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Cis–trans isomerization of $\{RuNO\}^6$-type nitrosylruthenium complexes containing 2-pyridinecarboxylate and structural characterization of a μ-H_3O_2 bridged dinuclear nitrosylruthenium complex

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cis-$[Ru(NO)Cl(pyca)_2]$ (pyca = 2-pyridinecarboxylate) ([**1**]), reacts with nucleophiles such as OH^- and N_3^- in H_2O to generate the dimeric nitrosylruthenium complex, $[\{Ru(NO)(pyca)_2\}_2(\mu\text{-}H_3O_2)]PF_6{\cdot}2H_2O$ ([**2**]$PF_6{\cdot}2H_2O$). The bridging unit of [**2**]PF_6 is a hydroxide hydrate anion ($H_3O_2^-$) composed of a hydroxo and an aqua moiety. Coordinated to each of the ruthenium centers are two pyca ligands in the *trans*-form with the pyridyl nitrogen atoms and the carboxylic oxygen atoms being at the *trans* position to each other (*trans*-form; *trans*(N,N), *trans*(O,O)-configuration). [**2**]PF_6 has also been isolated by the reaction of [**1**] with N_3^- in H_2O. The reaction of [**1**] with CH_3O^- in CH_3OH gives the *trans*-form nitrosylruthenium complex, *trans*-$[Ru(NO)(OCH_3)(pyca)_2]{\cdot}CH_3OH$ (*trans*(N,N), *trans*(O,O)-configuration) ([**3**]$\cdot CH_3OH$). The rare *cis–trans* isomerizations have thus occurred during the reaction between [**1**] (*cis*-form; *trans*(N,N), *cis*(O,O)-configuration) and OH^-, N_3^- or CH_3O^-.

Introduction

Metal nitrosyl complexes show interesting structures and reactivities, due to the specific interactions between metal ions and the nitrosyl ligand.[1,2] The bonding in the metal–nitrosyl moieties has been classified by the Enemark–Feltham notation, $\{M(NO)_x\}^n$, where n is the number of electrons in d orbitals of M and the π^* orbital of NO,[2] since assignment of the formal oxidation numbers to the metal and the nitrosyl ligand is unreasonable. A number of studies on metal nitrosyl complexes have been reported in connection with fundamental chemistry as well as with biological and environmental chemistry.[3] As for metal nitrosyl complexes, the relationship between chemical behaviors and physical properties such as $\nu(NO)$ and reduction potentials has been well studied.[4–9] Metal nitrosyl complexes having $\nu(NO) > 1886\ cm^{-1}$ behave as electrophiles and undergo nucleophilic reactions at the nitrosyl nitrogen.[5] The reaction of the $\{RuNO\}^6$-type nitrosylruthenium complexes with OH^- is well known as the nitrosyl–nitro acid–base equilibrium reaction to form the corresponding nitro complexes.[10] In our previous investigations, the nitrosyl ligand of $\{RuNO\}^6$-type complexes played an important role in stabilities of complexes and reactions such as a structural rearrangement of the co-existing ligand accompanying the reduction of the nitrosyl–ruthenium moiety.[11,12]

The reaction of *cis*-chlorobis(2-pyridinecarboxylate)nitrosylruthenium, *cis*-$[Ru(NO)Cl(pyca)_2]$ ([**1**]), with OH^- has been reported by Bottomley *et al.*[13] In that reaction, the nitrosyl–nitro conversion did not occur but a new nitrosylruthenium complex was formed. Unfortunately, however, the structure of the product was not reported nor were reactions of [**1**] with other nucleophiles investigated. The pyca ligand, which is an unsymmetrical and negatively charged bidentate ligand, affects the reactivity of the nitrosyl ligand and can give rise to at most six geometrical isomers of the formula of $[Ru(NO)(L)(pyca)_2]$, when L is a monodentate ligand. We report here the reactions of *cis*-$[Ru(NO)X(pyca)_2]^{n+}$ (*trans*(N,N), *cis*(O,O)-configuration) ($X = Cl^-$, NO_2^-, $n = 0$; $X = H_2O$, $n = 1$) with nucleophiles and the structure of the dinuclear nitrosylruthenium complexes whose stereochemical geometry has been changed by the rare geometrical isomerization.

