

## Dicyanoaurate(I) Salts with 1-Alkyl-3-methylimidazolium: Luminescence Properties Room-temperature and Liquid Forming

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Experimental details of salts **1-5** and selected crystal data for **1** and **2** (4 pages).

### General.

FT-IR spectra for KBr pellets were recorded on a Perkin-Elmer 1000 Series spectrophotometer in the region of 400-4000  $\text{cm}^{-1}$ . Fluorescence excitation and emission spectra using a quartz tube of 2 mm diameter were recorded on a Shimadzu RF-5300PC luminescence spectrophotometer. Energy-dispersive X-ray spectroscopy (EDS) was carried out on a JEOL JSM-5510LVN Scanning Electron Microscope. Glass transition ( $T_g$ , onset of the heat capacity change), crystallization ( $T_c$ , onset of the exothermic peak) and melting ( $T_m$ , onset of the endothermic peak) temperatures were determined from differential scanning calorimetry (DSC) thermograms (10  $^{\circ}\text{C min}^{-1}$  cooling/heating rate) on a Shimadzu DSC-60 instrument equipped with liquid nitrogen cryostatic cooling, and the temperature was calibrated with water and indium. Decomposition temperature ( $T_d$ , 10% of weight loss) was determined by thermogravimetric analyses (TGA, 5  $^{\circ}\text{C min}^{-1}$  heating rate) on a Shimadzu DTG-60 instrument, and the temperature was calibrated by indium. Density values were obtained by measuring the weight of the sample in a 1  $\text{cm}^3$  pycnometer held in the glovebox. X-ray diffraction data were collected on an automatic four circle diffractometer (MacScience, MXC<sup>x</sup>) with graphite monochromated Mo  $K\alpha$  radiation. A single crystal was mounted and sealed in a glass capillary of 0.5 mm diameter in the glovebox. Crystal structure was solved by direct method (SIR92) and refined by the full matrix least-squares method on  $F^2$  (SHELXL-93). The position of the hydrogen atoms was determined assuming  $\text{sp}^2$  or  $\text{sp}^3$  configuration with a C-H distance of 1.0 Å.

### Materials.

Potassium dicyanoaurate(I)  $\text{K}[\text{Au}(\text{CN})_2]$  was purchased from Mitsuwa Chemicals (99.5%) and used without purification.  $[\text{HMI}]\text{Cl}$ <sup>1</sup> was synthesized by neutralization of distilled *N*-methylimidazole with aqueous hydrochloric acid (99.999%), and purified by reprecipitation from acetonitrile/ethyl acetate.  $[\text{EMI}]\text{Cl}$  and  $[\text{BMI}]\text{Cl}$  were purchased from Tokyo Kasei (>97%) and Fluka (>95%), respectively, and purified by reprecipitation from

acetonitrile/ethyl acetate according to the literature procedure.<sup>2</sup> [C<sub>6</sub>MI]Cl and [C<sub>8</sub>MI]Cl were synthesized using Menschkin reactions of *N*-methylimidazole with 1-chlorohexane and 1-chlorooctane, respectively, dried *in vacuo* at 80 °C for two days, and decolorized by active charcoal. Solvents (acetonitrile, ethyl acetate, acetone, dichloromethane and water) were distilled prior to use. All manipulations for the sample preparation were carried out under an inert atmosphere of helium gas in a glovebox.

### Synthesis of [HMI][Au(CN)<sub>2</sub>] (1).

A mixture of K[Au(CN)<sub>2</sub>] (0.85 g, 3.0 mmol) and [HMI]Cl (0.33 g, 2.8 mmol) in acetone (100 cm<sup>3</sup>) was stirred under dark at RT for three days. Filtration and evaporation of the filtrate afford colorless polycrystals. Rod-shaped single crystals suitable for X-ray study were obtained by slow cooling of the ethyl acetate solution (0.48 g, 52% yield). IR (KBr)  $\nu_{\max}$ : 3135m, 3099s, 3065vw, 3048w (C–H aromatic); 2966m, 2867m (C–H aliphatic); 2162vw, 2146s, 2105wv (CN) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$ : 4.13 (s, 3H, CH<sub>3</sub>), 7.75 (s, 1H, CH), 7.76 (s, 1H, CH), 9.10 (s, 1H, NCHN) ppm. Anal. Calcd for C<sub>6</sub>H<sub>7</sub>N<sub>4</sub>Au<sub>1</sub>: C, 21.70; H, 2.12; N, 16.87; Cl, 0.00%. Found: C, 21.45; H, 2.18; N, 16.88; Cl, 0.00%. No trace of Cl and K was detected for EDS.

### Synthesis of [EMI][Au(CN)<sub>2</sub>] (2).

Plate-shaped single crystals were prepared by the procedure described above for **1** except that [EMI]Cl were used instead of [HMI]Cl. Yield 1.04 g (83%). IR (KBr)  $\nu_{\max}$ : 3167s, 3147m, 3116s (C–H aromatic); 2983s, 2956m, 2938w (C–H aliphatic); 2134s, 2093w (CN) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.67 (t, 3H, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 4.07 (s, 3H, CH<sub>3</sub>), 4.36 (q, 2H, *J* = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 7.33 (s, 1H, CH), 7.36 (s, 1H, CH), 8.97 (s, 1H, NCHN) ppm. Anal. Calcd for C<sub>8</sub>H<sub>11</sub>N<sub>4</sub>Au<sub>1</sub>: C, 26.68; H, 3.08; N, 15.56; Cl, 0.00%. Found: C, 26.51; H, 3.04; N, 15.66; Cl, 0.00%. No trace of Cl and K was detected for EDS.

