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Ionic Liquids from Copper(II) Complexes with Alkylimidazole-Containing Tripodal Ligands†

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Abstract

Five-coordinate copper(II) complexes [Cu(L)Cl]X bearing alkylimidazole-containing tripodal ligands were prepared, where L = bis(2-dimethylaminoethyl)-((1-alkylimidazol-2-yl)methyl)amine and X = bis(trifluoromethanesulfonyl)amide (Tf_2N) and PF_6. The salts with hexyl ([**1**]X), propyl ([**2**]X), and methyl ([**3**]X) substituents in the ligand were prepared, of which [**1**]Tf_2N and [**2**]Tf_2N were ionic liquids with high viscosity at room temperature. X-ray crystal structure determination at low temperature revealed that the coordination geometry around the metal ion in [**3**]Tf_2N was distorted trigonal bipyramidal, whereas that in [**2**]PF_6 was close to square pyramidal. UV-vis absorption spectra of these salts were consistent with the coordination structures.

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1. Introduction

Ionic liquids (ILs), salts with melting points below 100 °C, have received much attention because of their functionalities.[1] Most of them are onium salts with fluorinated anions, although functional ILs containing metal complexes[2,3] have been reported recently. We have prepared ILs from metallocenium cations[4] and cationic chelate complexes.[5] These ILs exhibit unconventional physical properties and chemical reactivities derived from the characteristic features of their constituent metal complexes. In this paper, we report the preparation and properties of ILs containing cationic copper complexes with tripodal tetradentate ligands.

Tris(2-dimethylaminoethyl)amine (abbreviated as Me_6tren) and its analogs are highly versatile tripodal ligands[6] that may be used to produce a variety of metal complexes. Among them, [Cu(Me_6tren)]X (X = anion) and related complexes are bioinorganically important complexes, and are the model compounds for the active sites of metalloenzymes.[7] Many five-coordinate complexes [Cu(Me_6tren)L]X (L = halogens, etc.) have been prepared and their structures and properties have been investigated.[8] Copper complexes with tripodal ligands catalyze various chemical reactions.[7d,9] As part of our continued investigation of the liquefaction of functional metal complexes, we aimed to prepare copper-containing ILs with tripodal ligands. Liquefaction of these complexes may lead to functional fluids exhibiting chemical reactivities and catalytic activities. For this purpose, we designed novel ligands bis(2-dimethylaminoethyl)-((1-R-imidazol-2-yl)methyl)amine, where R = hexyl ($\mathbf{L^1}$), propyl ($\mathbf{L^2}$), and methyl ($\mathbf{L^3}$) groups. We introduced the alkylimidazole moiety because alkylimidazolium cations produce ILs. Using these ligands, [Cu(L)Cl]X (L = $\mathbf{L^1}$–$\mathbf{L^3}$, X = bis(trifluoromethanesulfonyl)amide (Tf_2N) and PF_6) were prepared (Fig. 1), and their thermal properties and coordination structures were investigated. In addition, [Cu(Me_6tren)Cl]Tf_2N was prepared and structurally characterized for comparison.

2. Results and Discussion

Preparation and properties

The tripodal ligands **L^1**–**L^3** were prepared by reductive amination of alkylimidazolecarbaldehydes with bis(2-dimethylaminoethyl)amine.[10] The copper(II) complexes [**1**]Tf_2N–[**3**]Tf_2N and [Cu(Me_6tren)Cl]Tf_2N were prepared by the reaction of the ligands with Cu^{II} salts, followed by anion exchange using lithium bis(trifluoromethanesulfonyl)amide. [**1**]Tf_2N and [**2**]Tf_2N were obtained as green ionic liquids, although [**2**]Tf_2N crystallized over a few weeks. [**3**]Tf_2N and [Cu(Me_6tren)Cl]Tf_2N were obtained as blue crystals, and exhibited high melting points because of the absence of alkyl chains in the ligands. All of the salts were stable in air. Our efforts to obtain [Cu^I(**L1**)]Tf_2N failed because of disproportionation, as has been observed in [Cu^I(Me_6tren)]$^+$ and related complexes.[7b–d]