Experimental

Measurements and materials

IR spectra were recorded on a Perkin-Elmer FT-1650 FTIR spectrophotometer using samples prepared as KBr disks. Elemental analyses were performed by the Sophia University Analytical Facility. ^1H NMR and ^{13}C NMR spectra were obtained with a JEOL JML-LA500 spectrometer. Cyclic voltammetric measurements were made on CH_3CN and DMF containing $0.1\ mol\ dm^{-3}$ tetraethylammonium perchlorate, TEAP, (Nakarai Tesque. Ltd.) as supporting electrolyte with a platinum disk working electrode ($\phi = 1.6$ mm), and an $Ag|0.01\ mol\ dm^{-3}\ AgNO_3$ reference electrode using a BAS 100B/W Electrochemical Analyzer. At the end of each measurement, ferrocene was added as an internal standard to correct redox potentials. *cis*-$[Ru(NO)Cl(pyca)_2]$ ([**1**]) and *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ were prepared following literature procedures.[11,13] All other solvents and chemicals were of reagent quality and were used without further purification.

Preparation of *cis*-$[Ru(NO)(H_2O)(pyca)_2]ClO_4$

To a suspension of *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ 70 mg in $15\ cm^3$ water was added dropwise $0.7\ cm^3$ $HClO_4$ (60% solution), and the suspension was heated for 3 hours at 80 °C to give a yellow solution. The solution was concentrated to *ca.* $5\ cm^3$ on a hot plate. After the solution was cooled and 100 mg $NaClO_4$ was added, a yellow precipitate of *cis*-$[Ru(NO)(H_2O)(pyca)_2]ClO_4$ deposited. The product was collected by filtration, washed with water, ethanol and diethyl ether and dried *in vacuo* (70 mg, 85%), (Found: C, 29.24; H, 2.06; N; 8.86. Calc. for $C_{12}H_{10}N_3$-

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$O_{10}ClRu$: C, 29.25; H, 2.05; N, 8.53%); ν_{max}/cm^{-1} (NO) 1894; δ_H (d_6-DMSO) 8.11 (1H, t, py), 8.16 (1H, t, py), 8.27 (1H, t, py), 8.47 (1H, t, py), 8.57 (2H, t, py), 8.75 (1H, d, py), 9.05 (1H, d, py); δ_C (d_6-DMSO) 127.6 (py), 127.7 (py), 129.8 (py), 130.7 (py), 143.0 (py), 143.9 (py), 148.4 (py), 149.0 (py), 149.4 (py), 152.2 (py), 169.0 (COO^-), 171.3 (COO^-).

Reaction of [Ru(NO)Cl(pyca)$_2$] ([1]) in alkaline aqueous solution to form [{Ru(NO)(pyca)$_2$}$_2$(μ-H_3O_2)]PF_6·$2H_2O$ ([2]PF_6·$2H_2O$)

A suspension of [**1**] 300 mg in 0.05 mol dm^{-3} NaOH aqueous solution 40 cm^3 was heated for 30 min, giving a yellow solution (*ca.* pH 12). This solution was concentrated to *ca.* 5 cm^3 on a hot plate, and NH_4PF_6 was added. Allowing the solution to stand for 3 days resulted in the deposition of a yellow precipitate of [{Ru(NO)(pyca)$_2$}$_2$(μ-H_3O_2)]PF_6·$2H_2O$. The product was collected by filtration, washed with water, ethanol and diethyl ether and then dried *in vacuo* (210 mg, 60%), (Found: C, 29.67; H, 2.27; N, 8.47. Calc. for $C_{24}H_{23}N_6O_{14}F_6PRu_2$: C, 29.82; H, 2.40; N, 8.69%); ν_{max}/cm^{-1} (NO) 1896, 1910.

