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Article

Reactions of Acetonitrile Coordinated to a Nitrosylruthenium Complex with H_2O or CH_3OH under Mild Conditions: Structural Characterization of Imido-Type Complexes

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The reaction of *cis*-$[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ (bpy = 2,2′-bipyridine) in H_2O at room temperature proceeded to afford two new nitrosylruthenium complexes. These complexes have been identified as nitrosylruthenium complexes containing the N-bound methylcarboxyimidato ligand, *cis*-$[Ru(NO)(NH{=}C(O)CH_3)(bpy)_2]^{2+}$, and methylcarboxyimido acid ligand, *cis*-$[Ru(NO)(NH{=}C(OH)CH_3)(bpy)_2]^{3+}$, formed by an electrophilic reaction at the nitrile carbon of the acetonitrile coordinated to the ruthenium ion. The X-ray structure analysis on a single crystal obtained from CH_3CN–H_2O solution of *cis*-$[Ru(NO)(NH{=}C(O)CH_3)(bpy)_2](PF_6)_3$ has been performed: $C_{22}H_{20.5}N_6O_2P_{2.5}F_{15}Ru$, orthorhombic, *Pccn*, $a = 15.966(1)$ Å, $b = 31.839(1)$ Å, $c = 11.707(1)$ Å, $V = 5950.8(4)$ Å^3, and $Z = 8$. The structural results revealed that the single crystal consisted of 1:1 mixture of *cis*-$[Ru(NO)(NH{=}C(O)CH_3)(bpy)_2]^{2+}$ and *cis*-$[Ru(NO)(NH{=}C(OH)CH_3)(bpy)_2]^{3+}$ and the structural formula of this single crystal was thus $[Ru(NO)(NH{=}C(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$. The reaction of *cis*-$[Ru(NO)(CH_3CN)(bpy)_2]^{3+}$ in dry CH_3OH–CH_3CN at room temperature afforded a nitrosylruthenium complex containing the methyl methylcarboxyimidate ligand, *cis*-$[Ru(NO)(NH{=}C(OCH_3)CH_3)(bpy)_2]^{3+}$. The structure has been determined by X-ray structure analysis: $C_{25}H_{29}N_8O_{18}Cl_3Ru$, monoclinic, $P2_1/c$, $a = 13.129(1)$ Å, $b = 17.053(1)$ Å, $c = 15.711(1)$ Å, $\beta = 90.876(5)°$, $V = 3517.3(4)$ Å^3, and $Z = 4$.

Introduction

Nitric oxide coordinates to a metal center via the N atom to produce nitrosyl complexes. Physical properties, structural features, and reactivities of metal nitrosyl complexes may be explained by contributions of a donation of electron density from the NO ligand to the metal (σ-type bonding) and from the metal to the NO ligand (π-type back-bonding).[1–4] In our previous investigations on nitrosylruthenium complexes classifiable as $\{RuNO\}^6$-type by the Enemark–Feltham notation for metal nitrosyls,[5] polypyridinenitrosylruthenium complexes containing the nitrite ion, $[Ru(NO)(X)(L)_4]^{n+}$ ($X = NO_2^-$ or ONO^-, L = 1/2bpy, 1/2pyca (2-pyridinecarboxylato), or py), showed nitro–nitrito linkage isomerizations and stabilized labile nitrito-form complexes owing to a strong π-acceptor character of the

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nitrosyl ligand.[6] The nitrosyl ligand thus functioned as electron-withdrawing group in metal complexes.

Hydrolysis of the acetonitrile ligand coordinated to the bis(2,2′-bipyridine)nitrosylruthenium complex, *cis*-$[Ru(NO)(NCCH_3)(bpy)_2]^{3+}$, occurred at the acetonitrile carbon under mild conditions.[7] Hydrolysis of nitriles to amides was enhanced by coordination of nitriles to various metal centers such as Co,[8] Ni,[9] Mo,[10] Ru,[11,12] Rh,[13] Pd,[14] W,[15] Ir,[13] and Pt.[16] A number of investigations have reported isolation and identification of hydrolysis products coordinated to various metal ions. In such hydrolysis reactions, coordination of nitrile to transition metal ions resulted in an enhanced electrophilicity at the nitrile carbon by electron withdrawal from the metal ion, and thus protic nucleophiles such as water and alcohols attacked the nitrile carbon. In this paper, we report isolation and structural determination of the hydrolysis products of acetonitrile in the reactions of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2]^{3+}$ with water and methanol at room temperature.

Experimental Section

Materials. *cis*-$[Ru(NO)(OH_2)(bpy)_2](ClO_4)_3{\cdot}3H_2O$,[6a] *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](PF_6)_3$,[7] *cis*-$[Ru(NO)(bpy)_2(py)](PF_6)_2$,[17] *cis*-$[Ru(NO_2)(NCCH_3)(bpy)_2]PF_6$, and *cis*-$[Ru(NCCH_3)_2(bpy)_2](PF_6)_2$[18] were prepared according to the methods in the literature. CH_3CN and CH_3OH were purchased as the dehydrated grade.