We measured the temperature dependence of the viscosity of [**1**]Tf_2N. This was a Newtonian liquid with a very high viscosity (55.1 Pa s at 25 °C), which is larger than those of typical imidazolium ILs (e.g., [butylmethylimidazolium]Tf_2N: 49 mPa s)[11] by an order of 10^3. The activation energy (E_a) derived from the Arrhenius plot of viscosity was 99.5 kJ mol^{-1}, which is three times larger than the corresponding values for imidazolium ILs (E_a = 30–40 kJ mol^{-1}).[11] These tendencies probably reflect the high molecular weight and large molecular volume of the bulky cation. The temperature dependence was also fitted using the Vogel–Fulcher–Tammann (VFT) approximation ($\eta = \eta_0 \exp[DT_0/(T-T_0)]$),[12] where T_0 and D are the ideal glass-transition temperature and the degree of deviation from Arrhenius behavior, respectively (Fig. S1, ESI†). The best-fit parameters of the fitting were T_0 = 139.5 K (= −133.7 °C) and D = 25.4.

Thermal properties

Thermal properties of [**1**]Tf_2N–[**3**]Tf_2N were investigated by differential scanning calorimetry (DSC). Values of the melting point (T_m) and glass-transition temperature (T_g) of these salts are listed in Table 1. DSC traces of the salts are shown in Fig. S2 (ESI†). [**1**]Tf_2N did not crystallize upon cooling and showed a glass transition at –31 °C. The solid of [**2**]Tf_2N melted at 71.3 °C on heating, and the liquid showed only a glass transition at –16 °C on cooling. [**3**]Tf_2N melted at 108.4 °C, and on cooling the melt, partial crystallization occurred at around 75 °C and the residual liquid underwent a glass transition at 16 °C (Fig. S2c). The values of T_g/T_m were 0.75 ([**2**]Tf_2N) and 0.76 ([**3**]Tf_2N), which are larger than those predicted by the empirical relationship for molecular and ionic liquids (T_g/T_m = 0.67).[13] The melting point of [Cu(Me_6tren)Cl]Tf_2N was 198 °C.

[**2**]Tf_2N and [**3**]Tf_2N exhibited phase transitions in the solid state at –95.8 °C ($\Delta S = 1.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$) and –15.9 °C ($\Delta S = 1.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$), respectively. These small transition entropies indicate that structural changes at these transitions are only slight. Indeed, no structural change was detected for [**3**]Tf_2N by X-ray crystallography.

Table 1 Values of the melting point (T_m), melting enthalpy (ΔH_m), melting entropy (ΔS_m), and glass-transition temperature (T_g) of the salts prepared in this study.

Compound	T_m / °C	ΔH_m / kJ mol^{-1}	ΔS_m / J K^{-1} mol^{-1}	T_g / °C
[**1**]Tf_2N	–	–	–	–31
[**2**]Tf_2N	71.3	14.1	40.0	–16
[**3**]Tf_2N	108.4	28.5	74.3	16
[Cu(Me_6tren)Cl]Tf_2N	198 [a]			

[a] Observed under a microscope.

Crystal structures

Crystal structures of [**2**]PF_6, [**3**]Tf_2N, and [Cu(Me_6tren)Cl]Tf_2N were determined at 100 K. Molecular structures of the cations in [**2**]PF_6 and [**3**]Tf_2N are shown in Fig. 2. In [**3**]Tf_2N, the two dimethylaminoethyl groups in the cation were disordered over two sites. In [**3**]Tf_2N and [Cu(Me_6tren)Cl]Tf_2N, the anions adopted the transoid conformation, as often found in salts with Tf_2N.[14] The central nitrogen and oxygen atoms and the terminal trifluoromethyl groups were disordered over two sites (Fig. S3 in the ESI†).

Five-coordinate complexes usually adopt trigonal bipyramidal, square pyramidal, or intermediate coordination geometries.[15] The structural parameter $\tau = (\beta - \alpha)/60$, where α and β are the first and the second largest coordination angles, is an indicator of the geometry[16]; τ is equal to zero for a perfectly square pyramidal geometry, while it is unity for a perfectly trigonal bipyramidal geometry. The coordination geometry of [**2**]PF_6 was nearly square pyramidal (τ = 0.31), exhibiting a large N_{NMe2}–Cu–N_{NMe2} angle (154.3°). [**3**]Tf_2N exhibited a distorted trigonal bipyramidal geometry (τ = 0.72). The coordination geometry in [Cu(Me_6tren)Cl]Tf_2N was trigonal bipyramidal (τ = 0.98), probably because of the high ligand symmetry. These results are consistent with the general tendency of symmetric tripodal ligands having the same three ligating units to produce trigonal bipyramidal complexes ($\tau \approx 1$),[7b,8d-e,17] and the tendency of asymmetric ligands to produce complexes closer to square pyramidal geometries ($\tau < 0.4$).[18] Packing effects may also be responsible for the distorted structures in [**2**]PF_6 and [**3**]Tf_2N.

