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Synthesis and thermal properties of salts comprising cationic bis(oxazoline)-Au^{III} complexes and fluorinated anions

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Abstract

Salts comprising cationic bis(oxazoline) (box)-Au^{III} complexes and fluorinated anions were synthesized and their thermal properties were investigated. Cations that contain box ligands with butyl substituents (butyl-box) were used with either achiral-(*R*,*S*) ([**1**]$^{+}$) or chiral-(*S*,*S*) ([**2**]$^{+}$) configurations. [**1**][Tf_2N] (Tf_2N^{-} = bis(trifluoromethanesulfonyl)amide) is a solid that can also be classified as an ionic liquid (T_m = 62 °C, T_g = −11 °C). [**1**]X and [**2**]X (X = SbF_6^{-} and BF_4^{-}) exhibit melting points higher than 100 °C, where [**1**]X exhibits a higher melting point than [**2**]X. A salt with an ethyl-box ligand ([**3**][SbF_6]) exhibits no melting up to its decomposition temperature of 267 °C. Crystal structure determination revealed that the achiral cation in [**1**][BF_4] has a bent structure. The potential utility of [**1**][Tf_2N] for catalysis was demonstrated by the catalytic formation of an acetal from an alkyne.

Keywords: Bis(oxazoline) complexes; Metal complexes; Thermal properties; Ionic liquids; Catalytic activity

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1. Introduction

Metal complexes exhibit a variety of functions, including catalytic activities. Among the number of complex catalysts reported to date, metal complexes with bis(oxazoline) (box) ligands are a representative group of metal chelate catalysts [1,2]. Since box ligands have two asymmetric carbons, the resultant complexes have chiral and achiral isomers. Although complex catalysts are often prepared *in situ* in catalytic reactions and not isolated, X-ray structures of many box metal complexes have been determined to understand their stereochemistry. Their thermal properties, however, are not well understood.

We have developed a variety of ionic liquids containing functional metal complexes [3,4]. Ionic liquids are salts with melting points below 100 °C, and their unique characteristics have attracted much attention [5,6]. Ionic liquids with catalytic ability have been recently developed [7]; we previously synthesized ionic liquids from half-sandwich complexes that function as catalysts [8]. As such, we are interested in the possibility of ionic liquid formation from box complexes. In this study, therefore, we synthesized a series of Au^{III} complexes with a butyl-box ligand ($[Au^{III}Cl_2(\text{butyl-box})]X$, Fig. 1) and investigated their thermal properties. Au^{III}-containing complexes were chosen because of our recent work on the isolation and structural characterization of a related box-Au^{III} salt [9]. Counter anions Tf_2N^- (Tf_2N^- = bis(trifluoromethanesulfonyl)amide), SbF_6^-, and BF_4^- were used in this study. Although box-containing complexes with bulky substituents have often been used for catalytic reactions [1,2], butyl substituents were introduced into the box ligand to lower the melting points. To investigate the effect of chirality, cations with achiral (*R,S*)- and chiral (*S,S*)-configurations were employed, which are designated as [**1**]$^+$ and [**2**]$^+$, respectively (Fig. 1). A salt with ethyl substituents on the box ligand, $[Au^{III}Cl_2\{(S,S)\text{-ethyl-box}\}][SbF_6]$ ([**3**]$[SbF_6]$), was also synthesized to investigate the effect of the alkyl chain length on the complex. We attempted the synthesis of other salts with different substituents and anions; however, those results are not included in this study because we were unable to obtain sufficiently pure samples.

A search of the Cambridge Structural Database (CSD) revealed that structure determination of box-containing complexes is limited to chiral complexes. This is because of the interest in box complexes as asymmetric catalysts. Therefore, the crystal structure of [**1**][BF_4] was determined by X-ray crystallography to elucidate the stereochemistry of the achiral complex.

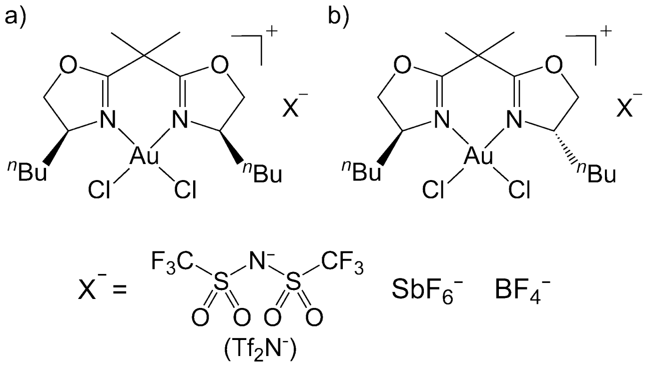

Figure 1. Structural formulas of salts of butyl-bis(oxazoline) (box)-Au^{III} complexes prepared in this study: (a) Achiral salts with the (*R*,*S*)-butyl-box ligand ([**1**]X) and (b) chiral salts with the (*S*,*S*)-butyl-box ligand ([**2**]X). The anions (X^-) are shown below the formulas.

