\text{PdS}_2$	$\text{C}_{21}\text{H}_{39}\text{F}_6\text{N}_3\text{O}_6\text{PdS}_2$
Formula weight	601.86	643.94	714.07
Temperature / $^{\circ}\text{C}$	-173	-173	-173
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
$a / \text{\AA}$	8.6854(11)	13.4591(18)	14.940(7)
$b / \text{\AA}$	10.5387(13)	12.0133(16)	17.007(8)
$c / \text{\AA}$	13.6525(17)	16.538(2)	25.222(12)
$\alpha / ^{\circ}$	104.6770(10)		99.486(6)
$\beta / ^{\circ}$	92.0660(10)	106.677(2)	97.232(7)
$\gamma / ^{\circ}$	112.0220(10)		102.134(7)
Volume / \AA^3	1108.6(2)	2561.6(6)	6094(5)
Z	2	4	8
$d_{\text{calcd}} / \text{g cm}^{-3}$	1.803	1.670	1.557
μ / mm^{-1}	1.110	0.966	0.821
Reflections collected	5547	13062	29791
Independent reflections	3976	5035	21217
	($R_{\text{int}} = 0.0339$)	($R_{\text{int}} = 0.0246$)	($R_{\text{int}} = 0.0761$)

Parameters	286	313	1433
R_1^a , $wR_2^b(I > 2\sigma(I))$	0.0262, 0.0690	0.0202, 0.0511	0.0653, 0.1433
R_1^a , wR_2^b (all data)	0.0265, 0.0694	0.0217, 0.0521	0.1061, 0.1652
Goodness-of-fit on F^2	1.113	1.049	1.005

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$$

Results and Discussion

Preparation and properties

The preparation scheme of **1–3** is shown in Fig. 2. These salts were prepared via the Tf_2N salts of dinuclear palladium complexes, where overall yields were: **1**: 42%, **2**: 17%, **3**: 19%. Salt **1** was also prepared by anion exchange of $[\text{Pd}(\text{acac})(\text{Me}_4\text{en})](\text{acac})$ prepared from $[\text{Pd}(\text{acac})_2]$ in a lower yield (24%). Although these salts formed as yellow solids, they melted below 100 °C (*vide infra*) and thus can be regarded as ionic liquids. The reaction of a chloroform solution of **1** with chlorine resulted in elimination of the acac ligand and produced $[\text{Pd}(\text{Me}_4\text{en})\text{Cl}_2]$,^{12,13} and no oxidative addition occurred.

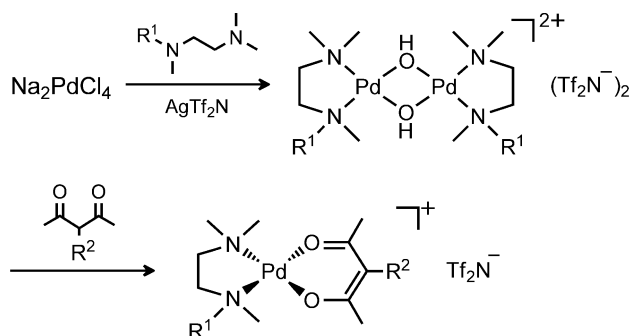


Fig. 2 Preparation scheme of complexes **1–3**.

Thermal properties

Thermal properties of complexes **1–3** were investigated by means of differential scanning calorimetry (DSC). The DSC traces are shown in Fig. S1 (ESI†). The melting points (T_m) and glass transition temperatures (T_g) of these and related salts are listed in Table 2. The melting points of **1–3**