The Cu–N bond lengths in [**3**]Tf_2N (Cu–N_{apical} = 2.08 Å, Cu–$N_{imidazole}$ = 2.00 Å, Cu–N_{NMe2} = 2.14 and 2.27 Å) and those in [**2**]PF_6 (Cu–$N_{imidazole}$ = 2.15 Å, Cu–N_{amine} = 2.11, 2.07, and 2.06 Å) are comparable to those in typical trigonal bipyramidal copper(II) complexes[7b,8d-e,17,19] and tetragonal copper(II) complexes[17] with similar τ values, respectively. In the latter salt, the Cu–$N_{imidazole}$ bond involving the axial nitrogen is longer than the Cu–N_{amine} bond.

Crystal structures of [**2**]PF_6 and [**3**]Tf_2N were also determined at 298 K, but no significant differences were observed compared with those at 100 K.

UV–vis–NIR spectra

The UV–vis–NIR absorption spectrum of [**1**]Tf_2N in the liquid state and those of [**2**]Tf_2N, [**3**]Tf_2N, and [**2**]PF_6 in the solid state were measured to obtain information on their coordination structures. All of the complexes exhibited an intense peak at around 300 nm and two broad peaks at around 740 and 940 nm (Fig. 3 and Table S1 in the ESI†). The former peak is assigned to the ligand-to-metal charge transfer transition,[20] whereas the latter peaks are ascribed to the d–d transitions.[8b–c,16–18a] It is reasonable that d–d transitions in [**1**]Tf_2N–[**3**]Tf_2N were observed between those in [Cu(Me_6tren)Cl]Cl (725 and 926 nm) and [Cu(tris((1-methylimidazol-2-yl)methyl)amine)Cl]PF_6 (830 and 1123 nm). The relative intensities of the two d–d transition peaks reflect the coordination geometries of the five-coordinate copper(II) complexes.[16–18a] The comparable peak heights observed for [**2**]PF_6 suggest that it had a square-pyramidal geometry, whereas the stronger peaks at around 940 nm in [**1**]Tf_2N–[**3**]Tf_2N suggest that they had trigonal bipyramidal geometries. The molecular structures determined crystallographically for [**2**]PF_6 and [**3**]Tf_2N, shown above, are fully consistent with these spectral features.

3. Conclusion

To develop metal-containing ILs with tripodal ligands, we designed alkylimidazole-containing tetradentate ligands and prepared their copper(II) complexes. The Tf_2N salts with hexyl and propyl substituents in the ligands were ILs with high viscosity at room temperature. The coordination structures of the crystalline complexes were found to be consistent with the UV–vis–NIR absorption spectra. Although we used only Cu^{II} ions in this study, preparation of related ILs with various metal ions is currently underway in our laboratory.

4. Experimental

General

Bis(2-dimethylaminoethyl)amine,[21] [Cu(Me_6tren)Cl]ClO_4,[7b] and 1-propylimidazole-2-carbaldehyde[22] were synthesized according to procedures described in the literature. 1-Hexylimidazole-2-carbaldehyde was synthesized similarly to 1-propylimidazole-2-carbaldehyde, using formylimidazole and iodohexane (ESI†). Other reagents were commercially available. ^1H NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Elemental analyses were performed using a Yanaco CHN MT5 analyzer. DSC measurements were performed in the temperature range –160 to 130 °C at a rate of 10 K min^{-1}, using a TA Instrument Q100 calorimeter. Infrared spectra were recorded using KBr plates analyzed on a Thermo Nicolet Avatar 360 spectrometer. UV–vis–NIR absorption spectra of the neat IL and crystalline salts as KBr pellets were measured on a JASCO V-570 UV/VIS/NIR spectrometer equipped with an integrating sphere (ISM–470). The viscosity was measured under a nitrogen atmosphere using a Toki Sangyo TV-22 viscometer with a 3° × R7.7 cone rotor, in the temperature range 10–50 °C.

