Crystal Structure of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}]^+$ (bpy = 2,2'-bipyridine) as a Key Intermediate in $\mathrm{CO_2}$/CO Conversion

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Molecular structure of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}]$ $(\mathrm{CF_3SO_3})(\mathrm{H_2O})$ (bpy = 2,2'-bipyridine) has revealed that protonation of $[\mathrm{Ru(\eta^1\text{-}CO_2)(bpy)_2(CO)}]$ as a key step in $\mathrm{CO_2}$/CO conversion shortens the Ru-C(O)OH bond distance compared with the Ru-$\mathrm{CO_2}$ one due to enhancement of dπ-pπ* interaction in the former.

Activation of $\mathrm{CO_2}$ on metal complexes is a subject of continuing importance in utilization of $\mathrm{CO_2}$ as C1 resources. The $\mathrm{CO_2}$/CO conversion under protic conditions is generally explained by an acid-base equilibrium among η^1-$\mathrm{CO_2}$, -C(O)OH and -CO metal complexes (eq 1), [1-6] and amphoteric reactivity of metal-C(O)OH complexes plays the key role in the smooth conversion from $\mathrm{CO_2}$ to CO on metals. The comparison of molecular structures of η^1-COOH and η^1-$\mathrm{CO_2}$ metal complexes, therefore, would serve to understand an enormous wide range of $\mathrm{p}K_\mathrm{a}$ values (from 2.5 to over 14) [2] of metal-C(O)OH complexes compared with those of organic carboxylic acids. As for the molecular structures of η^1-COOH and η^1-$\mathrm{CO_2}$ metal complexes, only *trans*-$[\mathrm{Pt(\eta^1\text{-}C(O)OH)(C_6H_5)(PEt_3)_2}]$, [7] $[\mathrm{Rh(\eta^1\text{-}CO_2)(Cl)(diars)_2}]$, [8] $[\mathrm{Co(salen)Na(\eta^1\text{-}CO_2)}]$, [9] and $[\mathrm{Ru(\eta^1\text{-}CO_2)(bpy)_2(CO)}]$ [10] have been determined by X-ray analysis. Although the molecular structure of $[\mathrm{Ru(bpy)_2(CO)(C(O)OCH_3)}]^+$ has been reported as a model of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}]^+$, [10] the comparison of the molecular structures of the latter with $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)}]$ would give more definitive knowledge concerning the unique equilibria among those two complexes and $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ in $\mathrm{H_2O}$ (eq. 1). [11]

$$[\mathrm{M{-}CO_2}]^{n+} \underset{\mathrm{OH^-}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{M{-}C(O)OH}]^{(n+1)+} \underset{\mathrm{OH^-}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{M{-}CO}]^{(n+2)+} \qquad (1)$$

Both $\mathrm{PF_6}$ and $\mathrm{BPh_4}$ salts of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}]^+$ are likely to disproportionate to $[\mathrm{Ru(bpy)_2(CO)_2}]^{2+}$ and $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)}]$ in solutions, which strongly hampered to grow single crystals of the hydroxycarbonyl complex. On the other hand, $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}](\mathrm{CF_3SO_3})$ obtained by a reaction of $[\mathrm{Ru(bpy)_2(CO)_2}](\mathrm{CF_3SO_3})_2$ with $\mathrm{Bu_4NOH}$ in $\mathrm{CH_3CN}$ gave brown yellow prismatic crystals as a monohydrated form by slow evaporation of the $\mathrm{H_2O/CH_3CN}$ solution (3: 1 v/v).

The molecular structure of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}]$ $(\mathrm{CF_3SO_3})(\mathrm{H_2O})$ (**1**) together with selected bond angles and distances is shown in Figure 1. [12] The C=O, C-O bond distances (1.242 and 1.345 Å, respectively) and the O-C-O angle (114°) of **1** are close to those of *trans*-$[\mathrm{Pt(\eta^1\text{-}C(O)OH)(C_6H_5)(PEt_3)_2}]$, which exists as a dimeric form through two hydrogen bondings between the hydroxycarbonyl moieties. On the other hand, the hydroxycarbonyl of **1** binds to hydrated water (O1-O5: 2.822(8) Å) which is also connected to triflate (O5-O4: 2.769(8) Å) with another hydrogen bonding. Furthermore, the hydrate water molecule is located in the neighborhood of the carbonyl oxygen of the hydroxycarbonyl group in another molecule of **1** (O5-O2': 3.040(8) Å) suggesting a weak intereaction between them. As a result, two molecules of **1** are related to an inversion center in a triclinic unit cell through a weak hydrogen bond. On the basis of Nakamoto's diagram [13] of hydrogen bond lengths vs. ν(OH) bands, two strong bands observed at 3416 and 3073 $\mathrm{cm^{-1}}$ in the IR spectrum of **1** in KBr disk are reasonably assigned to the ν(OH) bands of the strong hydroxycarbonyl-water (2.82 Å) and water-triflate (2.77 Å) hydrogen bondings, respectively, while no ν(OH) band assignable to the weak hydrogen bonding with the atomic distance of 3.04 Å appeared in the spectrum.