were 85.2 °C, 71.1 °C, and 62.3 °C, respectively (Table 2). The melting points decreased with an increase in the alkyl chain length of the ligands. On cooling from the liquid state, complex **1** crystallized at 57 °C, whereas **2** and **3** maintained the liquid state and exhibited glass transition temperatures of approximately –40 °C (Table 2). The values of T_g/T_m for **2** and **3** were close to 2/3, which is consistent with values observed in molecular and ionic liquids.¹⁴ Although **1** has no alkyl chains, its melting point was only 14 °C higher than that of **2**. This contrasts with the tendency of imidazolium and metallocenium ionic liquids to have significantly lower melting points due to the introduction of alkyl chains.^{1f, 4} Overall, the effect of the alkyl chain on the melting point is small compared with that in the imidazolium ILs, and this is probably owing to the large size of the cationic moiety. The relatively low melting point of **1** may be partly ascribed to the dimer-like arrangement of the cations in the solid state (*vide infra*) which have smaller Madelung energy gains. The crystal of **3** exhibited a phase transition at –19.0 °C ($\Delta H_m = 2.66 \text{ kJ mol}^{-1}$, $\Delta S_m = 10.4 \text{ J mol}^{-1} \text{ K}^{-1}$), while the other salts exhibited no solid-state phase transitions.

We reported previously that $[\text{M}(\text{acac})(\text{BuMe}_3\text{en})]\text{Tf}_2\text{N}$ ($\text{M} = \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$) are ionic liquids exhibiting glass transitions at –58 °C and –49 °C, respectively.^{5a} The corresponding Pd^{II} complex (**2**) exhibited the glass transition at a higher temperature (–38 °C), which is consistent with its greater molecular weight and molecular volume. However, the melting point of **1** (85.2 °C) was lower than that of the corresponding Cu^{II} complex, $[\text{Cu}(\text{acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (94.7 °C). The higher melting point of the latter salt may be ascribed to the affinity of the copper ion to the weakly coordinating Tf_2N anion.^{5a}

Table 2. Melting points (T_m), glass transition temperatures (T_g) and thermodynamic parameters of **1–3** and related complexes.

Compound	T_m (°C)	ΔH_m (kJ mol ^{–1})	ΔS_m (J mol ^{–1} K ^{–1})	T_g (°C)	T_g / T_m
$[\text{Pd}(\text{acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (1)	85.2	28.0	77.4		
$[\text{Pd}(\text{acac})(\text{BuMe}_3\text{en})]\text{Tf}_2\text{N}$ (2)	71.1	35.2	101.6	–38	0.68
$[\text{Pd}(\text{C}_8\text{-acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (3)	62.3	30.3	89.7	–40	0.70

[Cu(acac)(Me ₄ en)]Tf ₂ N ^a	94.7	22.9	62.0	
[Cu(acac)(BuMe ₃ en)]Tf ₂ N ^a				−49
[Ni(acac)(BuMe ₃ en)]Tf ₂ N ^a				−58

^a Ref. 5a

Crystal structures

Crystal structures of **1–3** were determined at −173 °C. The complexes crystallized in the space groups *P*−1, *P*2₁/*c*, and *P*−1, respectively. Packing diagrams of these salts are shown in Fig. 3. The asymmetric unit of **1** and **2** contained a pair of crystallographically independent cations and anions, while that of **3** contained four pairs of cations and anions (Fig. 3).

The cations exhibited square-planar geometry (Figs. S2 and S3, ESI†). The coordination plane and the acac ligand in **1** were parallel, while those in **2** and **3** were tilted by 15.0° and 2.9–10.2°, respectively. The Pd–N and Pd–O bond lengths in the cations were approximately 2.05 Å and 1.99 Å, respectively. These values are approximately 0.1 Å longer than those reported in Ni^{II} complexes such as [Ni(acac)(Me₄en)]BPh₄.¹⁵ The alkyl chain in **2** appeared to be extended perpendicular to the coordination plane, while those in **3** were tilted by approximately 30° from the coordination plane. The chains in cations I and II were straight, while those in cations III and IV were slightly bent (Fig. S3a, ESI†).

