Synthesis and Structural Characterization of *N*,*N*′-Dialkylimidazolium Tetrachloroplatinate and Monoaquatrichloroplatinate Salts

Wanzhi Chen and Kazuko Matsumoto*

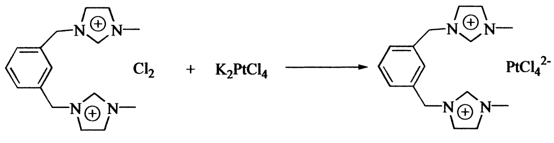
Department of Chemistry, School of Science and Engineering, Waseda University, and CREST, Japan Science and Technology Corp. (JST), Okubo, Shinjuku-ku, Tokyo 169-8555

(Received January 25, 2002)

N,*N*′-Dialkylimidazolium salts, $[m\text{-}C_6H_4(CH_2ImMe)_2][PtCl_4]$ (Im = imidazolium) (**1**) and $[Mes_2Im][PtCl_3(H_2O)]$ (Mes_2Im = *N*,*N*′-di(2,4,6-trimethylphenyl)imidazolium) (**2**), were prepared and characterized by X-ray diffraction. Compound **2** is the first structurally characterized aquatrichloroplatinate compound.

The synthesis of *N*,*N*′-dialkylimidazolium salts (ionic liquids) is currently an area of intense research activity.[1–3] *N*,*N*′-dialkylimidazolium salts can be used as non-aqueous ionic solvents for many catalytic organic processes.[1] A palladium/imidazolium salt system catalyzes dehalogenation of aryl halides,[4] and a palladium/phosphine-imidazolium system promotes highly efficient Heck reactions of aryl bromides with *n*-butyl acrylate, which have been reported very recently.[5] It has recently been demonstrated that ionic liquids are important alternatives to water as solvents for two-phase catalytic oligomerization, hydroformylation, and hydrogenation of olefins by transition metal complexes.[6] *N*,*N*′-Dialkylimidazolium salts containing transition-metal complexes, especially platinum group metal complexes, are of great interests regarding their potential catalytic applications. However, relatively few studies have been carried out on the use of ionic liquids for the synthesis and characterization of coordination complexes.[7]

We report here the synthesis and structural characterization of two novel *N*,*N*′-dialkylimidazolium chloroplatinate salts of the type $[m\text{-}C_6H_4(CH_2ImMe)_2][PtCl_4]$ (Im = imidazolium) (**1**) and $[Mes_2Im][PtCl_3(H_2O)]$ (Mes_2Im = *N*,*N*′-di(2,4,6-trimethylphenyl)imidazolium) (**2**). Interestingly, compound **2** is a rare example of an aquaplatinum complex that is probably stabilized by the ionic liquid.

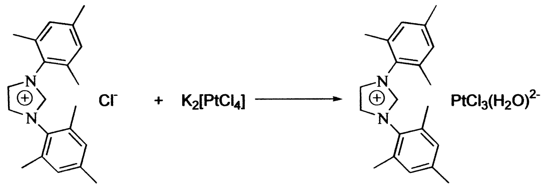


(1)

When the ionic liquid $[m\text{-}C_6H_4(CH_2ImMe)_2]Cl_2$ was treated with $K_2[PtCl_4]$ in water, a tetrachloroplatinate salt, $[m\text{-}C_6H_4(CH_2ImMe)_2][PtCl_4]$ (**1**), was immediately afforded quantitatively as red crystals. As expected, the complex consists of a $[PtCl_4]^{2-}$ and $[m\text{-}C_6H_4(CH_2ImMe)_2]^{2+}$ ionic pair (Eq. 1). The X-ray crystallography of **1** reveals that the square planar geometry of the Pt atom remains unchanged. The molecule has a crystallographic inversion center at the platinum atom, and thus the asymmetric unit contains a half molecule of $[m\text{-}C_6H_4(CH_2ImMe)_2][PtCl_4]$. The Pt–Cl bond distances (average 2.309 Å) are consistent with those of $[EMIM]_2[PtCl_4]$ (EMIM = *N*-ethyl-*N*′-methylimidazolium) (2.308 Å), which has been described most recently.[7]

The crystal packing is determined by the presence of several weak CH···Cl interactions, each Cl atom of the tetrachloroplatinates being involved in such interactions with H atoms of phenyl and imidazolate groups (Fig. 1(a)).

Under the same reaction conditions as for **1**, the reaction of $[Mes_2Im]Cl$ and $K_2[PtCl_4]$ in water led to the isolation of $[Mes_2Im][PtCl_3(H_2O)]$ (**2**) as red crystals quantitatively. Unexpectedly, one of the chloride atoms of $[PtCl_4]^{2-}$ is replaced by one molecule of water (Fig. 2). The coordination geometry of the platinum atom is thus regarded as a slightly distorted square plane. The Pt–Cl distances (average 2.287 Å) *cis* to water become shorter than those of **1**, and the Pt–Cl distance *trans* to water is much shorter, being 2.248(3) Å.