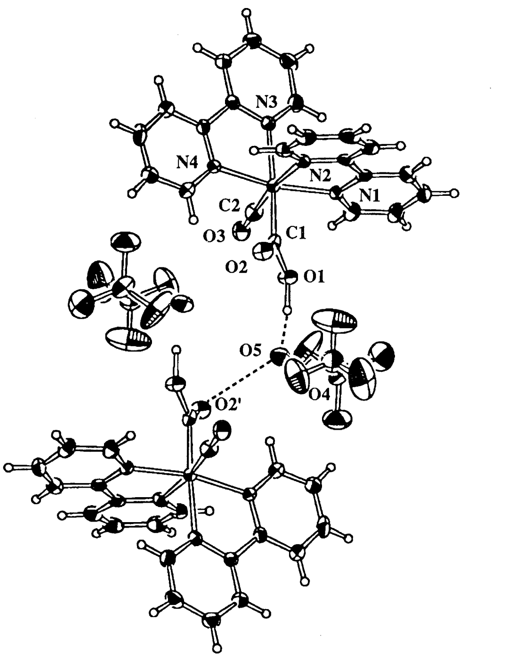

Figure 1. The molecular structure of $[\mathrm{Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)}](\mathrm{CF_3SO_3})(\mathrm{H_2O})$ (1) drawing in 30% probability. Selected bond lengths(Å) and angles(°): Ru-C1 2.003(7), Ru-C2 1.786(7), Ru-N1 2.046(5), Ru-N2 2.109(5), Ru-N3 2.146(5), Ru-N4 2.062(5), C1-O1 1.345(7), C1-O2 1.242(7), O1-O5 2.822(8), O5-O4 2.769(8), O5-O2' 3.040(8), O1-C1-O2 114.9(6).

The Ru-N bond distances of **1** are largely influenced by the π-acceptor and σ-donor characteristic of the CO and COOH moieties. The Ru-N1 and Ru-N4 bond distances of 2.046 and 2.062 Å (trans to bpy) are significantly shorter than the Ru-N2 and Ru-N3 distances of 2.109 and 2.146 Å (trans to CO and C(O)OH) (Figure 1). On the basis of the fact that the average of the Ru-N bond length of 2.054 Å (trans to bpy) of **1** is same as that of $[\mathrm{Ru(bpy)_2Cl_2}]$ (2.054 Å), the distinct lengthening of the Ru-N bond trans to the CO and C(O)OH moieties of **1** suggests a

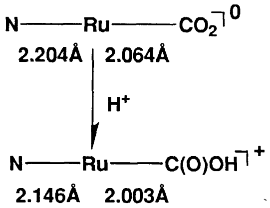

Figure 2. Contraction of the Ru-C(O)OH and Ru-bpy (trans to C(O)OH) bonds in $[Ru(bpy)_2(CO)(C(O)OH)]^+$ by protonation of $[Ru(bpy)_2(CO)(CO_2)]$.

low π-acceptor ability of bpy compared with that of CO and C(O)OH ligands. The difference in the Ru-N2 and Ru-N3 bond distances of 2.109 and 2.146 Å of **1** (trans to CO and C(O)OH), on the other hand, would be ascribed to a strong σ-donor ability of the C(O)OH moiety compared with the neutral CO ligand.

The most notable feature in the comparison of the molecular structure of **1** with the deprotonated $[Ru(bpy)_2(CO)(\eta^1\text{-}CO_2)]$ (**2**)[10] is that not only the Ru-C(O)OH but also the Ru-N3 bond distances (trans to C(O)OH) of **1** (2.003 and 2.146 Å) are much shorter than the Ru-CO_2 and Ru-N ones (trans to CO_2) of **2** (2.064 and 2.204 Å, respectively) (Figure 2). The shortening of the Ru-C(O)OH bond of **1** compared with the Ru-CO_2 one of **2** is explained by an increase in a π-acceptor ability of the C(O)OH moiety. The decrease in the electron density of Ru of **1**, therefore, may be compensated by a σ-donor ability of bpy. Thus, protonation of Ru-CO_2 causes an intramolecular electron transfer from the bpy to the C(O)OH moiety through Ru. The present study revealed that the diffusion controlled interconversion between **1** and **2** in H_2O is largely assisted by synergetic σ-donor and π-acceptor characteristics of bpy.

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12 Anal. Found: C 42.28, H 2.96, N 8.63 (%). Calcd for $C_{23}H_{18}N_4O_6F_3SRu(H_2O)$: C 42.27, H 2.93, N 8.57. IR (KBr): ν(OH) 3416 and 3073 cm^{-1}, ν(C≡O) 1952.2 cm^{-1}, ν(C=O) 1583.7 cm^{-1}. Crystal data for **1**: $C_{23}H_{19}O_7N_4F_3SRu$, triclinic, $P\bar{1}$, a = 11.988(3) Å, b = 13.424(2) Å, c = 8.700(1) Å, α = 96.90(1)°, β = 110.43(1)°, γ = 72.02(2)°, V = 1247.9(5) $Å^3$, Z = 2, crystal size 0.20 × 0.20 × 0.10 mm. 7599 reflections (6° < θ < 60°), 7275 independent (*Rini* = 0.061). All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation. All calculations were carried out with TEXSAN. Hydrogen atoms were placed in idealized positions and included in the structure factor calculation. The final cycle of full-matrix least-squares refinement was based on 3861 observed reflections ($I > 3.00\sigma(I)$) and 352 variable parameters and converged with $R = 0.058$, $Rw = 0.042$.

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