Preparation of ligands

(a) Bis(2-dimethylaminoethyl)-((1-hexylimidazol-2-yl)methyl)amine (**L^1**). Under a nitrogen atmosphere, 1-hexylimidazole-2-carboxaldehyde (0.71 g, 3.94 mmol) was added dropwise to a solution of bis(2-dimethylaminoethyl)amine (0.620 g, 3.94 mmol) and $NaBH(OAc)_3$ (1.22 g, 5.75 mmol) in dichloromethane (50 mL). The reaction mixture turned into a pale brown suspension and evolved gas. The suspension was stirred for 24 h at 50 °C, and then cooled to room temperature. A saturated aqueous solution of NaOH was added to the cooled suspension. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The organic phase and the extract were combined, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was dissolved in concentrated hydrochloric acid (10 mL) and washed with dichloromethane. The aqueous phase was basified by adding small portions of NaOH, and then extracted with diethyl ether. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The product was obtained as a yellow oil (0.471 g, yield 37%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.89 (t, 3H, J = 6.8 Hz), 1.21 (br, 6H), 1.72 (m, 2H), 2.20 (s, 12H), 2.34 (t, 4H, J = 7.2 Hz), 2.60 (t, 4H, J = 7.2 Hz), 3.73 (s, 2H), 4.04 (t, 2H, J = 7.6 Hz), 6.86 (d, 1H, J = 1.2 Hz), 6.91 (d, 1H, J = 1.6 Hz).

(b) Bis(2-dimethylaminoethyl)-((1-propylimidazol-2-yl)methyl)amine (**L^2**). This ligand was prepared

as described for **L^1**, using 1-propylimidazole-2-carboxaldehyde (0.48 g, 3.47 mmol) instead of 1-hexylimidazole-2-carboxaldehyde. The product was obtained as a yellow oil (0.278 g, yield 29%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.94 (t, 3H, J = 6.8 Hz), 1.79 (m, 2H), 2.17 (s, 12H), 2.35 (t, 4H, J = 7.2 Hz), 2.60 (t, 4H, J = 7.2 Hz), 3.74 (s, 2H), 4.04 (t, 2H, J = 7.2 Hz), 6.86 (d, 1H, J = 1.2 Hz), 6.92 (d, 1H, J = 1.6 Hz).

*(c) Bis(2-dimethylaminoethyl)-((1-methylimidazol-2-yl)methyl)amine (**L^3**).* This ligand was prepared as described for **L^1**, using 1-methylimidazole-2-carboxaldehyde (0.67 g, 4.25 mmol) instead of 1-hexylimidazole-2-carboxaldehyde. The reaction mixture was stirred for 35 h at 50 °C, and then a saturated aqueous solution of $NaHCO_3$ was added to quench the reaction. The product was obtained as a yellow oil (0.22 g, yield 23%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.23 (s, 12H), 2.43 (t, 4H, J = 6.8 Hz), 2.67 (t, 4H, J = 7.0 Hz), 3.71 (s, 3H), 3.76 (s, 2H), 6.84 (d, 1H, J = 1.2 Hz), 6.90 (d, 1H, J = 0.8 Hz).

Preparation of copper(II) complexes

*(a) [Cu(**L^1**)Cl]Tf_2N ([**1**]Tf_2N).* An aqueous solution (2 mL) of $CuCl_2 \cdot 2H_2O$ (48 mg, 0.28 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (105 mg, 0.28 mmol) was added to a solution of **L^1** (165 mg, 0.50 mmol) in methanol (2 mL), and the reaction mixture was stirred for 5 min. Methanol (5 mL) and $LiTf_2N$ (0.20 g, 0.75 mmol) were then added successively to the solution and the resulting mixture was stirred for 15 min. The reaction mixture was then concentrated under reduced pressure, and the obtained crude product was dissolved in dichloromethane and washed with water. When an emulsion was formed, brine was added to the solution and the mixture was allowed to stand for a few minutes. The organic phase was separated, dried over magnesium sulfate, and concentrated under reduced pressure. The residual liquid was dissolved in methanol and washed repeatedly with hexane. The methanol phase was separated, concentrated under reduced pressure, and washed repeatedly with diethyl ether. The obtained liquid was dried under vacuum at room temperature, and then dried by repeated

freeze–pump–thaw cycles to completely remove residual solvents. The product was obtained as a viscous turquoise-blue liquid (366 mg, yield 63%). Anal. Calcd. for $C_{20}H_{37}ClCuF_6N_6O_4S_2$ (702.66): C, 34.19; H, 5.31; N, 11.96. Found: C, 34.39; H, 5.33; N, 11.88. The color of the product changed from turquoise-blue to green when stored for over a week at room temperature under a nitrogen atmosphere. The IR and UV spectra and elemental analysis results were identical before and after this change. The reason for this change is unknown but it may be ascribed to a change in the coordination environment or partial elimination of the axial chloride ligands in the cation.