2. Results and Discussion

2.1. Preparation

Complexes [**1**]X and [**2**]X ($X^- = Tf_2N^-$, SbF_6^-, and BF_4^-) were synthesized by the reaction of the butyl-box ligand, K[$AuCl_4$], and a salt of the anion in acetonitrile. [**3**][SbF_6] was prepared by the same method. We failed to purify a pale yellow oil of [**2**][Tf_2N]; the results are not included here. Other salts were obtained as pale yellow solids after recrystallization. These salts were soluble in dichloromethane and polar solvents, such as alcohol; however, they appeared to be rather unstable in polar solvents.

2.2. Thermal properties

The thermal properties of these salts were investigated by differential scanning calorimetry (DSC). DSC traces are shown in Fig. S1 (electronic supporting information). The melting points (T_m), glass transition temperatures (T_g), and relevant parameters of the salts are listed in Table 1. In [**1**]X, the melting points increases with decreasing anion size ($Tf_2N^- > SbF_6^- > BF_4^-$). [**1**][$Tf_2N$] ($T_m$ = 62.0 °C, T_g = −11 °C) can be regarded as an ionic liquid but is a solid at room temperature. The rather high melting point of [**1**][Tf_2N] is likely caused by the large polarity, planar shape, and heavy molecular weight of the cation, considering the thermal properties of ionic liquids of pincer complexes [10]. The SbF_6^- and BF_4^- salts exhibit melting points higher than 100 °C, and the achiral salts exhibit higher melting points than the chiral salts. The melting point of [**1**][SbF_6] (T_m = 131.5 °C) is higher than that of [**2**][SbF_6] (T_m = 115.4 °C) and that of [**1**][BF_4] (T_m = 173.0 °C) is higher than that of [**2**][BF_4] (T_m = 101 °C). For the melting entropies (ΔS), the value for [**1**][Tf_2N] is larger (110 J mol^{-1} K^{-1}) than those for [**1**][X] (X = BF_4^-, SbF_6^-; ~55 J mol^{-1} K^{-1}); this result is consistent with the flexibility of the Tf_2N anion.

When cooled from a melt, the salts do not crystallize but exhibit glass transitions (T_g = −29–30 °C). The glass transition temperatures were much higher than those of the free box ligands. The box ligands are liquids and do not crystallize at low temperatures, undergoing glass transitions at −79 °C ((*R*,*S*)-butyl-box) and −77 °C ((*S*,*S*)-butyl-box).

All the salts bearing butyl substituents on the ligand exhibit melting as described above, but the salt with ethyl substituents on the ligand [**3**][SbF_6] did not show melting upon heating, only decomposition at 267 °C. This result demonstrates the effectiveness of introducing butyl substituents on the box ligand for lowering the melting point.

Among the salts synthesized, [**2**][SbF_6] and [**3**][SbF_6] exhibit a phase transition in the solid state at 73.8 °C (ΔS = 1.7 J mol^{-1} K^{-1}) and 69.3 °C (ΔS = 10.6 J mol^{-1} K^{-1}), respectively.

Table 1.

Melting points (T_m), melting enthalpies (ΔH) and entropies (ΔS), and glass transition temperatures (T_g) of the salts synthesized in this study

Compound	T_m (°C)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	T_g (°C)
[**1**][Tf_2N]	62.0	35.8	105.8	–11
[**1**][SbF_6]	131.5	22.2	54.4	30
[**1**][BF_4]	173.0	25.9	57.9	25
[**2**][SbF_6]	115.4	22.0	55.3	–29
[**2**][BF_4][a]	101[b]			
[**3**][SbF_6]	267 (dec.)[b]			

[a]Elemental analysis data deviated by 0.7% from the calculated value for the salt. [b]Visually observed under a microscope.