The cations in **1** and **3** exhibited centrosymmetric dimer-like arrangements (Fig. 3). The coordination planes in the dimers were separated by 3.38 Å in **1** and 3.45 and 3.07 Å in **3**. Complex **2** exhibited no such dimer arrangement and this was attributed to steric hindrance effects. The dimer-like arrangements are found also in related complexes such as [Ni(acac)(Me₄en)]BPh₄¹⁵ (interdimer distance: 3.56 Å) and [Cu(acac)(phen)]BPh₄¹⁶ (interdimer distance: 3.38 Å), whereas [Ni(3,5-heptanedionate)(Me₄en)]BPh₄¹⁷ does not form such arrangements due to the effect of larger steric hindrance. The dimer-like arrangement observed in the current work is likely favored because the cations have dipole moments along the molecular long axes. The dipole moments of mixed-ligand complexes may be disadvantageous in decreasing the melting points and viscosities of

the liquids.

The Tf_2N anions adopted the *cisoid* conformation in **1** and *transoid* conformation in **2** and **3** (Fig. 4 and Fig. S3, ESI†). The Tf_2N anion often exhibits energetically favorable *transoid* conformations,¹⁸ but the *cisoid* conformation is stabilized by intermolecular interactions.¹⁹ In the crystals of **1–3**, there were intermolecular $\text{CH}\cdots\text{O}_{\text{Tf}_2\text{N}}$ contacts (2.54–2.72 Å) that were 0.1 Å shorter than the van-der-Waals distance, which may have stabilized the *cisoid* conformation in **1**. The negatively charged moieties of the anion ($-\text{SO}_2-\text{N}-\text{SO}_2-$) are thus surrounded by hydrogen atoms of the cations and have no contacts with the metal centers, as seen in the long $\text{Pd}-\text{N}_{\text{Tf}_2\text{N}}$ distances of 4.46 Å, 6.60 Å, and 4.83–5.77 Å, for **1**, **2**, and **3**, respectively. Complex **2** exhibited $\text{F}\cdots\text{F}$ contacts between the anions that were 0.3 Å shorter than van-der-Waals distance.

The crystal of **3** exhibited a phase transition at -19°C . Structure determination at -10°C did not give satisfactory results as extensive disorder of the alkyl chains and Tf_2N anions was observed. The disorder is consistent with the rather large transition entropy ($\Delta S_m = 10.4 \text{ J mol}^{-1} \text{ K}^{-1}$). Above the transition temperature, the unit cell volume was reduced to one fourth of that at -173°C , while the space group was unchanged ($P-1$). The molecular structures were averaged owing to the disorder, giving only one pair of crystallographically independent cation and anion.