### Synthesis of [BMI][Au(CN)<sub>2</sub>] (3).

A mixture of K[Au(CN)<sub>2</sub>] (3.0 g, 10 mmol) and [BMI]Cl (1.7 g, 9.9 mmol) in acetone (150 cm<sup>3</sup>) was stirred under dark at RT for three days. Filtration and evaporation of the filtrate afford translucent liquid including a small amount of chloride (<1 wt%), which was removed by washing with acetone (2×30 cm<sup>3</sup>). The resulting liquid was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) and washed with water (5×30 cm<sup>3</sup>). The organic layer was

collected, dried over anhydrous  $\text{MgSO}_4$ , and evaporated *in vacuo* to yield pale yellow viscous liquid (3.03 g, 79% yield). IR (KBr)  $\nu_{\text{max}}$ : 3151m, 3109m (C–H aromatic); 2960s, 2933w, 2873m (C–H aliphatic); 2140s, 2101vw (CN)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.95 (t,  $J = 7.6$  Hz, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.41 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.93 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.10 (s, 3H,  $\text{CH}_3$ ), 4.39 (t, 2H,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 7.74 (s, 1H, CH), 7.80 (s, 1H, CH), 9.10 (s, 1H, NCHN) ppm. Anal. Calcd for  $\text{C}_{10}\text{H}_{15}\text{N}_4\text{Au}_1$ : C, 30.94; H, 3.89; N, 14.43; Cl, 0.00%. Found: C, 30.67; H, 3.70; N, 14.51; Cl, 0.00%. No trace of Cl and K was detected for EDS.

#### Synthesis of $[\text{C}_6\text{MI}][\text{Au}(\text{CN})_2]$ (4).

Pale yellow viscous liquid was prepared by the procedure described above for **3** except that  $[\text{C}_6\text{MI}]\text{Cl}$  were used instead of  $[\text{BMI}]\text{Cl}$ . Yield 2.75 g (68%). IR (KBr)  $\nu_{\text{max}}$ : 3151m, 3109m (C–H aromatic); 2956m, 2930s, 2859s (C–H aliphatic); 2156w, 2141s, 2101vw (CN)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.91 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 1.37 (m, 6H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 1.95 (m, 2H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 4.04 (s, 3H,  $\text{CH}_3$ ), 4.26 (t,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ ), 7.41 (s, 1H, CH), 7.43 (s, 1H, CH), 8.97 (s, NCHN) ppm. Anal. Calcd for  $\text{C}_{12}\text{H}_{19}\text{N}_4\text{Au}_1$ : C, 34.62; H, 4.60; N, 13.46; Cl, 0.00%. Found: C, 34.52; H, 4.58; N, 13.41; Cl, 0.00%. No trace of Cl and K was detected for EDS.

#### Synthesis of $[\text{C}_8\text{MI}][\text{Au}(\text{CN})_2]$ (5).

Pale yellow liquid was prepared by the procedure described above for **3** except that  $[\text{C}_8\text{MI}]\text{Cl}$  were used instead of  $[\text{BMI}]\text{Cl}$ . Yield 3.28 g (75%). IR (KBr)  $\nu_{\text{max}}$ : 3151m, 3109m (C–H aromatic); 2955w, 2927s, 2856s (C–H aliphatic); 2141s, 2101vw (CN)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.89 (t, 3H,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 1.33 (m, 10H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 1.94 (m, 2H,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 4.05 (s, 3H,  $\text{CH}_3$ ), 4.25 (t,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$ ), 7.38 (s, 1H, CH), 7.41 (s, 1H, CH), 8.97 (s, NCHN) ppm. Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{N}_4\text{Au}_1$ : C, 37.84; H, 5.22; N, 12.61; Cl, 0.00%. Found: C, 37.83; H, 5.25; N, 12.50; Cl, 0.00%. No trace of Cl and K was detected for EDS.

### Selected crystallographic data of 1 and 2.

compound	[HMI][Au(CN) <sub>2</sub> ] (1)	[EMI][Au(CN) <sub>2</sub> ] (2)
empirical formula	C <sub>6</sub> H <sub>7</sub> N <sub>4</sub> Au <sub>1</sub>	C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> Au <sub>1</sub>
formula weight	332.12	360.17
crystal system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	6.915(1)	8.370(2)
<i>b</i> , Å	7.014(2)	19.900(4)
<i>c</i> , Å	10.590(2)	6.672(2)
$\alpha$ , °	100.18(2)	90
$\beta$ , °	97.31(2)	107.84(2)
$\gamma$ , °	117.66(2)	90
<i>V</i> , Å <sup>3</sup>	434.7(2)	1057.9(4)
<i>Z</i>	2	4
<i>d</i> <sub>c</sub> , g cm <sup>-3</sup>	2.538	2.261
$\lambda$ , Å	0.71073	0.71073
$\mu$ , mm <sup>-1</sup>	16.9	13.8
criterion for obsd reflections	$F^2 \geq 4\sigma(F^2)$	$F^2 \geq 4\sigma(F^2)$
no. of intensity measd	1199	1387
no. of refined params	101	120
GOF on <i>F</i> <sup>2</sup>	1.450	1.207
<i>R</i>	0.056	0.043
<i>wR</i> (all data)	0.195	0.131

	[HMI][Au(CN) <sub>2</sub> ] (1)	[EMI][Au(CN) <sub>2</sub> ] (2)
	Distances / Å	
Au1–C11	1.984(21)	2.003(13)
Au1–C12	1.952(21)	1.996(14)
C11–N11	1.139(25)	1.124(15)
C12–N12	1.173(26)	1.127(15)
	Angles / °	
C11–Au1–C12	177.0(7)	178.4(5)
Au1–C11–N11	176.7(18)	176.0(12)
Au1–C12–N12	177.1(18)	178.9(13)

### References.

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