Reaction of [1] with NaN_3 in water to form ([2]PF_6·$2H_2O$)

A suspension of [**1**] 20 mg and NaN_3 15 mg in H_2O 20 cm^3 was heated for 30 min to give a yellow solution (*ca.* pH 7). The solution was concentrated to *ca.* 5 cm^3 on a hot plate. After the solution was cooled, NH_4PF_6 was added. A yellow precipitate of [**2**]PF_6 deposited by allowing the solution to stand for 3 days. The product was collected by filtration, washed with water, ethanol and diethyl ether and dried *in vacuo* (10 mg, 43%).

Reaction of [1] with $NaOCH_3$ in methanol to form *trans*-[Ru(NO)(OCH_3)(pyca)$_2$] ([3])

A suspension of [**1**] 100 mg and $NaOCH_3$ 14 mg in methanol 20 cm^3 was refluxed for an hour until a yellow solution was obtained. The solution was reduced to *ca.* 5 cm^3, and diethyl ether was added to give a yellow precipitate. The product was collected by filtration, washed with diethyl ether and dried *in vacuo* (90 mg, 94%), (Found: C, 38.38; H, 2.62; N, 10.43. Calc. for $C_{13}H_{11}N_3O_6Ru$: C; 38.43, H; 2.73, N; 10.34%); ν_{max}/cm^{-1} (NO) 1838; δ_H (CD_3CN) 2.19 (3H, s, CH_3), 7.87 (2H, t, 5-py), 8.19 (2H, d, 3-py), 8.33 (2H, t, 4-py), 8.76 (2H, d, 6-py); δ_C (CD_3CN) 56.9 (CH_3), 128.3 (py), 129.9 (py), 143.4 (py), 150.8 (py), 152.0 (py), 172.7 (COO^-).

Reaction of [{Ru(NO)(pyca)$_2$}$_2$(μ-H_3O_2)]PF_6·$2H_2O$ ([2]PF_6·$2H_2O$) in acidic aqueous solution to form *trans*-[Ru(NO)(H_2O)(pyca)$_2$]ClO_4·$0.5H_2O$ ([4]ClO_4·$0.5H_2O$)

To a suspension of [**2**]PF_6·$2H_2O$ 180 mg in water 20 cm^3 was added $HClO_4$ 0.6 cm^3, and the suspension was heated at 80 °C for 3 hours to give a yellow solution. This solution was concentrated to *ca.* 5 cm^3 on a hot plate, and $NaClO_4$ was added to give a precipitate. The product was collected by filtration, washed with water, ethanol and diethyl ether and dried *in vacuo* (120 mg, 64%), (Found: C, 28.71; H, 2.20; N, 8.33. Calc for $C_{12}H_{11}N_3O_{10.5}ClRu$: C, 28.73; H, 2.21; N, 8.37%); ν_{max}/cm^{-1} (NO) 1940 cm^{-1}; δ_H (d_6-DMSO) 8.10 (2H, t, 5-py), 8.27 (2H, d, 3-py), 8.53 (2H, t, 4-py), 8.82(2H, d, 6-py); δ_C (d_6-DMSO) 127.3 (py), 129.7 (py), 143.6 (py), 149.7 (py), 150.5 (py), 170.9 (COO^-).