*(b) [Cu(**L**^{2})Cl]Tf$_2$N ([**2**]Tf$_2$N).* This salt was prepared as described for [**1**]Tf$_2$N, using **L**$^{\mathbf{2}}$. The product was obtained as a viscous green liquid, which solidified over several weeks at room temperature under a nitrogen atmosphere. The product was obtained as a green solid (140 mg, yield 42%). Anal. Calcd. for $C_{17}H_{31}ClCuF_6N_6O_4S_2$ (660.59): C, 30.91; H, 4.73; N, 12.72. Found: C, 30.93; H, 4.71; N, 12.68.

*(c) [Cu(**L**^{3})Cl]Tf$_2$N ([**3**]Tf$_2$N).* This salt was prepared as described for [**1**]Tf$_2$N, using **L**$^{\mathbf{3}}$. The product was obtained as a viscous green liquid, which was recrystallized by slow diffusion of diethyl ether into an acetone solution of the crude product. Turquoise-blue prismatic crystals were obtained (7 mg, yield 17%), together with green solids. Anal. Calcd. for $C_{15}H_{27}ClCuF_6N_6O_4S_2$ (632.53): C, 28.48; H, 4.30; N, 13.29. Found: C, 28.42; H, 4.25; N, 13.26.

*(d) [Cu(**L**^{2})Cl]PF$_6$ ([**2**]PF$_6$).* An aqueous solution (2 mL) of $CuCl_2{\cdot}2H_2O$ (86 mg, 0.47 mmol) and an aqueous solution (5 mL) of KPF_6 (110 mg, 0.60 mmol) were successively added to **L**$^{\mathbf{2}}$ (130 mg, 0.46 mmol), and the reaction mixture was stirred for 30 min. The resultant mixture was extracted with dichloromethane, and the organic phase was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The residual turquoise-blue liquid was recrystallized by slow diffusion of diethyl ether and hexane into an acetone solution. The product was obtained as light-blue block crystals (87.8 mg, yield 36%). Anal. Calcd. for $C_{15}H_{31}ClCuF_6N_5P$ (525.40): C, 34.29; H, 5.95; N, 13.33. Found: C, 33.17; H, 5.76; N, 12.87.

(e) [Cu(Me$_6$tren)Cl]Tf$_2$N. LiTf$_2$N (72 mg, 0.25 mmol) was added to an aqueous solution (7 mL) of [Cu(Me$_6$tren)Cl]ClO$_4$ (71 mg, 0.17 mmol) under stirring, and the solution was further stirred for 5 min. The reaction mixture was then extracted with dichloromethane and the organic phase was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The obtained light-green powder was recrystallized by slow diffusion of diethyl ether and hexane into an acetone solution. The product was obtained as light-green plate crystals (43 mg, yield 42%). Anal. Calcd. for $C_{14}H_{30}ClCuF_6N_5O_4S_2$ (609.54): C, 27.61; H, 4.99; N, 11.52. Found: C, 27.59; H, 4.96; N, 11.49.

X-ray structure determination

Single crystals of [**2**]PF$_6$, [**3**]Tf$_2$N, and [Cu(Me$_6$tren)Cl]Tf$_2$N were obtained by slow diffusion of diethyl ether and hexane into a dichloromethane solution, ether into an acetone solution, and diethyl ether and hexane into an acetone solution, respectively. XRD data were collected on a Bruker APEX II Ultra CCD diffractometer at 100 K, using Mo Kα radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and analysis statistics for these compounds are listed in Table 2. All calculations were performed using SHELXL.[23] The nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted at calculated positions. Empirical absorption corrections (SADABS)[24] were applied. The packing diagrams were drawn using Ortep 3 for Windows.[25] CCDC 930374 ([**2**]PF$_6$), 930375 ([**3**]Tf$_2$N), and 930376 ([Cu(Me$_6$tren)Cl]Tf$_2$N) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2 Crystallographic parameters for [**2**]PF$_6$, [**3**]Tf$_2$N, and [Cu(Me$_6$tren)Cl]Tf$_2$N.

