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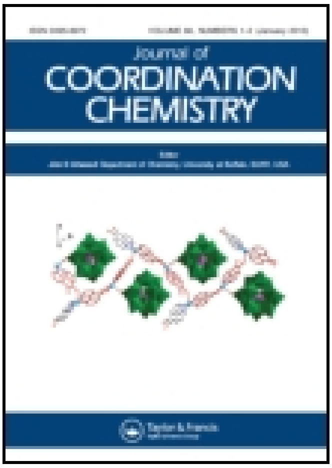

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Ionic liquids from the cationic cobalt(III) Schiff base complex, [Co(acacen)L_2][Tf_2N] (acacen = N,N′-bis(acetylacetone)ethylenediamine, Tf_2N = bis(trifluoromethanesulfonyl)amide)

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Ionic liquids from the cationic cobalt(III) Schiff base complex, $[Co(acacen)L_2][Tf_2N]$ (acacen = *N*,*N′*-bis(acetylacetone) ethylenediamine, Tf_2N = bis(trifluoromethanesulfonyl)amide)

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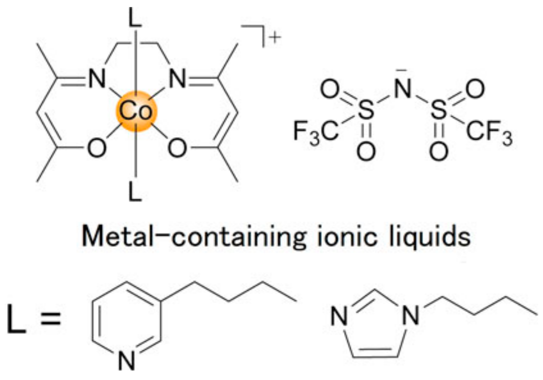

Ionic liquids comprising cationic cobalt(III) complexes $[Co(acacen)L_2][Tf_2N]$ (L = 3-butylpyridine (**1**), 1-butylimidazole (**2**); acacen = *N*,*N′*-bis(acetylacetone)ethylenediamine, Tf_2N = bis(trifluoromethanesulfonyl)amide) were prepared. **1** is a liquid at room temperature and exhibits a glass transition at −12 °C, whereas **2** is a solid at room temperature with a melting point of 74.6 °C and glass transition temperature of −15 °C upon cooling from the melt. These salts are reddish brown diamagnetic materials that are stable against air and water; these properties differ from those of the corresponding iron(III) salt. Desorption of the axial ligands of **1** and **2** occurs at 180 and 207 °C, respectively.

Keywords: Ionic liquid; Thermal properties; Acacen; Schiff base; Axial ligand

1. Introduction

Ionic liquids are salts with melting points below 100 °C; they have attracted significant attention because of their various applications [1–7]. Although most ionic liquids are onium salts, ionic liquids with metal-containing anions [8–12] or cations [13–16] have been

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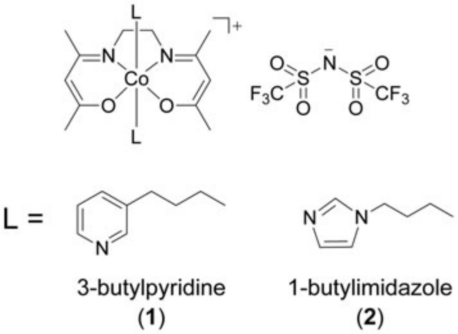

Figure 1. Structural formula of [Co(acacen)L_2][Tf_2N] (L = 3-butylpyridine (**1**) or 1-butylimidazole (**2**)).

developed recently and have attracted attention due to the properties contributed by the metal ions, such as magnetism and catalytic activity. We previously developed functional ionic liquids using cationic metal complexes, including metallocenium cations [17–21] and metal chelate cations [22, 23].

N,*N′*-Bis(acetylacetone)ethylenediamine (acacen) is a tetradentate Schiff base ligand that has been used to prepare various metal complexes [24]. Previously, we prepared [Fe(acacen)(1-butylimidazole)$_2$][Tf_2N] (Tf_2N = bis(trifluoromethanesulfonyl)amide), which is a paramagnetic ionic liquid that exhibits spin-crossover phenomena [25]. However, this liquid is highly sensitive to air and moisture, and thermally unstable because of desorption of the axial ligands. In this study, we prepared [Co(acacen)L_2][Tf_2N] (L = 3-butylpyridine or 1-butylimidazole) (figure 1), which contains cobalt(III). The resultant diamagnetic ionic liquids are stable, which enabled investigation of their thermal properties. Several [Co(acacen)L_2]$^+$ complexes (L = *N*-donor ligands) have been reported, and their crystal structures and electrochemical properties have been investigated [26, 27].