Syntheses and Reactions of Complexes. *Caution! Although the complexes as perchlorate salts described below are stable, they are potentially explosive and should be handled with care.*

***cis*-$[Ru(NO)(im)(bpy)_2](ClO_4)_3$ (im = Imidazole).** A 100 mg (0.12 mmol) amount of *cis*-$[Ru(NO)(OH_2)(bpy)_2](ClO_4)_3{\cdot}3H_2O$ was dissolved in H_2O (30 cm^3) to give an orange solution. To the orange aqueous solution was added 175 mg (2.57 mmol) of imidazole. The solution was heated, and its volume was reduced to ca. 10 cm^3 on a hot plate (ca. 60 °C). The solution was cooled to room temperature and allowed to stand for overnight to precipitate *cis*-$[Ru(NO_2)(im)(bpy)_2](ClO_4)_2$ as a brown powder. The product was collected and washed with cold water and was then suspended in 3 mol dm^{-3} hydrochloric acid solution (5 cm^3). The suspension was stirred at room temperature overnight to become an orange solution. Solid $NaClO_4{\cdot}H_2O$ was added to the solution to form a salmon-colored precipitate. The product was collected, washed with cold water, and dried. Yield: 50 mg (50%). Anal. Found: C, 33.88; N, 12.04; H, 2.38. Calcd for $C_{23}H_{20}O_{13}N_7Cl_3Ru$: C, 34.11; N, 12.11; H, 2.49. $\nu(NO) = 1938\ cm^{-1}$.

***cis*-$[Ru(NCCH_3)(im)(bpy)_2](ClO_4)_2{\cdot}H_2O$.** A 150 mg (0.21 mmol) amount of *cis*-$[Ru(NO)(im)(bpy)_2](ClO_4)_2$ was dissolved in CH_3CN, and NaN_3 (13.7 mg, 0.21 mmol) was added to the solution. The solution was stirred for 1 h at room temperature. The volume of the solution was reduced to ca. 3 cm^3, and diethyl ether was then added to form a reddish-brown precipitate. The product was collected, washed with water, and dried. Yield: 106 mg (77%). Anal. Found: C, 40.65; N, 13.48; H, 3.70. Calcd for $C_{25}H_{25}O_9N_7Cl_2Ru$: C, 40.61; N, 13.26; H, 3.41. FAB-MS: *m*/*e* 622 (M − ClO_4).

***cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF6)_2$ (py = Pyridine).** This complex was prepared by a procedure similar to that for *cis*-$[Ru(NCCH_3)(im)(bpy)_2](ClO_4)_2{\cdot}H_2O$, using *cis*-$[Ru(NO)(bpy)_2(py)](PF_6)_2$ (200 mg, 0.21 mmol) as starting material. Yield: 148 mg (86%). Anal. Found: C, 39.09; N, 10.16; H, 3.16. Calcd for $C_{27}H_{26}ON_6P_2F_{12}Ru$: C, 39.38; N, 10.20; H, 2.94. FAB-MS: *m*/*e* 679 (M − PF_6), 534 (M − $2PF_6$).

Isolation of Products Generated by the Reaction of Acetonitrileruthenium Complexes with Water. Reaction of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](PF_6)_3$ with water was performed by the same procedure described in the previous report.[7] A 100 mg amount of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](PF_6)_3$ was dissolved in H_2O (5 cm^3), and the solution was stirred at room temperature for 3 h. The solution was dried using a rotary evaporator, and the resultant solid material was washed with ether. The solid material underwent column chromatography (SiO_2; 1:1 $CH_3CN-CH_2Cl_2$ (v/v)), and the yield of the product obtained as the third band, *cis*-$[Ru(NO)(NHC(O)CH_3)(bpy)_2](PF_6)_2$, was 43%. $\nu(NO) = 1924\ cm^{-1}$.

Reactions of acetonitrileruthenium complexes *cis*-$[Ru(NCCH_3)(im)(bpy)_2](ClO_4)_2{\cdot}H_2O$, *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2$, *cis*-$[Ru(NO_2)(NCCH_3)(bpy)_2]PF_6$, and *cis*-$[Ru(NCCH_3)_2(bpy)_2](PF_6)_2$ with water were carried out as follows: The complex was dissolved in water, and the solution was stirred for several days. The volume of the solution was reduced until a precipitate appeared, or solid

