A New Water-soluble and Acid-stable Dinuclear Organoiridium Dinitrate Complex

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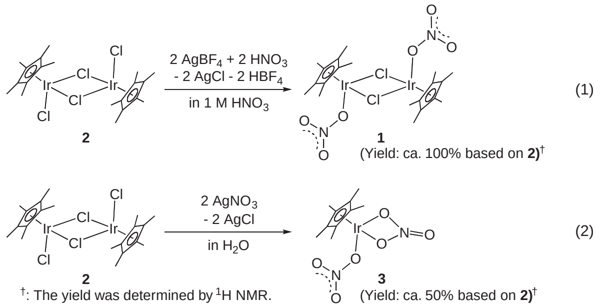
A new water-soluble and acid-stable dinuclear organoiridium(III) dinitrate complex $[\{Cp^*Ir(NO_3)\}_2(\mu\text{-}Cl)_2]$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) was synthesized by the reaction of a water-insoluble organoiridium(III) complex $[(Cp^*IrCl)_2(\mu\text{-}Cl)_2]$ (**2**) with two equivalents of $AgBF_4$ in aqueous nitric acid (1 M HNO_3/H_2O) at 23 °C for 12 h. The structure of **1** with two monodentate NO_3^- ligands is discussed in comparison with structure of a mononuclear organoiridium(III) complex with one monodentate and one bidentate NO_3^- ligands, $[Cp^*Ir(NO_3)_2]$ (**3**).

Reactions catalyzed by water-soluble organometallic complexes in water are undergoing very rapid growth because of many potential advantages such as alleviation of environmental problems associated with the use of organic solvents and reaction-specific pH selectivity.[1,2] Development of organometallic catalysts to be used in water under acidic or basic conditions is a worthy endeavor. We previously reported a water-soluble and acid-stable "mononuclear" organoiridium(III) dinitrate complex (with one monodentate and one bidentate NO_3^- ligands), $[Cp^*Ir^{III}(NO_3)_2]$ (**3**, $Cp^* = \eta^5\text{-}C_5Me_5$),[2] whose structure was determined by X-ray analysis.[2,3] However, the corresponding water-soluble and acid-stable "dinuclear" organoiridium(III) dinitrate complex has yet to be reported.

We report herein synthesis and structure of a water-soluble dinuclear organoiridium(III) dinitrate complex (with two monodentate NO_3^- ligands), $[\{Cp^*Ir^{III}(NO_3)\}_2(\mu\text{-}Cl)_2]$ (**1**), which is stable in aqueous nitric acid (1 M HNO_3/H_2O). Complex **1** was synthesized by the reaction of a well-known water-insoluble organoiridium(III) complex $[(Cp^*Ir^{III}Cl)_2(\mu\text{-}Cl)_2]$ (**2**) with two equivalents of $AgBF_4$ in 1 M HNO_3/H_2O. The structure of **1** was determined by X-ray analysis, IR, and ^1H NMR spectroscopy, and electrospray ionization mass spectrometry (ESI-MS). The NO_3^- ligands of **1** and **3** could serve as water-soluble ligands,[2,4,5] which were isotopically labeled by $N^{18}O_3^-$ (50% ^{18}O), and were characterized by IR spectroscopy.

Complex **2** was prepared by the method described in the literature.[6] To a suspension of the water-insoluble **2** in 1 M HNO_3/H_2O was added two equivalents of $AgBF_4$ at 23 °C. The mixture was stirred for 12 h giving a pale yellow solution and a precipitate of AgCl, which was removed by filtration. On evaporation of the solvent, a dark yellow powder of **1** was obtained at about 100% yield based on **2** (determined by ^1H NMR, eq 1). In contrast to **2**, complex **1** is soluble in water (6.5 mg/10 mL at pH 3 at 23 °C) and acid-stable (below 1 M HNO_3/H_2O). The reaction of **2** with two equivalents $AgNO_3$ in H_2O, however, gave **3** at about 50% yield based on **2** (determined by ^1H NMR, eq 2). The use with a little $AgNO_3$ in eq 2 causes the fall of the yield of the product of **3**. It should be noted that no reaction between **2** and aqueous nitric acid (1 M HNO_3/H_2O) has occurred in the absence of the silver salt.



†: The yield was determined by ^1H NMR.