	[**2**]PF_6	[**3**]Tf_2N	[Cu(Me_6tren)Cl]Tf_2N
Empirical formula	$C_{15}H_{31}ClCuF_6N_5P$	$C_{15}H_{27}ClCuF_6N_6O_4S_2$	$C_{14}H_{30}ClCuF_6N_5O_4S_2$
Formula weight	525.41	632.54	609.54
Temperature / K	100	100	100
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P–1 (No. 2)	P–1 (No. 2)	$P2_1/c$ (No. 14)
a / Å	8.4294(14)	8.1069(14)	12.236(5)
b / Å	10.0642(16)	8.5666(15)	15.751(5)
c / Å	13.427(2)	20.655(4)	16.495(5)
α / °	102.327(2)	87.973(2)	
β / °	99.113(2)	79.639(2)	128.831(19)
γ / °	90.022(2)	63.172(2)	
Volume / $Å^3$	1098.1(3)	1257.5(4)	2476.5(15)
Z	2	2	4
d_{calcd} / g cm^{-3}	1.589	1.671	1.635
μ / mm^{-1}	1.251	1.220	1.234
Reflections collected	5303	5996	11662
Independent reflections	3803	4318	4375
Parameters	267	525	412
R_1^a, wR_2^b ($I > 2\sigma(I)$)	0.0229, 0.0584	0.0486, 0.1173	0.0610, 0.1482
R_1^a, wR_2^b (all data)	0.0244, 0.0596	0.0518, 0.1204	0.0687, 0.1511
Goodness-of-fit on F^2	1.037	1.031	1.050

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

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Notes and references

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†Electronic Supplementary Information (ESI) available: Preparation of 1-alkylimidazole-2-carbaldehyde; temperature dependence of the viscosity of [**1**]Tf_2N (Fig. S1); DSC traces of [**1**]Tf_2N, [**2**]Tf_2N, and [**3**]Tf_2N (Fig. S2); ORTEP drawings of the anions in [**3**]Tf_2N and [Cu(Me_6tren)Cl]Tf_2N (Fig. S3); and UV–vis–NIR absorption energies of [**1**]Tf_2N, [**2**]Tf_2N,

[**3**]Tf_2N, and [**2**]PF_6 (Table S1). See DOI: 10.1039/b000000x/

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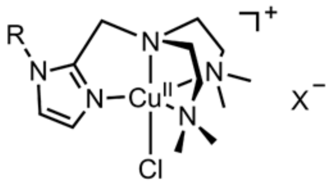

	R
[**1**]Tf$_2$N	hexyl
[**2**]Tf$_2$N	propyl
[**3**]Tf$_2$N	methyl
[**2**]PF$_6$	propyl

Fig. 1 Structural formulae of salts prepared in this study.

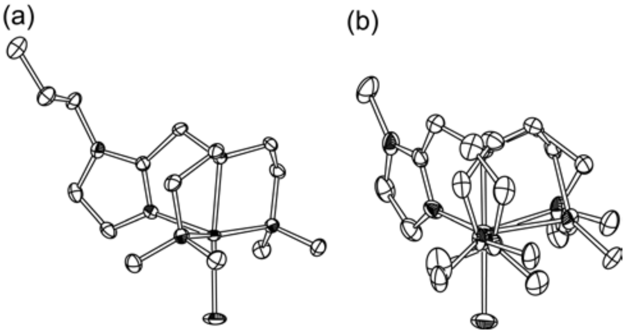

Fig. 2 ORTEP diagrams of the cations in (a) [**2**]PF$_6$ and (b) [**3**]Tf$_2$N. The dimethylaminoethyl moieties are disordered over two sites in (b).