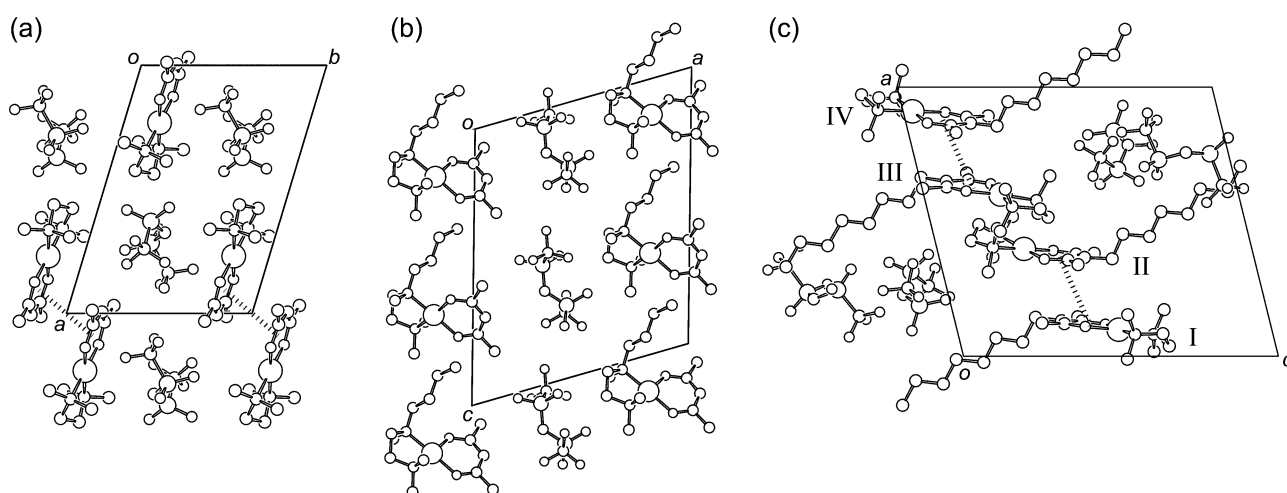


Fig. 3 Packing diagrams of (a) **1**, (b) **2**, and (c) **3**. Dotted lines for **1** and **3** indicate dimer-like arrangement of the cations. I–IV denote crystallographically independent cations in **3**.

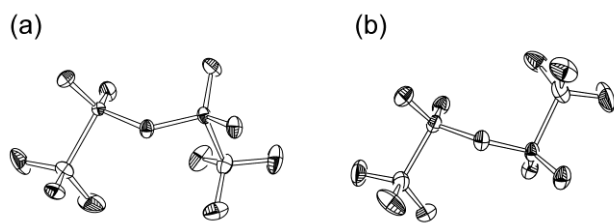


Fig. 4 ORTEP drawings of the anions in (a) **1** and (b) **2**.

Conclusion

Ionic liquids comprising cationic palladium chelate complexes with diamine and diketonato ligands were prepared. Although previously reported Cu^{II} and Ni^{II} complexes bearing alkyl chains were liquids, the corresponding Pd^{II} complexes described in the current work were solids at room temperature. The higher observed crystallinity as well as the higher melting points and glass transition temperatures are partly ascribed to larger molecular weights and volumes. X-ray crystal structure determination revealed the tendency of dimer-like arrangement of the cations and the absence of direct cation–anion interactions in the solid state. The dipole moment of this type of mixed-ligand cations likely lead to dimer formation, which may be disadvantageous for decreasing the melting points and viscosities of the liquids.

Ionic liquids containing platinum group metals could be useful for metal nanoparticle preparation and electroplating. Our initial motivation was to develop ionic liquids that are useful for Pd nanoparticle preparation and oxidative addition of halogens to tune liquid properties, but the palladium complexes prepared in this study did not exhibit such properties. Future developments of ionic liquids containing platinum ion may show promise for oxidative addition and catalytic activities.

Acknowledgments

This work was financially supported by MEXT KAKENHI grant number No. 24350073. We thank Dr. Y. Furuie for elemental analyses.

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Table of contents entry

Ionic liquids containing cationic palladium chelate complexes were prepared, and their thermal properties and crystal structures were investigated.



Ionic liquids from cationic palladium(II) chelate complexes: Preparation, thermal properties, and crystal structures†