2.3. Crystal structure

The crystal structure of [**1**][BF_4] containing the achiral ligand was determined by X-ray crystallography. As per our knowledge, there are no X-ray structures of achiral box ligand-containing complexes reported to date. An ORTEP drawing of the cation is shown in Fig. 2a. The complex has a square-planar coordination geometry, whereas the ligand exhibits a bent structure (Fig. 2b). The two oxazoline rings make an angle of 145°. The central six-membered ring involving the Au ion forms a boat conformation, and the angle between the mean plane of the ring and the coordination plane is ~20°. The butyl groups are extended outside of the coordination plane. The cation and anion form an ion-pair-like arrangement with a distance of 4.39 Å between the metal and anion centers. The structure contrasts with that of [$Au^{III}Cl_2${(*R,R)*-benzyl-box}][SbF_6] containing a chiral ligand, which we previously reported [9]. In this complex, the ligand is almost planar and the substituents are oriented above and below the coordination plane. Moreover, the ion pairing is less prominent because of the more symmetric cationic structure concomitant with symmetric cation–anion arrangements. Indeed, chiral box complexes usually exhibit a planar ligand conformation in the solid state [1]. Although the bent structure of the achiral cation as shown here may partially result from the packing effects, the higher melting points of the achiral complexes compared with those of chiral complexes may be ascribed to a more effective ion-pair formation resulting from the less symmetrical structure of the achiral cation.

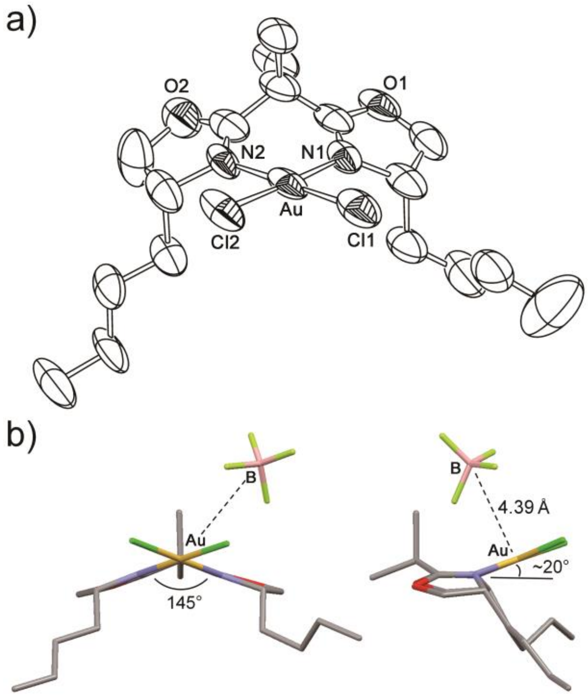

Figure 2. (a) ORTEP drawing of cation in [**1**][BF_4]. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. (b) Cation–anion arrangement viewed from two directions.

2.4. Catalytic reaction

The catalytic activities of box-Au^{III} complexes have been previously demonstrated [9]. To investigate the potential utility of the ionic liquid [**1**][Tf_2N] for catalysis, the conversion of an alkyne to an acetal, a simple reaction catalyzed by Au^{III} catalysts [11], was examined. Heating a solution of phenylacetylene (PhC≡CH) with a slight excess of methanol in the presence of [**1**][Tf_2N] (2 mol%) for 1 h at 60 °C produced 1,1-dimethoxyethylbenzene ($PhCCH_3(OCH_3)_2$) in 77% yield. No additional solvent was used in the reaction. The solution was initially homogeneous, whereas the product separated from the ionic liquid upon consumption of the methanol. The use of 0.2 mol% catalyst gave a lower yield of ~40%. The catalytic activity was thus demonstrated, although the yield was lower than that for a reaction using Na[$AuCl_4$] as the catalyst (96%) [11]. The lower yield may be partly attributed to the gradual decomposition of the catalyst, forming black precipitate. This tendency likely results from the instability of the Au^{III}-containing complex.

3. Conclusion

Salts of cationic Au^{III} complexes containing butyl-box ligands were prepared and their thermal properties were investigated. [**1**][Tf_2N] is regarded as an ionic liquid; however, its melting point is higher than room temperature. Once melted, [**1**][Tf_2N] maintains its liquid state at room temperature. Moreover, its rather high melting point can be attributed to the planar shape, large polarity, and heavy molecular weight of the cation. The melting points of SbF_6^- and BF_4^- salts are higher than 100 °C, and the salts from the chiral (*S*,*S*)-butyl-box complex exhibit lower melting points than the achiral (*R*,*S*)-butyl-box complex. The achiral complex exhibits a bent structure in [**1**][BF_4] in the solid state. The salts from the less symmetrical achiral complex likely contain stronger electrostatic interactions, yielding high melting points. The Tf_2N^- salt exhibits catalytic activity for the conversion of an alkyne to an acetal; however, gradual decomposition of the catalyst occurs during the reaction. Indeed, a similar problem has been observed in catalytic reactions using ionic liquids from half-sandwich catalysts [8]. The use of a more robust catalytic species may be needed to enable recycling of the catalyst.