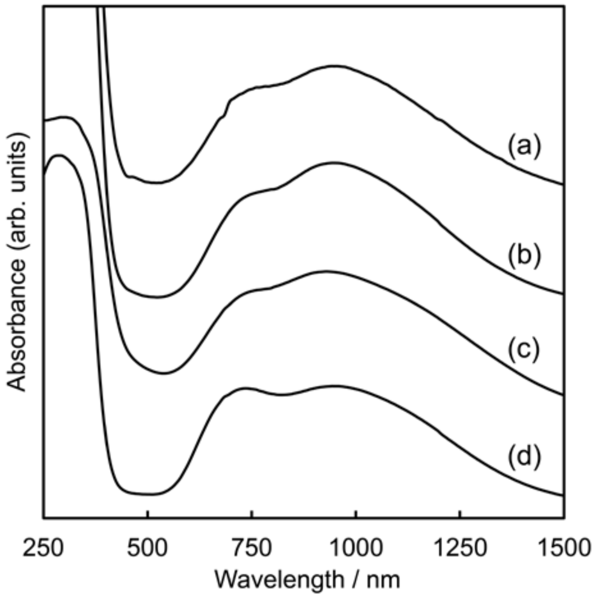

Fig. 3 UV–vis–NIR absorption spectra of (a) [**1**]Tf$_2$N in the liquid state, and (b) [**2**]Tf$_2$N, (c) [**3**]Tf$_2$N, and (d) [**2**]PF$_6$ in the solid state.

Electronic Supplementary Information

Ionic Liquids from Copper Complexes with Alkylimidazole-Containing Tripodal Ligands

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Preparation of 1-alkylimidazole-2-carbaldehyde

Under a nitrogen atmosphere, 1-iodohexane (1.53 mL, 10.4 mmol) was added to a mixture of formylimidazole (1.00 g, 10.4 mmol), K_2CO_3 (1.73 g, 12.5 mmol), and DMF (20 mL). The reaction mixture was stirred for 24 h at 50 °C, and then cooled to room temperature and filtered. The precipitate was dissolved in ethyl acetate and washed repeatedly with brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The residual yellow oil was dissolved in concentrated hydrochloric acid (10 mL) and washed with hexane. The aqueous phase was basified by addition of a saturated aqueous solution of NaOH, and then extracted with diethyl ether. The organic phase was dried over magnesium sulfate and concentrated under reduced pressure to give the desired product as a yellow oil (0.429 g, yield 12.3%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (m, 3H), 1.30 (m, 6H), 1.76 (m, 2H), 4.39 (t, 2H, J = 7.2 Hz), 7.15 (s, 1H), 7.29 (s, 1H), 9.81 (s, 1H).

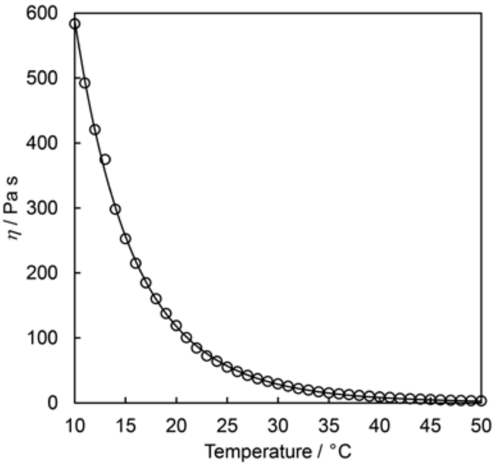

Fig. S1 Temperature dependence of the viscosity of [**1**]Tf_2N measured at 10–50 °C. Solid lines are the fitting curves using the VFT equation.