(2)

Platinum(II) is classified as a soft metal center which forms stable complexes with polarizable ligands.[8] It has long been known that $[PtCl_3(H_2O)]^-$ ion exists in aqueous solution (Eq. 2). The hydrolysis of $[PtCl_4]^{2-}$ is extensive at 25 °C, and thus a 10^{-3} M solution of $K_2[PtCl_4]$ contains only 5% of $[PtCl_4]^{2-}$ with 53% of mono- and 42% of diaqua species.[9] However, $[PtCl_3(H_2O)]^-$ compound has never been isolated and structurally characterized in the solid state. In contrast, $K[PtCl_3(C_2H_4)]$, Zeise salt,[10] is the most famous one, and $[PtCl_3(dmso)]^-$,[11] $[PtCl_3(amine)]^-$,[12] $[PtCl_3(NCR)]^-$ and $[PtCl_3\{HNC(OMe)R\}]^-$,[13] and $[PtCl_3(pyrimidine)]^{2-}$ [14] are all known. The $[Pt(H_2O)_4]^{2+}$ can be obtained by interaction of $K_2[PtCl_4]$ and $AgClO_4$ in water.[9]

Significantly, the crystal packing is governed by OH···Cl and CH···Cl interactions, i.e., the imidazolium cations are linked through hydrogen bonds with $[PtCl_3(H_2O)]^-$ (Fig. 1(b)). These interactions make hydrogen-bond networks between imidazolium cations and $[PtCl_3(H_2O)]^-$ ion in **2**. Obviously, the network structures are stabilized by these weak interactions.

Experimental

Preparation of 1. Addition of $K_2[PtCl_4]$ (100 mg, 0.24 mmol) in 2 mL of H_2O to a solution of $[m\text{-}C_6H_4(CH_2ImMe)_2]Cl_2$[15] in 3 mL of H_2O resulted in an immediate precipitation of a red sol-

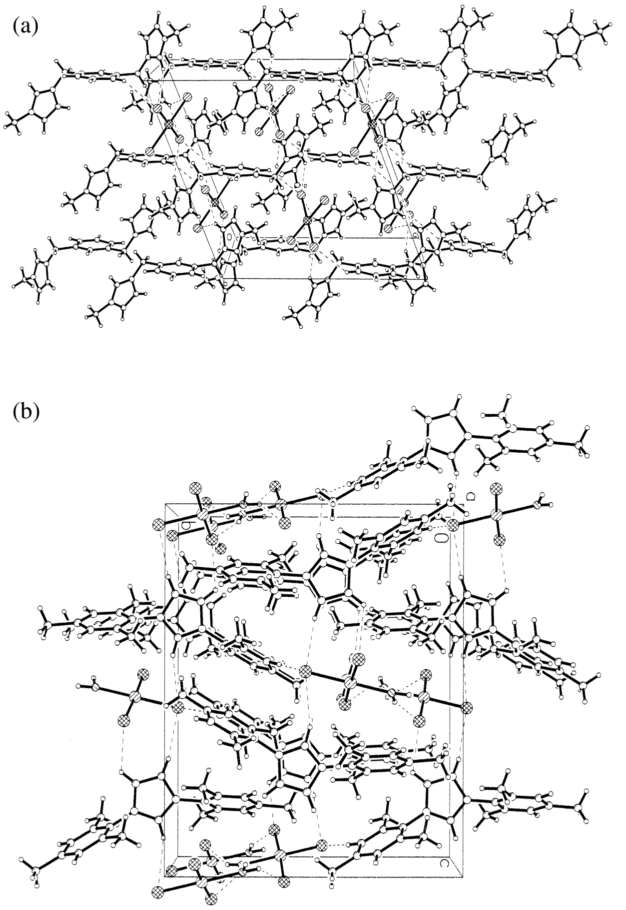


Fig. 1. Diagram of (a) **1** and (b) **2** showing the hydrogen bonding interactions between imidazolium cation and chloroplatinate anion.

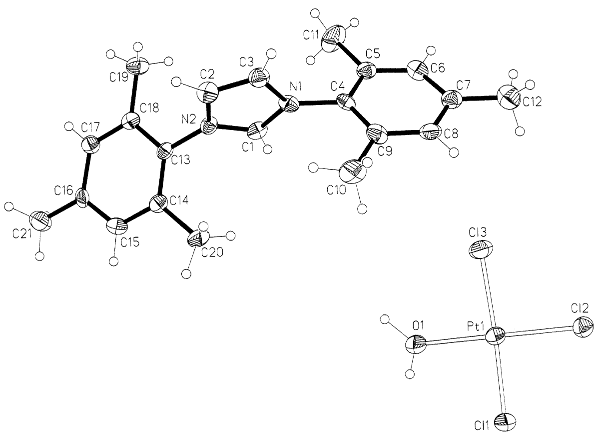


Fig. 2. Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability.

id. It was collected by filtration and washed with H_2O and acetone. Single crystals suitable for X-ray diffraction analysis were obtained by layering $K_2[PtCl_4]$ aqueous solution onto [*m*-$C_6H_4(CH_2ImMe)_2]Cl_2$ solution in water. Yield: (96.0%). Anal. Calcd for $C_{16}H_{20}Cl_4N_4Pt$: C, 31.75; H, 3.33; N, 9.26%. Found: C, 31.33; H, 3.14; N, 9.29%.