4. Experimental Section

4.1. General

Silver bis(trifluoromethanesulfonyl)amide was prepared according to the literature [12].

The box ligands were prepared using the general procedure described for bis(oxazolines) [13] and were purified using silica gel chromatography (eluent: hexane/ethyl acetate: 5/1–10/1 + 1% triethylamine). Other reagents were commercially available. ^{1}H NMR spectra were measured using a JEOL JNM-ECL-400 spectrometer. Elemental analysis was performed using a Yanaco CHN MT-5 recorder. DSC measurements were conducted using a TA Instrument Q100 differential scanning calorimeter. TG analysis was conducted using a Rigaku TG8120 at 1 K min^{-1} under nitrogen atmosphere.

*4.2. Preparation of [AuCl$_2${(R,S)-butyl-box}]X ([**1**]X; X = Tf$_2$N$^-$, SbF$_6^-$, BF$_4^-$)*

An acetonitrile solution (10 mL) of (*R,S*)-butyl-box (51.6 mg, 0.175 mmol) and an acetonitrile solution (10 mL) of KAuCl$_4$ (64.3 mg, 0.170 mmol) were mixed, to which a solution of Ag[Tf$_2$N] (106 mg, 0.273 mmol) in acetonitrile was added. After stirring the solution in the dark for a day, a small amount of lithium chloride was added to the solution. Then, the solution was filtered through a short plug of celite and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane, washed several times with water, dried over magnesium sulfate, and evaporated. The residue was dissolved in methanol and washed several times with hexane, and the methanol layer was separated and evaporated. Recrystallization of the resultant yellow oil from ethanol (−50 °C) produced the desired compound i.e., a pale yellow powder (29 mg, yield 20%). ^{1}H NMR (CDCl$_3$, ppm, 400 MHz): δ = 0.94 (t, 6H, *J* = 7.0 Hz), 1.23–1.40 (m, 8H), 1.81 (s, 3H), 1.92 (m, 2H), 1.98 (s, 3H), 2.10–2.12 (m, 2H), 4.85–4.97 (m, 6H). Anal. found: C 27.43, H 3.78, N 4.92%; calcd. for $C_{19}H_{30}AuCl_2F_6N_3O_6S_2$: C 27.09, H 3.59, N 4.99%.

[**1**][SbF$_6$] was synthesized by the same procedure as used for the synthesis of [**1**][Tf$_2$N] using silver hexafluoroantimonate. Recrystallization of the product from ethanol (−50 °C) produced a pale yellow powder (Yield ~20%).^{1}H NMR (CDCl$_3$, ppm, 400 MHz): δ = 0.94 (t,

6H, *J* = 7.2 Hz), 1.29–1.45 (m, 8H), 1.78 (s, 3H), 1.95 (m, 2H), 1.98 (s, 3H), 2.12–2.15 (m, 2H), 4.79–4.89 (m, 4H), 4.99–4.94 (m, 2H). Anal. found: C 25.74, H 3.81, N 3.51%; calcd. for $C_{17}H_{30}AuCl_2F_6N_2O_2Sb$: C 25.58, H 3.79, N 3.51%.

[**1**][BF_4] was synthesized by the same procedure as used for the synthesis of [**1**][Tf_2N] using silver tetrafluoroborate. Slow diffusion of ether into a dichloromethane solution of the product gave a pale yellow powder (yield 71%). ^1H NMR ($CDCl_3$, ppm, 400 MHz): $\delta = 0.93$ (t, 6H, *J* = 7.0 Hz), 1.29–1.43 (m, 8H), 1.81 (s, 3H), 1.94 (s, 3H), 2.08–2.17 (m, 4H), 4.81–4.95 (m, 6H). Anal. found: C 31.61, H 4.92, N 4.61%; calcd. for $C_{17}H_{30}AuBCl_2F_4N_2O_2$: C 31.46, H 4.66, N 4.32%.