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Table 1. Crystallographic Data for *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2 \cdot CH_3CN$, *cis*-$[Ru(NO)(NHC(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$, and *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3 \cdot 2CH_3NO_2$

formula	$C_{29}H_{27}N_7F_{12}P_2Ru$	$C_{22}H_{20.5}N_6O_2P_{2.5}F_{15}Ru$	$C_{25}H_{29}N_8O_{18}Cl_3Ru$
fw	864.58	864.42	936.98
cryst system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	Pccn	$P2_1/c$
color of cryst	red	red	orange
a, Å	11.948(2)	15.966(1)	13.129(1)
b, Å	23.969(3)	31.839(1)	17.053(1)
c, Å	12.937(2)	11.707(1)	15.711(1)
β, deg	112.14(1)		90.876(5)
V, Å^3	3431.7(9)	5950.8(4)	3517.3(4)
Z	4	8	4
T, °C	25	-140	-150
D_{calcd}, g cm^{-3}	1.67	1.93	1.77
μ(Mo Kα), cm^{-1}	6.49	7.91	7.64
R1[a]	0.068	0.031	0.044
GOF	1.38	0.74	1.02

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $I < 2\sigma(I)$.

NH_4PF_6 or $NaClO_4$ was added to the solution after reducing the volume. The solid material was collected and dried.

The product from the reaction of *cis*-$[Ru(NCCH_3)(im)(bpy)_2](ClO_4)_2 \cdot H_2O$ was *cis*-$[Ru(H_2O)(im)(bpy)_2](ClO_4)_2 \cdot H_2O$. Anal. Found: C, 38.37; N, 11.73; H, 3.30. Calcd for $C_{23}H_{24}O_{10}N_6Cl_2Ru$: C, 38.56; N, 11.73; H, 3.38. FAB-MS: *m*/*e* 599 (M − H_2O − ClO_4), 500 (M − H_2O − $2ClO_4$).

The reactions of *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2$ afforded the starting complex and those of *cis*-$[Ru(NO_2)(NCCH_3)(bpy)_2]PF_6$ and *cis*-$[Ru(NCCH_3)_2(bpy)_2](PF_6)_2$ afforded the corresponding aquaruthenium complexes, *cis*-$[Ru(NO_2)(H_2O)(bpy)_2]PF_6$ and *cis*-$[Ru(H_2O)_2(bpy)_2](PF_6)_2$, respectively.

Isolation of *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3$ Generated by the Reaction of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](ClO_4)_3$ with Methanol. A 100 mg (0.13 mmol) amount of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](ClO_4)_3$ was dissolved in CH_3OH-CH_3CN (v/v = 2:1, 15 cm^3). The solution was stirred for 2 days at room temperature to give a yellow solution. The volume of the solution was reduced by a rotary evaporator, and the product was collected, washed with water, and dried. Yield: 78 mg (75%). Anal. Found: C, 33.77; N, 10.48; H, 3.03. Calcd for $C_{25}H_{23}O_{14}N_6Cl_3Ru$: C, 33.90; N, 10.31; H, 2.84. FAB-MS: *m*/*e* 616 (M − $2ClO_4$), 517 (M − $3ClO_4$). ν(NO) = 1942 cm^{-1}.

Physical Measurements. Infrared spectra were obtained on KBr pellets with a Perkin-Elmer FT-1650 spectrometer. Elemental analyses were performed by the Sophia University Analytical Facility. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JMN-LA-500 spectrometer. UV−vis spectra were recorded on a Shimadzu MultiSpec-1500. Electrochemical measurements were carried out in a cell equipped with a Pt-disk working electrode (i.d. = 1.6 mm), a Pt-wire auxiliary electrode, and an Ag|0.01 mol dm^{-3} $AgNO_3$ reference electrode purchased from BAS Corp. Cyclic voltammograms in CH_3CN containing TEAP (0.1 mol dm^{-3}) were obtained by a BAS 100B/W electrochemical analyzer.

Rate Studies. A citric acid−Na_2HPO_4 buffer solution containing 1.0 mol dm^{-3} $NaClO_4$ was first prepared, and to this buffer solution was added a certain amount of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](ClO_4)_3$, so that the concentration of the complex became 1.6×10^{-4} mol dm^{-3}. Hydrolysis of the complex commenced immediately, and the formation of the products was monitored by measuring the absorbance at 320 nm with spectrometer. The temperature of the solution was kept constant at 25 °C during the whole process of the monitoring. The obtained data were analyzed to estimate the observed rate constants of hydrolysis, k_{obs}, based on the method of Zanella and Ford.[12] Experiments were repeatedly conducted with buffer solutions with different pH values between 2 and 4. This pH range was chosen because it was known that the complex reacted with OH^- at the nitrogen atom of the nitrosyl ligand above pH 5 (the nitrosyl−nitro acid−base conversion reaction).[19]