2. Experimental

2.1. *General*

N,*N′*-Bis(acetylacetone)ethylenediamine was prepared according to the published procedure [27]. Other reagents were commercially obtained. ^{1}H NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Elemental analyses were performed using a Yanaco CHN MT-5 instrument. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q100 differential scanning calorimeter from −150 to 100 °C with a scan rate of 10 K $\min^{-1}$. Thermogravimetric analysis (TG) was performed using a Rigaku TG8120 under nitrogen with a scan rate of 10 K $\min^{-1}$.

2.2. *Preparation of [Co(acacen)(3-butylpyridine)$_2$][Tf_2N] (1)*

A methanol solution of $CoCl_2{\cdot}6H_2O$ (99.2 mg, 0.42 mM) and acacen (77.1 mg, 0.34 mM) was refluxed for 30 min at 70 °C under nitrogen. After the addition of a methanol solution of 3-butylpyridine (0.15 mL, 1.02 mM), the mixture was refluxed for an additional hour and then cooled to room temperature. The reaction mixture was stirred overnight at room temperature with oxygen bubbled through the solution. After evaporation of the solvent, the residue was washed with water and ether, extracted with dichloromethane, and dried over $MgSO_4$. This procedure gave [Co(acacen)(3-butylpyridine)$_2$]Cl as a reddish brown solid in a yield of 70% (142 mg). $LiTf_2N$ (84.0 mg, 0.30 mM) was added to an aqueous solution of the obtained salt (142 mg, 0.24 mM). The mixture was stirred for 10 min, extracted with dichloromethane, and dried over $MgSO_4$. Evaporation of the solvent gave the desired product as a red–brown liquid in a yield of 77% (155 mg), which was further dried *in vacuo* at 60 °C overnight. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) = 7.85 (s, 2H), 7.75 (d, 2H, $J = 6.0$), 7.59 (d, 2H, $J = 8$), 7.27 (t, 2H, $J = 6.6$), 4.99 (s, 2H), 3.73 (s, 4H), 2.59 (t, 4H, $J = 7.4$), 2.29 (s, 6H), 2.10 (s, 6H), 1.54 (q, 4H, $J = 7.4$), 1.32–1.23 (m, 4H), 0.91 (t, 6H, $J = 7.2$). Anal. Calcd for $C_{32}H_{44}F_6MnN_5O_6S_2$: C, 46.21; H, 5.33; N, 8.42. Found: C, 46.44; H, 5.49; N, 8.29.

2.3. *Preparation of [Co(acacen)(1-butylimidazole)$_2$][Tf$_2$N] (2)*

Complex **2** was prepared using the same procedure described for complex **1** with 1-butylimidazole instead of 3-butylpyridine. The Tf_2N salt was purified by column chromatography (alumina, eluent: dichloromethane and ethanol). The yields of the chloride and Tf_2N salts were 83 and 88%, respectively. The Tf_2N salt was obtained as a liquid but soon crystallized at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) = 7.22 (s, 2H), 6.88 (s, 2H), 6.64 (s, 2H), 4.99 (s, 2H), 3.95 (t, 4H, $J = 7.4$), 3.53 (s, 4H), 2.34 (s, 6H), 2.18 (s, 6H), 1.69 (q, 4H, $J = 9.8$), 1.29–1.20 (m, 4H), 0.91 (t, 6H, $J = 5.8$). Anal. Calcd for $C_{28}H_{42}F_6CoN_7O_6S_2$: C, 41.53; H, 5.23; N, 12.11. Found: C, 41.78; H, 5.33; N, 11.91.

3. Results and discussion

Chloride salts of the desired compounds were obtained by reacting acacen, cobalt chloride, and the axial ligands, followed by oxidation in air. Reddish brown salts **1** and **2** were obtained by metathesis of the chloride salts with $LiTf_2N$. In contrast to the corresponding iron(III) complex reported previously [25], these liquids were stable against air and moisture.