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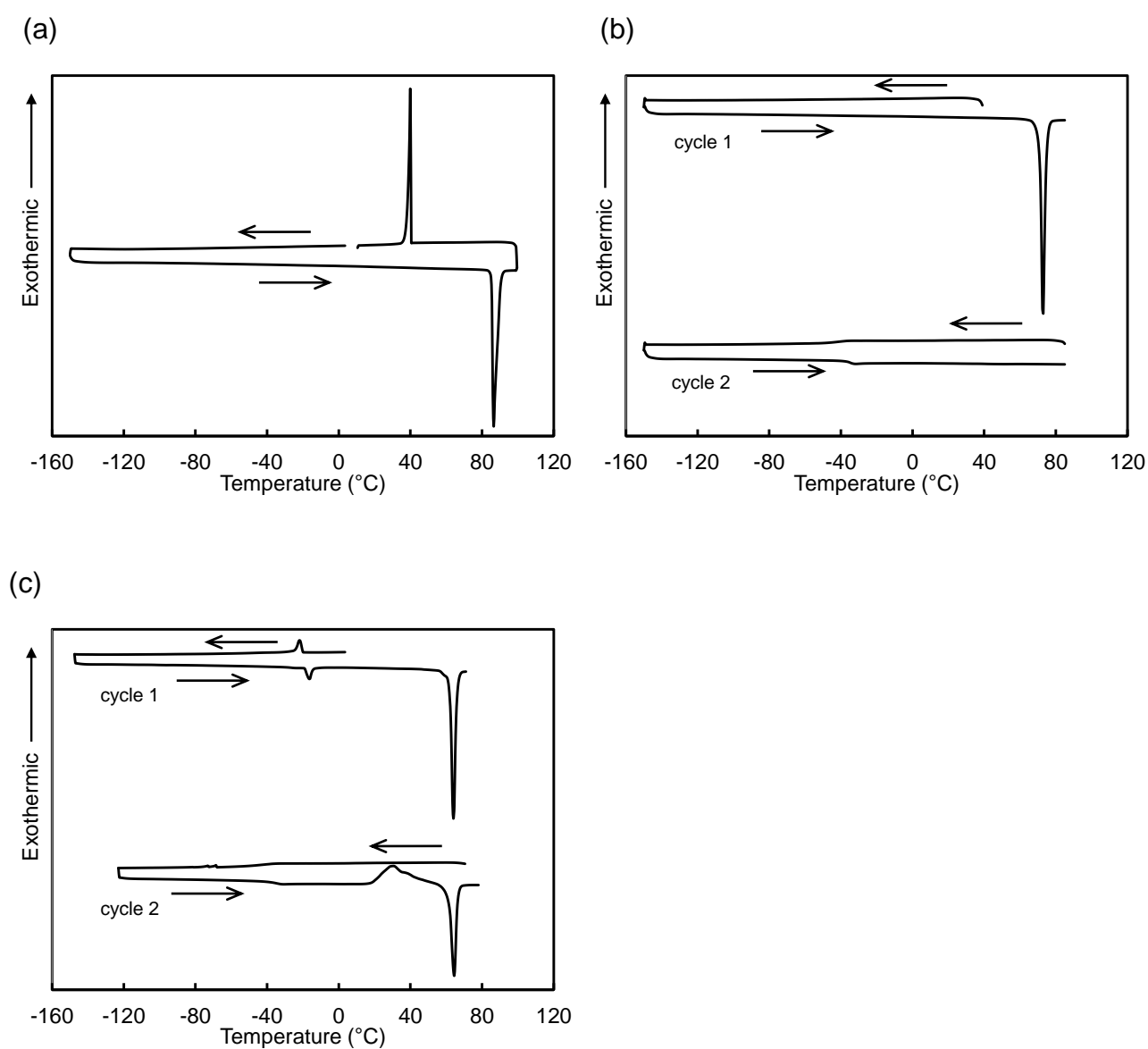


Fig. S1 DSC traces of (a) $[\text{Pd}(\text{acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (**1**), (b) $[\text{Pd}(\text{acac})(\text{BuMe}_3\text{en})]\text{Tf}_2\text{N}$ (**2**), and (c) $[\text{Pd}(\text{C}_8\text{-acac})(\text{Me}_4\text{en})]\text{Tf}_2\text{N}$ (**3**).