X-ray Crystallographic Studies. Single crystals of *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2 \cdot CH_3CN$, *cis*-$[Ru(NO)(NHC(O)CH_3)(bpy)_2](PF_6)_3$, and *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3 \cdot 2CH_3NO_2$ were grown by vapor diffusion of Et_2O into CH_3CN, CH_3CN-H_2O (v/v = 1:1), and CH_3NO_2 solutions of the complexes, respectively. The crystallographic data are summarized in Table 1. The data for *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2 \cdot CH_3CN$ were collected on a Rigaku AFC5S automated four-circle diffractometer, and those of *cis*-$[Ru(NO)(NHC(O)CH_3)(bpy)_2](PF_6)_3$ and *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3 \cdot 2CH_3NO_2$, on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromatized Mo Kα radiation (0.710 69 Å). All the calculations were carried out on an O_2 workstation of Silicon Graphics Corp., using the TEXSAN crystallographic software package of Molecular Structure Corp. The structures were solved by a Patterson method or direct methods and were expanded using Fourier techniques. For *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2 \cdot CH_3CN$, empirical absorption corrections were applied, and for *cis*-$[Ru(NO)(NHC(O)CH_3)(bpy)_2](PF_6)_3$ and *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3 \cdot 2CH_3NO_2$ numerical absorption corrections were applied using Lorentz−polarization and absorption. The structures were refined with the full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically.

Results and Discussion

Syntheses of (Acetonitrile)ruthenium Complexes. (Acetonitrile)ruthenium complexes, except *cis*-$[Ru(NO)(NCCH_3)(bpy)_2]^{3+}$, have been synthesized by the reactions of *cis*-$[Ru(NO)X(bpy)_2]^{n+}$ with sodium azide in acetonitrile solution (eq 1). These reactions are characteristic reactions of $\{RuNO\}^6$-type complexes with the azide ion via initial attack on the nitrosyl nitrogen with the evolution of dinitrogen and nitrous oxide.[18]

$$cis\text{-}[Ru(NO)X(bpy)_2]^{n+} + N_3^- + CH_3CN \rightarrow cis\text{-}[Ru(NCCH_3)X(bpy)_2]^{(n-1)+} + N_2 + N_2O \quad (1)$$

While the present four (acetonitrile)ruthenium complexes (X = NO_2^-, im, py, and CH_3CN), where the nitrosyl ligand

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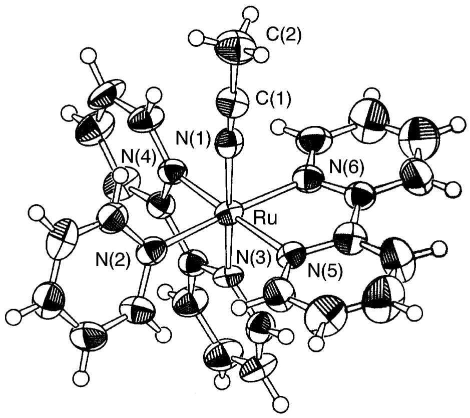

Figure 1. Structure of *cis*-$[Ru(NCCH_3)(py)(bpy)_2]^{2+}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) of *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2{\cdot}CH_3CN$

Ru−N(1)	2.034(7)	Ru−N(2)	2.118(7)
Ru−N(3)	2.041(6)	Ru−N(4)	2.063(6)
Ru−N(5)	2.075(6)	Ru−N(6)	2.056(7)
N(1)−C(1)	1.11(1)	C(1)−C(2)	1.49(1)
Ru−N(1)−C(1)	174.9(7)	N(1)−C(1)−C(2)	177.5(10)

is not coligated to the ruthenium ion, were synthesized by the use of the characteristic reaction of eq 1, the bis(acetonitrile)ruthenium complex *cis*-$[Ru(NCCH_3)_2(bpy)_2](PF_6)_2$ was synthesized by the reported convenient method.[20] Since a suitable sized and high-quality single crystal was difficult to obtain, the structural analysis of *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2{\cdot}CH_3CN$ was carried out using a small single crystal. The structure is shown in Figure 1, and the selected bond distances and angles are listed in Table 2. The geometry around the ruthenium ion is a distorted octahedron, and the CH_3CN and py ligands are located at cis positions to each other. The CH_3CN ligand linearly coordinates to the ruthenium ion in the usual manner. (Acetonitrile)ruthenium complexes used in this investigation seem to have the same coordination geometry and coordination mode as that of *cis*-$[Ru(NCCH_3)(py)(bpy)_2]^{2+}$. An acetonitrile molecule can coordinate to metal centers as η^1-$NCCH_3$ (end-on) by σ-bonding through the nitrogen lone pair. In several transition metal complexes, back-bonding forms between the metal d orbitals and the π^* orbital of the acetonitrile. The C−N bond distances of the CH_3CN molecule coordinated to the ruthenium ion have been reported to be 1.06−1.15 Å, shorter than that of the free CH_3CN molecule,[7,21] and those values depend on the degree of π-back-bonding between the ruthenium center and the CH_3CN ligand. The N−C bond distance of *cis*-$[Ru(NCCH_3)(py)(bpy)_2]^{2+}$, 1.11(1) Å, is the usual one for the N−C distance of CH_3CN coordinated to the Ru(II) center, and on the basis of the oxidation potentials of the ruthenium centers, this complex most probably has π-back-bonding. On the other hand, the previously reported acetonitrile complex *cis*-$[Ru(NO)(NCCH_3)(bpy)_2]^{3+}$ has a remarkably short C−N bond, 1.08(2) Å,[7] indicating that π-back-bonding between the ruthenium center and the acetonitrile ligand is very weak owing to the strong π-acceptor character of the nitrosyl ligand.