Complex **1** was successfully crystallized from a 1 M HNO_3/H_2O solution of **1**.[7] The structure of **1** was determined by X-ray analysis as shown in Figure 1. Complex **1** has a dinuclear framework with a crystallographic inversion center. Ir atom adopts distorted-octahedral coordination which is surrounded by one Cp^*, one NO_3^- ligand with a monodentate fashion, and two bridging Cl^- ligands. All bond lengths between Ir atom and carbons of the Cp^* ring of **1** in the solid state are within 2.126–2.141 Å. A similar framework is found in a dinuclear organorhodium(III) nitrate complex $[\{Cp^*Rh^{III}(NO_3)\}_2(\mu\text{-}Cl)_2]$ (**4**), whose structure was previously determined by X-ray analysis.[8] Ir···Ir distance {3.6428(4) Å} in **1** is slightly longer than Rh···Rh distance {3.590(4) Å} in **4**. The Ir–O bond length {2.112(3) Å} of **1** for monodentate coordination mode is shorter than that (average 2.1745 Å) of **3** for bidentate coordination modes.[2]

It is known that the monodentate NO_3^- ligand exhibits characteristic three stretching bands, i.e., asymmetric stretching vibration $\nu_a(NO_2)$ in the range of ca. 1410–1570 cm^{-1}, symmetric stretching vibration $\nu_s(NO_2)$ at ca. 1250–1320 cm^{-1}, and

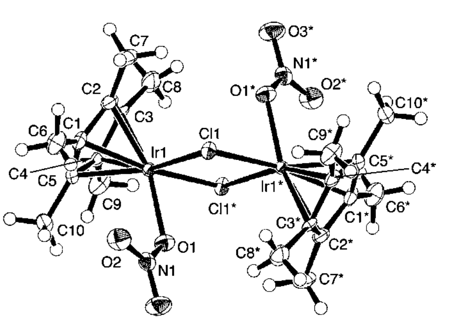


Figure 1. An ORTEP drawing of **1**. Selected interatomic distances (l/Å) and angles (ϕ/deg): Ir1–C1 = 2.141(4), Ir1–C2 = 2.136(4), Ir1–C3 = 2.134(4), Ir1–C4 = 2.126(4), Ir1–C5 = 2.139(4), Ir1–Ir1* = 3.6428(4), Ir1–Cl1 = 2.430(1), Ir1–Cl1* = 2.439(1), Ir1–O1 = 2.112(3), O1–N1 = 1.253(5), O2–N1 = 1.237(5), O3–N1 = 1.268(5), Ir1–Cl1–Ir1* = 96.85(4), Cl1–Ir1–Cl1* = 83.15(4), Ir1–O1–N1 = 120.8(3).

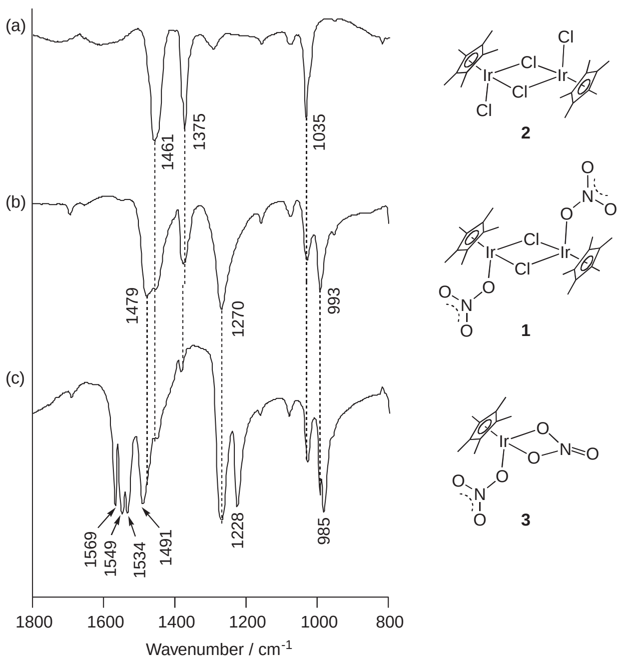


Figure 2. IR spectra in mineral oil of **2** (a), **1** (b), and **3** (c).