*4.3. Preparation of [$AuCl_2${(S,S)-butyl-box}]X ([**2**]X; X = SbF_6, BF_4)*

[**2**][SbF_6] was synthesized by the same procedure as used for the synthesis of [**1**][Tf_2N] using (*S,S*)-butyl-bis(oxazoline) and silver hexafluoroantimonate. Recrystallization of the resultant yellow oil from ethanol (−50 °C) produced a pale yellow powder (yield 9%). ^1H NMR ($CDCl_3$, ppm, 400 MHz): $\delta = 0.93$ (t, 6H, *J* = 6.8 Hz), 1.37–1.40 (m, 8H), 1.77 (m, 8H), 2.01 (m, 2H), 4.37–4.45 (m, 4H), 4.90 (t, 2H, *J* = 8.6 Hz). Anal. found: C 25.48, H 3.97, N 3.59%; calcd. for $C_{17}H_{30}AuCl_2F_6N_2O_2Sb$: C 25.58, H 3.79, N 3.51%.

[**2**][BF_4] was synthesized by a similar procedure but the corresponding nitrate salt was first prepared using silver nitrate and then the solid was subjected to anion exchange using sodium tetrafluoroborate in acetonitrile. After evaporation of the solvent, the product was dissolved in dichloromethane and washed with water; the product was then dissolved in methanol and washed several times with hexane. The product was obtained as a yellow powder (yield 28%). ^1H NMR ($CDCl_3$, ppm, 400 MHz): $\delta = 0.91$ (t, 6H, *J* = 6.4 Hz), 1.26–1.51 (m, 8H), 1.54–1.77 (m, 8H), 1.90 (m, 2H), 3.28–3.73 (m, 2H), 4.11–5.00 (m, 4H).

Anal. found: C 30.75, H 4.76, N 4.07%; calcd. for $C_{17}H_{30}AuBCl_2F_4N_2O_2$: C 31.46, H 4.66, N 4.32%. The elemental analysis results deviated by 0.71%, but purification by recrystallization was not possible.

*4.4. Preparation of [AuCl$_2${(S,S)-ethyl-box}][SbF$_6$] ([**3**][SbF$_6$])*

[**3**][SbF_6] was synthesized by the same procedure as used for [**1**][Tf_2N] using (*S,S)*-ethyl-bis(oxazoline) and silver hexafluoroantimonate. Recrystallization of the product from ethanol (−50 °C) produced a pale yellow powder (yield 24%). ^{1}H NMR (CD_2Cl_2, ppm, 400 MHz): δ = 0.97 (t, 6H, *J* = 7.4 Hz), 1.77 (m, 2H), 1.81 (s, 6H), 2.11–2.14 (m, 2H), 4.72–4.73 (m, 2H), 4.86–4.87 (m, 4H). Anal. found: C 21.43, H 3.10, N 4.19%; calcd. for $C_{13}H_{22}AuCl_2F_6N_2O_2Sb$: C 21.04, H 2.99, N 3.78%.

4.5. Catalytic reaction

Under a nitrogen atmosphere, [**1**][Tf_2N] (19.2 mg, 0.0228 mmol, ca. 2 mol%) and phenylacetylene (0.125 mL, 1.32 mmol) were dissolved in methanol (0.092 mL, 3.62 mmol) and the solution was stirred for 1 h at 60 °C. Then, the product was extracted with hexane and filtered through a short plug of celite. Removal of the solvent left 182.8 mg of a yellow liquid of 1,1-dimethoxyethylbenzene, which contained a small amount of phenylacetylene. The yield was determined by ^{1}H NMR (yield 77%).

4.6. X-ray crystallography

Single crystals of [**1**][BF_4] suitable for X-ray crystallography were prepared by slow diffusion of diethyl ether to a dichloromethane solution of the salt. X-ray diffraction data were collected on a Bruker APEX II Ultra CCD diffractometer using Mo K_α radiation (λ = 0.71073 Å) at −173°C. All calculations were performed using SHELXL [14]. Empirical absorption correction was applied. Crystallographic parameters: $C_{17}H_{30}AuBCl_2F_4N_2O_2$, $M_W = 649.11$, $Z = 8$, $D_{calcd.} = 1.845$ g cm^{-3}, monoclinic, space group $C2/c$, with unit cell $a = 22.688(5)$ Å, $b = 14.477(5)$ Å, $c = 14.231(5)$ Å, $\beta = 91.569(5)°$, and $V = 4672(3)$ Å^3. $R_1(I > 2\sigma(I)) = 0.0714$, $wR_2 = 0.1980$, 4909 independent reflections (R(int) = 0.0434), 266 parameters. Ortep-3 [15] was used to produce molecular graphics.