Table 3. Electrochemical Data[a] for Ruthenium Complexes

complex	Ru(II)/ Ru(III)[b]	$(RuNO)^{2+}$/ $(RuNO)^{+}$ [b]	$(RuNO)^{+}$/ (RuNO)[c]
$[Ru(NCCH_3)(im)(bpy)_2](ClO_4)_2$	0.85		
$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2$	1.01		
$[Ru(NCCH_3)(NO_2)(bpy)_2]PF_6$	0.86		
$[Ru(NCCH_3)_2(bpy)_2](PF_6)_2$	1.10		
$[Ru(NO)(NCCH_3)(bpy)_2](PF_6)_3$		0.19	−0.71
$[Ru(NO)(NHC(O)CH_3)(bpy)_2](PF_6)_2$		−0.41	−1.16
$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3$		−0.07	−0.86

[a] Vs Ag|0.01 mol dm^{-3} $AgNO_3$. [b] $E_{1/2} = (E_{p,c} + E_{p,a})/2$. [c] Irreversible oxidation wave.

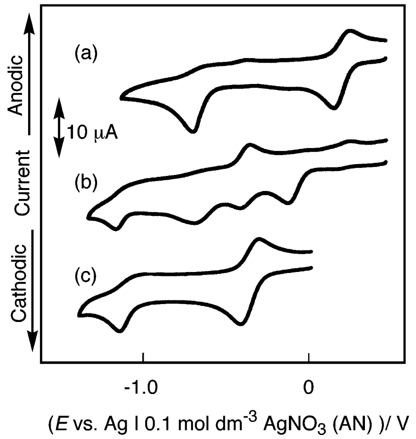

Figure 2. Cyclic voltammograms of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2](PF_6)_3$ (a) and reaction products with water after the 3 h of standing (b) and the product, *cis*-$[Ru(NO)(NH{=}C(O)CH_3)(bpy)_2](PF_6)_2$, purified by column chromatography (c) in CH_3CN containing TEAP (0.1 mol dm^{-3}).

Cyclic voltammograms of the four (acetonitrile)ruthenium complexes having no nitrosyl ligand show reversible redox couples between Ru(II) and Ru(III) as summarized in Table 3. These oxidation waves are observed in the relatively high potential region of the oxidation from Ru(II) to Ru(III), indicating the CH_3CN ligand functions as an electron-withdrawing ligand. A comparison of these oxidation potentials reveals that the decreasing order of electron-withdrawing nature is $CH_3CN > py > NO_2^- \sim im$. The CV of *cis*-$[Ru(NO)(NCCH_3)(bpy)_2]^{3+}$ in CH_3CN shows a reversible redox couple of $(RuNO)^{3+/2+}$ at $E_{1/2} = 0.19$ V and an irreversible reduction wave of $(RuNO)^{2+/+}$ at $E_{p,c} = -0.71$ V, assignable to the nitrosyl ligand base reductions (Figure 2a), and a characteristic nitrosyl stretching band, $\nu(NO)$, is observed at 1962 cm^{-1}. The reduction potentials appear in the highest potential region, and the stretching vibration is

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at the highest wavenumber for *cis*-[Ru(NO)X(bpy)$_2$]$^{n+}$-type complexes. Thus, the results of CV, IR, and structural parameters suggest that the electron density of the nitrosyl ligand and also that of the ruthenium center are low and the CH_3CN ligand is not affected by the back-donation from the ruthenium center.

Reaction of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$]$^{3+}$ with Water. The acetonitrile ligand of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$]$^{3+}$ easily reacts with H_2O to form the corresponding imido-type ligand by a nucleophilic attack of H_2O or OH^- at the nitrile carbon. An aqueous solution of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$](ClO$_4$)$_3$ is allowed to stand for 3 h at room temperature and concentrated until a precipitate appears. The pH of the starting aqueous solution is 2.5 and changes to 1.8 after the solution stands for 3 h. The previously reported reactions of nitrile coordinated to the ruthenium(III) center in water were carried out in a pH region higher than that for neutral conditions.[11] The pH value of the present reaction solution indicates the acetonitrile ligand of this ruthenium complex is highly activated by the strong π-acceptor character of the nitrosyl ligand. The value of the observed rate constant, k_{obs}, of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$](PF$_6$)$_2$ is an increasing function of the pH of the reaction solution between 2.3 and 4.1 and varies from 3.6×10^{-4} to 1.4×10^{-3} s^{-1} at 25 °C. These k_{obs} values of the present reaction are about the same as those of the reactions of [Ru(NCCH$_3$)(NH$_3$)$_5$]$^{3+}$ under basic conditions[11d] and larger than those under acidic conditions (pH 2−3).[12] The vary fact that it is pH dependent indicates the hydrolysis reaction of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$](PF$_6$)$_2$ is contributed not only by the acid-hydrolysis path but also, presumably slightly, by the base-hydrolysis path and there may be some following and/or side reactions such as protonation and isomerization reactions of hydrolysis products. Further discussion on the present hydrolysis using the rate data seems difficult.