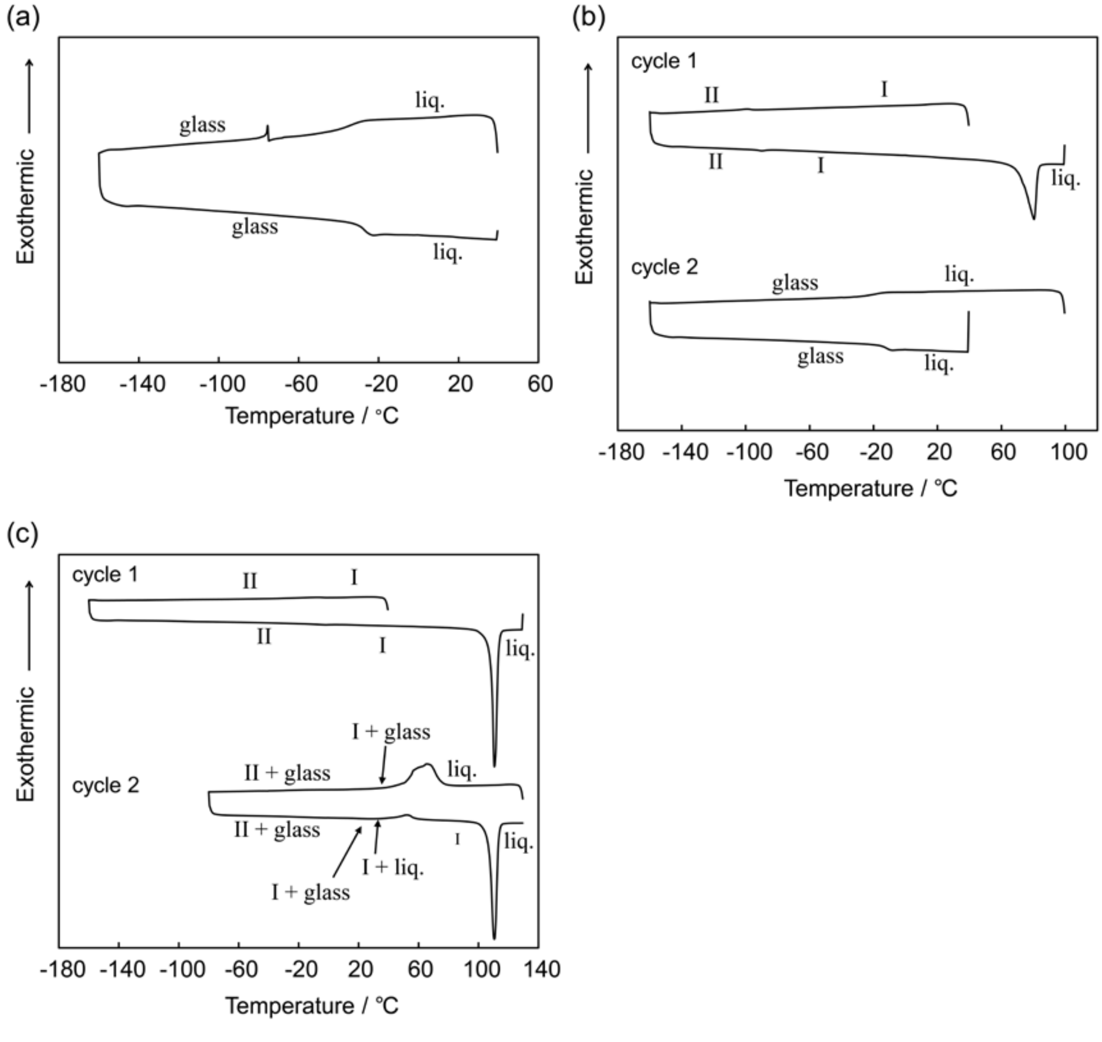

Fig. S2 DSC traces of (a) [**1**]Tf_2N, (b) [**2**]Tf_2N, and (c) [**3**]Tf_2N. The first and second cooling-heating cycles are shown in Figs. (b) and (c). I and II denote different crystal phases.

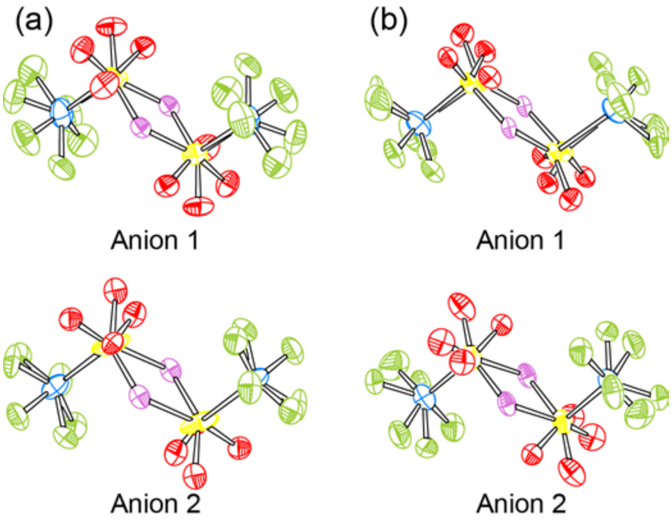

Fig. S3 ORTEP drawings of the anions in (a) [**3**]Tf_2N and (b) [Cu(Me_6tren)Cl]Tf_2N.

Table S1 Absorption maxima in the UV–vis–NIR spectra of [**1**]Tf_2N (liquid), [**2**]Tf_2N, [**3**]Tf_2N, and [**2**]PF_6 (solids).

	λ_{LMCT} / nm	$\lambda_{\mathrm{d–d}}$ / nm
[**1**]Tf_2N	302	743, 930
[**2**]Tf_2N	312	751, 944
[**3**]Tf_2N	289	735, 944
[**2**]PF_6	307	734, 943