Preparation of 2. The compound was prepared as described for [*m*-$C_6H_4(CH_2ImMe)_2][PtCl_4]$ by using $[Mes_2Im]Cl$[16] instead of [*m*-$C_6H_4(CH_2ImMe)_2]Cl_2$. Single crystals suitable for X-ray diffraction analysis were obtained by layering $K_2[PtCl_4]$ aqueous solution onto $[Mes_2Im]Cl$ solution in water. Yield: 96.5%. Anal. Calcd for $C_{21}H_{27}Cl_3N_2OPt$: C, 40.36; H, 4.36; N, 4.48%. Found: C, 40.01; H, 4.48; N, 4.57%.

X-ray Structure Determination. The chosen crystals were covered with polyfluoroether, and mounted on a glass fiber. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at room temperature. Crystallographic data for **1**: $C_{16}H_{20}Cl_4N_4Pt$, fw = 605.25, monoclinic, *C*2/*c*, a = 14.4184(12) Å, b = 10.3160(9) Å, c = 13.8489(11) Å, β = 110.1720(10)°, V = 1933.5(3) Å^3, Z = 4, D_{calc} = 2.079 Mg/m^3, 5844 reflections collected, 2222 unique (R_{int} = 0.0478), goodness-of-fit 0.971. $R1$, $wR2$ [$I > 2\sigma(I)$] 0.0312, 0.0788; $R1$, $wR2$ (all data) 0.0453, 0.0842. For **2**: $C_{21}H_{27}Cl_3N_2OPt$, fw = 624.89, orthorhombic, $P2_12_12_1$, a = 8.5173(15) Å, b = 14.703(3) Å, c = 18.341(3) Å, V = 2296.8(7) Å^3, Z = 4, D_{calc} = 1.807 Mg/m^3, 13764 reflections collected, 5077 unique (R_{int} = 0.0777), goodness-of-fit 1.028. $R1$, $wR2$ [$I > 2\sigma(I)$] 0.0505, 0.1187; $R1$, $wR2$ (all data) 0.0658, 0.1243.

References

1 H. Olivier, *J. Mol. Catal.*, **146**, 285 (1999).

2 Recent reviews see: a) T. Walton, *Chem. Rev.*, **99**, 2071 (1999). b) D. Bourissou, O. Guerret, F. P. Gabbai, and G. Bertrand, *Chem. Rev.*, **100**, 39 (2000).

3 T. Weskamp, V. P. W. Böhm, and W. A. Hermann, *J. Organomet. Chem.*, **600**, 12 (2000).

4 M. S. Viciu, G. A. Grasa, and S. P. Nolan, *Organometallics*, **20**, 3607 (2001).

5 C. Yang, H. M. Lee, and S. P. Nolan, *Org. Lett.*, **3**, 1511 (2001).

6 J. E. L. Dulius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, and A. De Cian, *Organometallics*, **17**, 815 (1998).

7 M. Hasan, I. V. Kozhevnikov, M. Rafiq, H. Siddiqui, C. Femoni, A. Steiner, and N. Winterton, *Inorg. Chem.*, **40**, 795 (2001).

8 D. M. Roundhill, in "Comprehensive Coordination Chemistry," ed by. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon (1987), Vol. 5, p. 353.

9 F. A. Cotton, G. Wilkinson, C. A. Murrillo, and M. Bochmann, "Advanced Inorganic Chemistry," 6th ed, Wiley-Interscience (1999), p. 1071.

10 D. Seyferth, *Organometallics*, **20**, 2 (2001).

11 a) Y. N. Kykushikin, Y. E. Vyazmenski, and L. I. Zorina, *Russ. J. Inorg. Chem.* (Engl. Trans), **13**, 1573 (1968). b) R. Melanson and F. D. Rochon, *Can. J. Chem.*, **53**, 2371 (1975).

12 L. Nguyen, J. Kozelka, and C. Bois, *Inorg. Chim. Acta*, **190**, 217 (1991).

13 R. Cini, P. A. Caputo, F. P. Intini, and G. Natile, *Inorg. Chem.*, **34**, 1130 (1995).

14 N. Nédélec and F. D. Rochon, *Inorg. Chem.*, **40**, 5236 (2001).

15 W. Chen, K. Matsumoto, *J. Organomet. Chem.*, in press.

16 L. Jafarpour, E. D. Stevens, and S. P. Nolan, *J. Organomet. Chem.*, **606**, 49 (2000).