The CV of the precipitate, obtained from the solution of [Ru(NO)(NCCH$_3$)(bpy)$_2$](PF$_6$)$_2$ after standing for 3 days, shows four new reduction waves at $E_{p,a} = -0.12$, -0.41, -0.68, and -1.16 V vs. Ag|0.01 mol dm^{-3} AgNO$_3$(AN) in addition to a small wave of the starting (acetonitrile)-ruthenium complex at $E_{p,c} = 0.15$ V as shown in Figure 2b. This indicates that the precipitate is a mixture of two new nitrosylruthenium complexes formed by the reaction of the acetonitrile ligand with H_2O. The CV pattern of CV(b) in Figure 2 is independent of the reaction time from 1 h to a few days, although the amount of the starting complex remaining varies with varying reaction time. From the mixture, a new nitrosylruthenium complex, which shows two reduction waves at -0.41 and -1.16 V (Figure 2c), is isolated by column chromatography (SiO$_2$; 1:1 $CH_3CN-CH_2Cl_2$ (v/v)) as described in the Experimental Section and precipitated as ClO$_4$ or PF$_6$ salt using NaClO$_4$ or NH$_4$PF$_6$ as a precipitating agent. Unfortunately the other new nitrosylruthenium complex that shows reduction waves at -0.12 and -0.68 V cannot be isolated from the mixture by column chromatography. The IR spectra of the isolated complex show the strong stretching bands assigned to ν(NO) at 1919 cm^{-1} and ν(CO) at 1579 cm^{-1} for the ClO$_4$ salt and 1924 and 1577 cm^{-1} for the PF$_6$ salt. Signals of the bpy ligands in the ^{1}H and ^{13}C NMR spectra are consistent with the cis-form configuration. The elemental analysis and the FAB mass spectrum of the PF$_6$ salt, coupled with these IR and NMR data, determine its chemical formula as *cis*-[Ru(NO)(NH=C(O)CH$_3$)(bpy)$_2$](PF$_6$)$_2$. The chemical formula of the other new nitrosylruthenium complex is inferred from the X-ray crystallography of the isolated complex, which will be discussed in detail in a later section, and from the CV pattern of single crystals of the PF$_6$ salt prepared in the same manner as that for the X-ray crystallography. The CV pattern obtained is the same as that of Figure 2b, indicating the single crystals consist not only of *cis*-[Ru(NO)(NH=C(O)CH$_3$)(bpy)$_2$](PF$_6$)$_2$ but also of another nitrosylruthenium complex. This CV result, coupled with the result of the X-ray crystallography, suggests that the other new nitrosylruthenium complex, which cannot be isolated chromatographically, is *cis*-[Ru(NO)(NH=C(OH)CH$_3$)(bpy)$_2$]$^{3+}$, a protonated species of *cis*-[Ru(NO)(NH=C(O)CH$_3$)(bpy)$_2$]$^{2+}$. Thus, the reaction products of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$]$^{3+}$ with water are identified as nitrosylruthenium complexes containing methylcarboxyimidato and methylcarboxyimido acid ligands that form by the reaction of acetonitrile at the nitrile carbon, and these methylcarboxyimidato and methylcarboxyimido acid complexes exist as an equilibrium mixture in aqueous solution.

Reaction of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$]$^{3+}$ with Methanol. The reaction of *cis*-[Ru(NO)(NCCH$_3$)(bpy)$_2$](ClO$_4$)$_3$ with methanol is performed in the mixed solvent CH_3OH-CH_3CN (2:1 (v/v)) owing to the low solubility of the complex in methanol. This reaction proceeds slowly as the reaction with water but gives a single new nitrosylruthenium complex. The use of the dehydrated solvent is of great importance, and water contamination increases the amounts of impurity products formed by the reaction with water. For the new complex, a strong NO stretching vibrational mode, ν(NO), is observed at 1942 cm^{-1}, and the CV shows a reversible couple at $E_{1/2} = -0.07$ V and an irreversible wave at $E_{p,c} = -0.86$ V assignable to (RuNO)$^{3+/2+}$ and (RuNO)$^{2+/+}$, respectively. The ^{1}H and ^{13}C NMR spectra and the X-ray structural analysis reveal that the configuration of bpy ligands is a cis form. The formed ruthenium complex is formulated as the nitrosylruthenium containing a methyl methylcarboxyimidate ligand, *cis*-[Ru(NO)(NH=C(OCH$_3$)CH$_3$)(bpy)$_2$](ClO$_4$)$_3$.