stretching vibration ν(NO) at ca. 920–1050 cm^{-1}.[9,10] The chelating bidentate NO_3^- ligand also exhibits characteristic stretching bands, i.e., ν(NO) at ca. 1440–1650 cm^{-1}, $\nu_a(NO_2)$ at ca. 1220–1350 cm^{-1}, and $\nu_s(NO_2)$ at ca. 970–1050 cm^{-1}.[9,11,12]

Figure 2 illustrates the IR spectra in mineral oil in the range of 800–1800 cm^{-1} of **2**, **1**, and **3**, whose structures are depicted to the right of each IR spectrum. These results indicate that the IR spectra of nitrate complexes could be used to distinguish between monodentate NO_3^- ligand and bidentate NO_3^- ligand. Figure S1a[13] shows the IR spectrum in mineral oil in the range of 800–1800 cm^{-1} of **1** with $N^{16}O_3^-$ ligands. The peaks at 1479, 1270, and 993 cm^{-1} were assigned to $\nu_a(NO_2)$, $\nu_s(NO_2)$, and ν(NO), respectively. This assignment is made by isotopic substitution of $N^{18}O_3^-$ (50% ^{18}O) for $N^{16}O_3^-$, which results in the predicted isotope shift to 1466, 1258 (and 1247), and 980 cm^{-1}, respectively (Figure S1b).[13] Figure S2[13] shows the IR spectra in mineral oil in the range of 800–1800 cm^{-1} of $N^{16}O_3^-$ and $N^{18}O_3^-$ (50% ^{18}O) derivatives of **3**. In Figure S2a,[13] the peaks at 1491–1569 cm^{-1} were assigned to ν(NO). They shift to 1483–1562 cm^{-1} by isotopic substitution of $N^{18}O_3^-$ (50% ^{18}O) for $N^{16}O_3^-$ (Figure S2b).[13] The peaks at 1228 and 985 cm^{-1} in Figure S2a[13] were assigned to $\nu_a(NO_2)$ and $\nu_s(NO_2)$, respectively, based on the respective shift to 1222 and 975 (and 953) cm^{-1} by isotopic substitution of $N^{18}O_3^-$ (50% ^{18}O) for $N^{16}O_3^-$. It is noteworthy that IR spectra of **1** and **3** of KBr disks (prepared by pressing KBr pellets) show the absorption of uncoordinating NO_3^- anions at 1384 cm^{-1}.[3,4,8,12] Therefore, we did not use KBr and performed the IR measurement with mineral oil.

Figure S3[13] shows ^{1}H NMR spectrum of **1** in 0.1 M DNO_3/D_2O (at pD 1). The signal at 1.62 ppm corresponds to the Cp* protons $\{C_5(CH_3)_5\}$ of **1**, which is different from the signal at 1.63 ppm of the Cp* protons of the mononuclear complex **3**. The positive-ion ESI mass spectrum of the same crystal used in the X-ray analysis of **1** in 0.1 M HNO_3/H_2O (100 μM, pH 1) shows the consistency with the formulation and the dinuclearity of **1**. A signal at m/z 788.0 {relative intensity (I) = 13% in the range of m/z 100–1000, Figure S4a[13]}, has a characteristic distribution of isotopomers (Figure S4b)[13] that matches well with the calculated isotopic distribution for $[\mathbf{1}-NO_3]^+$ (Figure S4c).[13]

In summary, we have synthesized and characterized a new water-soluble and acid-stable dinuclear organoiridium(III) dinitrate complex **1**, providing a candidate as a water-soluble and acid-stable catalyst in a variety of chemical transformations in water under acidic conditions, e.g., hydrogenation of aqueous nitric acid.

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7 Crystal data for **1**: $C_{20}H_{30}Cl_2Ir_2N_2O_6$, $M_r = 849.81$, monoclinic, space group $P2_1/n$ (No. 14), $a = 8.252(2)$ Å, $b = 10.500(2)$ Å, $c = 14.721(3)$ Å, $\beta = 103.668(2)°$, $V = 1239.4(4)$ Å^3, $Z = 2$, $D_{calcd} = 2.277$ g cm^{-3}, $T = 123$ K, $R1 = 0.027$, $R_w = 0.072$ based on 2808 reflections $\{I > 2.0\sigma(I)\}$ and 145 variable parameters. The crystal data for **1** have been deposited with the Cambridge Crystallographic Data Center as a supplementary publication No. CCDC-659583.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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