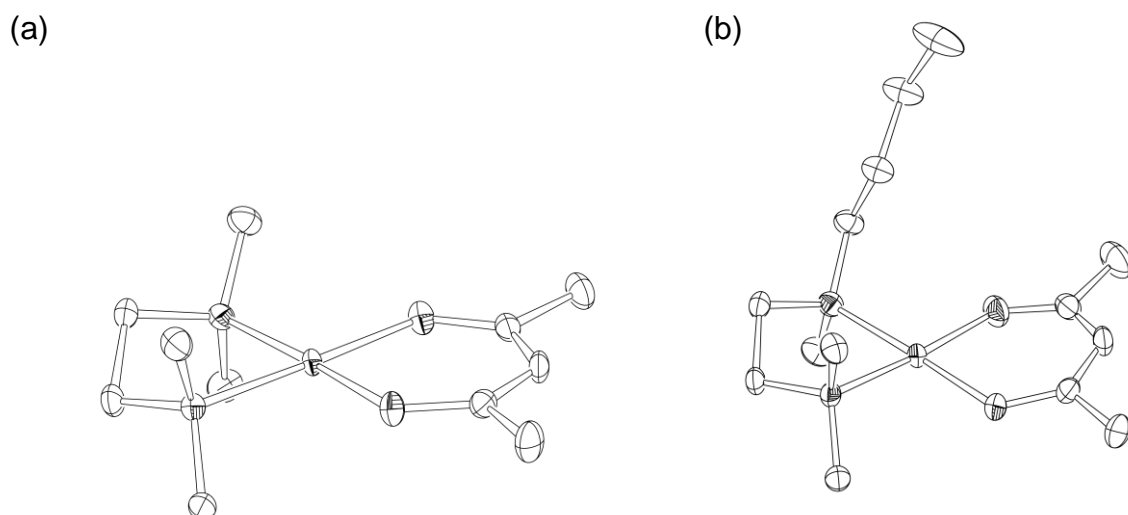


Fig. S2 ORTEP drawings of the cations in (a) **1** and (b) **2**.

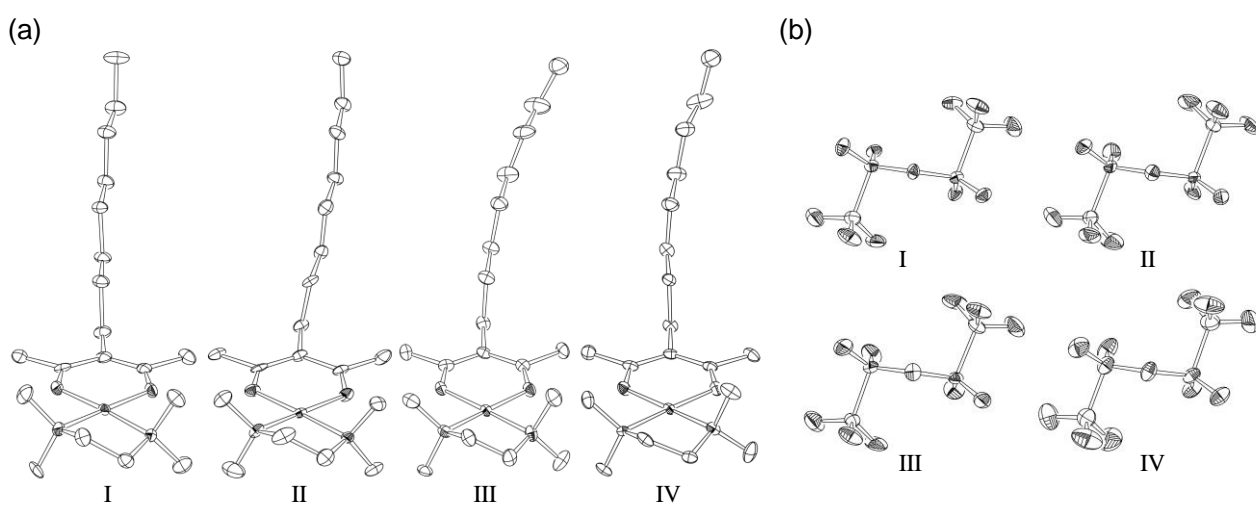


Fig. S3 ORTEP drawings of the crystallographically independent (a) cations and (b) anions in **3**.