Structural Characterization of Imido-Type Complexes. A single crystal of *cis*-[Ru(NO)(NHC(O)CH$_3$)(bpy)$_2$](PF$_6$)$_2$ is obtained by vapor diffusion of ether into a CH_3CN solution of the complex containing a few drops of water. In the absence of water, no single crystal is obtained for use in X-ray single-crystal analysis as needed. This result supports the identification of the second new nitrosylruthenium complex formed as [Ru(NO)(NH=C(OH)CH$_3$)(bpy)$_2$]$^{3+}$ described in the earlier section. The single crystal is mounted on a grass fiber, and the data are collected at −140 °C. The structure of this ruthenium complex cation is shown in Figure 3, and the selected bond distances and angles are listed in Table 4. Non-hydrogen atoms are found by Fourier tech-

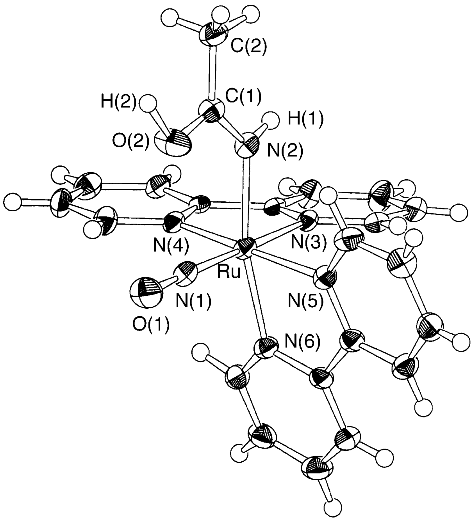
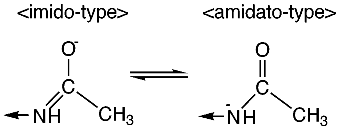


Figure 3. Structure of *cis*-$[Ru(NO)(NHC(OH_{0.5})CH_3)(bpy)_2]^{2.5+}$.

Table 4. Selected Bond Distances (Å) and Angles (deg) of *cis*-$[Ru(NHC(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$

Ru−N(1)	1.763(3)	Ru−N(2)	2.049(3)
Ru−N(3)	2.091(2)	Ru−N(4)	2.068(3)
Ru−N(5)	2.073(3)	Ru−N(6)	2.089(3)
N(1)−O(1)	1.143(3)	N(2)−C(1)	1.290(5)
C(1)−O(2)	1.288(4)	C(1)−C(2)	1.500(5)
Ru−N(1)−O(1)	177.6(3)	Ru−N(2)−C(1)	131.1(2)
N(2)−C(1)−O(2)	119.0(3)	N(2)−C(1)−C(2)	122.6(3)

Scheme 1. Resonance Structures of the Acetoamidato and the Methylcarboxyimidato Ligands



niques and refined anisotropically. Three PF_6^- anions are found against the ruthenium complex cation. Two P atoms of these are sited on general positions, and one of the P atoms is on a special position with an occupancy of 0.5. All hydrogen atoms are found by difference Fourier techniques. The hydrogen atom of the imido acid, H(2), is located at a special position with an occupancy of 0.5. Thus, the structural chemical formula is $[Ru(NO)(NHC(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$, and methylcarboxyimidato complex $[Ru(NO)(NH{=}C(O)CH_3)(bpy)_2]^{2+}$ and methylcarboxyimido acid complex $[Ru(NO)(NH{=}C(OH)CH_3)(bpy)_2]^{3+}$ cations exist in the unit cell with 1:1 ratio. This result is also evidence in support of the need of water for the formation of single crystals.

The cation has the expected octahedral coordination geometry around the ruthenium atom, and the nitrosyl and imido-type ligands exist at cis positions to each other. The nitrosyl moiety (Ru−N = 1.763(3) Å, N−O = 1.143(3) Å, and Ru−N−O = 177.6(3)°) is essentially linear as expected for the $\{RuNO\}^6$ configuration. The structural parameters of two bpy ligands are similar to those of previously reported ruthenium complexes.[6d,7,20,22] The imido-type ligand has two resonance structures as shown in Scheme 1. It is noteworthy that the bond distance of N(2)−C(1), 1.290(5) Å, is shorter and that of C(1)−O(2), 1.288(4) Å, is longer than those of the corresponding amido-type ligands.[23] The N(2)−C(1) bond distance of this complex is similar to that of the structurally characterized NH═C moiety coordinated to the metal center, 1.25−1.31 Å,[24] indicating the bond between N(2) and C(1) is a double bond. The hydrogen atom, H(1), bonded to the nitrogen atom, N(2), is coplanar with N(2), C(1), and O(2), and H(2) bonded to O(2) is found with an occupancy of 0.5 by difference Fourier techniques. It may be concluded that the structure of this ligand is an imido-type structure rather than an amido-type one.