Appendix A. Supplementary data

CCDC 854789 contains the supplementary crystallographic data for [**1**][BF_4]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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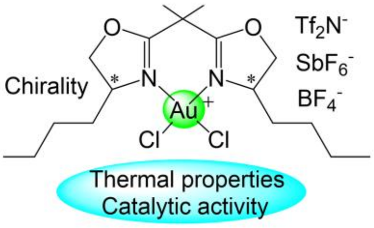

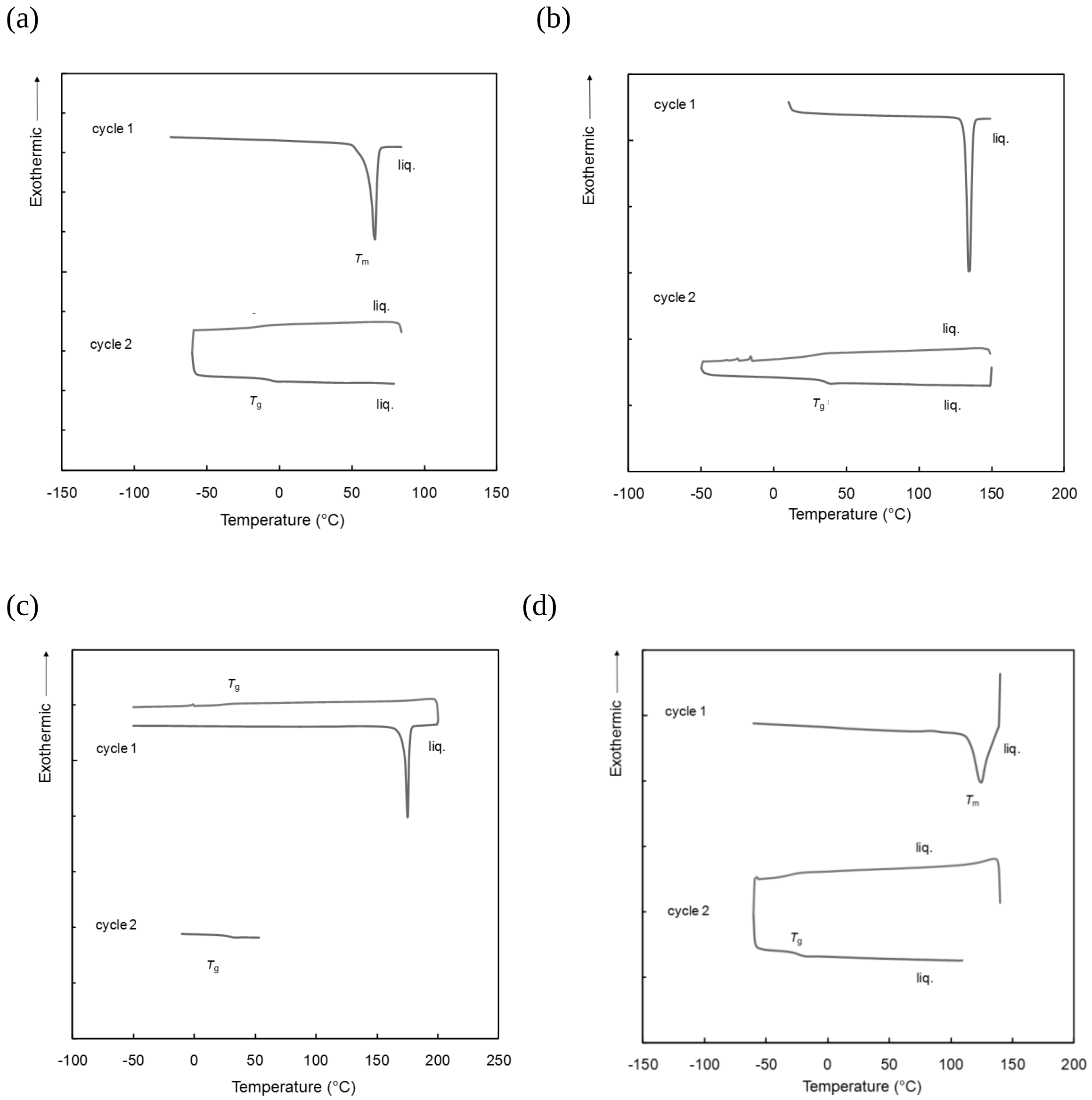

Figure S1. DSC traces of (a) [**1**][Tf_2N], (b) [**1**][SbF_6], (c) [**1**][BF_4], and (d) [**2**][SbF_6].