DSC traces of these salts recorded during heating are shown in figure 2. **1** is a liquid at room temperature and exhibited a glass transition at −12 °C. In contrast, **2** is a solid at room temperature, which melts at 74.6 °C ($\Delta H = 50.0\ \mathrm{kJ\ M^{-1}}$, $\Delta S = 141.2\ \mathrm{J\ K^{-1}\ M^{-1}}$). This salt does not crystallize after melting, and exhibits a glass transition at −15 °C. The relationship between the melting point and glass transition temperature ($T_g/T_m = 0.74$) slightly deviates from the empirical relationship of $T_g/T_m = 2/3$ [28, 29]; this may be due to a decrease in the melting point caused by slight desorption of axial ligands near the melting temperature. The glass transition temperature of [Fe(acacen)(1-butylimidazole)$_2$][Tf$_2$N] (−31 °C) is lower than that of the present cobalt complex **2** [25].

TG traces of these salts are shown in figure 3. The decomposition temperatures (−3 wt%) of **1** and **2** are 180 and 207 °C, respectively, and are ascribed to desorption of the axial ligands. The higher thermal stability of the latter is likely due to the stronger coordination ability of imidazole than pyridine, as reported for [Co(acacen)L$_2$]BPh$_4$ (L = 1-methylimidazole or pyridine) [26]. The cobalt complexes are much more stable than [Fe(acacen)(1-butylimidazole)$_2$][Tf$_2$N], which begins to decompose at 50 °C [25]. The increased stability is ascribed to the inertness of cobalt(III) towards substitution.

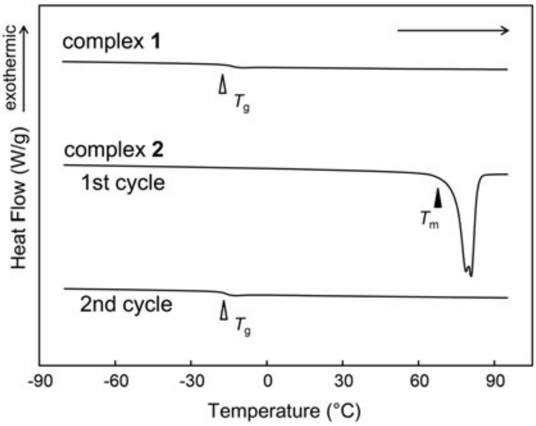

Figure 2. DSC curves for **1** and **2** obtained during heating.

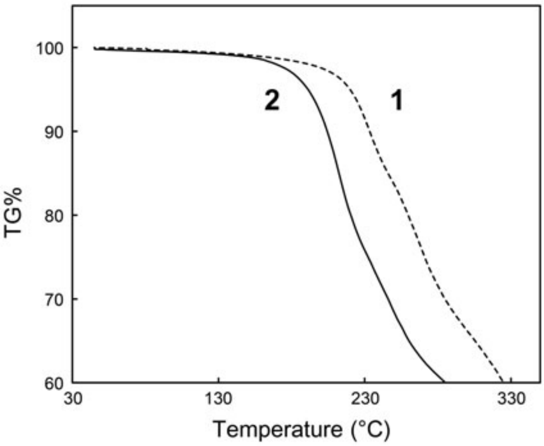

Figure 3. Thermogravimetric traces of **1** (dotted line) and **2** (solid line).

We previously prepared Tf_2N salts of cationic manganese salen (salen = *N*,*N′*-bis(salicylideneaminato)ethylene) complexes and investigated the dependence of the decomposition temperatures on the axial ligands [30]; the decomposition temperatures of the complexes with 1-butylimidazole and 3-butylpyridine axial ligands were 156 and 106 °C, respectively. Again, this is likely due to the increased coordination ability of imidazole over that of pyridine. Although the melting points of these salts are high, the acacen complexes are ionic liquids because of their smaller molecular weights and weaker intermolecular interactions. It is expected that the corresponding manganese(III) acacen ionic liquids would be less stable than the cobalt(III) complexes prepared in this study.

4. Conclusion

We prepared two ionic liquids from acacen complexes containing cobalt(III) as the metal center. These salts are much more stable than the corresponding iron(III) salts against air, moisture, and heat because of the inertness of the cobalt(III) against substitution. The use of metal ions that are inert towards substitution and axial ligands with stronger coordination abilities are important for the development of stable ionic liquids containing tetradentate ligands such as acacen. An investigation of complexes without axial ligands is currently in progress to improve the stability of the ionic liquids.

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