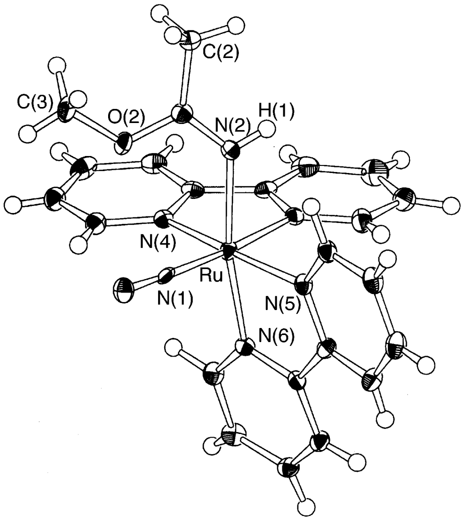


Figure 4. Structure of *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2]^{3+}$.

The single crystal of *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3\cdot 2CH_3NO_2$ is mounted in a loop. The structure of this ruthenium complex cation is shown in Figure 4, and the selected bond distances and angles are listed in Table 5. The cation has the expected octahedral coordination geometry around the ruthenium atom, and the nitrosyl and the methyl methylcarboxyimidate ligand exist at cis positions to each other and so are the two bpy ligands. The nitrosyl ligand linearly coordinates to the ruthenium atom, and the structural parameters of two bpy ligands are similar to those of the present imido-type complex, $[Ru(NO)(NHC(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$. The bond distances and angles of the imido ester ligand of this complex (N(2)−C(1), 1.289(5), and C(1)−O(2), 1.318(5) Å) are the same as those of the imido-

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Table 5. Selected Bond Distances (Å) and Angles (deg) of *cis*-$[Ru(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3$

Ru−N(1)	1.763(4)	Ru−N(2)	2.071(3)
Ru−N(3)	2.074(3)	Ru−N(4)	2.068(3)
Ru−N(5)	2.076(3)	Ru−N(6)	2.074(3)
N(1)−O(1)	1.141(4)	N(2)−C(1)	1.289(5)
C(1)−O(2)	1.318(5)	C(1)−C(2)	1.490(6)
O(2)−C(3)	1.451(5)		
Ru−N(1)−O(1)	177.6(3)	Ru−N(2)−C(1)	128.8(3)
N(2)−C(1)−O(2)	115.8(4)	N(2)−C(1)−C(2)	122.8(4)
C(1)−O(2)−C(3)	120.0(3)		

type complex. These values also indicate that the structure of this ligand is an imido ester structure.

Conclusion

In general, the hydrolysis of nitriles is catalyzed by acids or bases, and the base-catalyzed hydrolysis is facilitated by their coordinating to a high-valent transition metal to give the corresponding amidato complex. The order of the observed rates of hydrolysis on the nitrosylruthenium complex under acidic conditions in this study is the same as that on the Ru(III) center under basic conditions. The hydrolysis precedes the methanolysis in the case of the reaction with methanol contaminated by water, and the methanolysis does not need a base while the reported alcoholysis proceeds in the presence of a catalytic amount of base. These results indicate the degree of activation of acetonitrile coordinated to the nitrosylruthenium complex is equivalent to that of acetonitrile coordinated to Ru(III) center.[11] Although the assignment of the formal oxidation number to the Ru center and the NO ligand is irrational, the oxidation state of the Ru center is not estimated to be high from the diamagnetic properties of this (acetonitrile)nitrosylruthenium complex. Therefore, this hydrolysis is induced by the electron-attracting nature of $(RuNO)^{3+}$ moiety.

The formations of the acetoamidato complexes and the resonance structures of the acetoamidato and the methylcarboxyimidato ligands shown in Scheme 1 have been reported in the hydrolysis of acetonitrile coordinated to the metal center.[25] The present reaction products of coordinated acetonitrile with water and methanol can be identified as imido-type complexes rather than amido-type ones. Although the imido-type complex is synthesized by the reaction of the iridium complex with acetoamide,[12a] the present formation of the methylcarboxyimidato ligand in the reaction of coordinated acetonitrile with water is a novel synthetic route. Finally, it may be concluded that activation of the coordinated acetonitrile and stability of the imido-type structure in the product are caused by the electronic features of the $(RuNO)^{3+}$ moiety.

Supporting Information Available: Crystallographic details for *cis*-$[Ru(NCCH_3)(py)(bpy)_2](PF_6)_2 \cdot CH_3CN$, *cis*-$[Ru(NO)(NHC(OH_{0.5})CH_3)(bpy)_2](PF_6)_{2.5}$, and *cis*-$[Ru(NO)(NHC(OCH_3)CH_3)(bpy)_2](ClO_4)_3 \cdot 2CH_3NO_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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