X-Ray crystallography

A single crystal of [**2**]PF_6·$2H_2O$ was obtained by slow evaporation of an alkaline solution of [**1**] and that of [**3**]·CH_3OH by recrystallization from the methanol solution of [**3**]. The intensity data were collected on a Rigaku RAXIS–RAPID Imaging Plate diffractometer with graphic monochromatized MoKα radiation (0.71069 Å). All the calculations were carried out on an O_2 Workstation (Silicon Graphics Corporation) using the TEXSAN crystallographic software package.[14] The structures were solved by a direct method, expanded using Fourier techniques and refined using full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. For [**2**]PF_6·$2H_2O$ the hydrogen atoms, except the two hydrogen atoms bonded to the free water molecule, were located in the final difference Fourier map. For [**3**]·CH_3O all hydrogen atoms were located in the final difference Fourier map. The crystallographic data of [**2**]PF_6·$2H_2O$ and [**3**]·CH_3OH are summarized in Table 1.

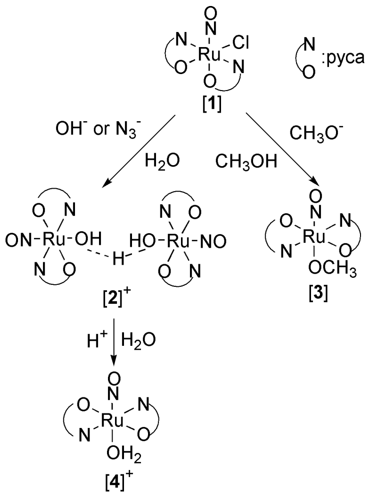
CCDC reference numbers 177496 and 177497.

See http://www.rsc.org/suppdata/dt/b2/b200417h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Reaction of *cis*-[Ru(NO)Cl(pyca)$_2$] [1] with nucleophiles in water

The {RuNO}^{6}-type nitrosylruthenium complexes are well known to react with nucleophiles at the nitrosyl nitrogen atom under mild experimental conditions.[4–6] The electrophilic reactivity of the nitrosyl complex is correlated with the electron density of the nitrogen atom of the nitrosyl ligand, which is reflected in the ν(NO) and reduction potentials. The ν(NO) of [**1**] is observed at 1890 cm^{-1}, and its cyclic voltammogram in CH_3CN shows a reversible redox couple at $E_{1/2} = -0.71$ V and an irreversible reduction wave at $E_{pc} = -1.48$ V (see Table 2), assigned to the reductions based on the nitrosyl ligand, $(RuNO)^{3+/2+}$ couple and $(RuNO)^{2+/+}$ reduction, respectively. These data indicate that [**1**] is a typical nitrosylruthenium complex of {RuNO}^{6}-type, and is at the boundary between those reactive and unreactive to nucleophiles at the nitrogen atom of the nitrosyl ligand. The reactions discussed in this paper are summarized in Scheme 1.



Scheme 1

The reaction of [**1**] in alkaline aqueous solution (pH 12) has been performed under the same conditions as reported by Bottomley *et al.*[13] Although they mentioned, based on the elemental analysis, that the reaction product was a μ-hydroxo dimer, [{Ru(NO)(pyca)$_2$}$_2$(μ-OH)]PF_6·$2H_2O$, our reaction product can be identified as a hydroxide hydrate anion ($H_3O_2^-$) bridged nitrosylruthenium dimer, [{Ru(NO)(pyca)$_2$}$_2$(μ-H_3O_2)]PF_6·$2H_2O$ ([**2**]PF_6·$2H_2O$) by the IR measurement, the elemental analysis, and X-ray crystallography. The structure of the complex cation of [**2**]PF_6 is shown in Fig. 1 and selected bond distances and angles are listed in Table 3. This cation consists of two nitrosylruthenium units, Ru1 and Ru2, which are linked to each other through a strong hydrogen bond between O2 and O8, 2.427(3) Å. This bridging unit is regarded as hydroxide hydrate anion, $H_3O_2^-$, being composed of hydroxo and aqua

Table 1 Crystallographic data for [**2**]PF_6·$2H_2O$ and [**3**]·CH_3OH

	[**2**]PF_6·$2H_2O$	[**3**]·CH_3OH
Formula	$C_{24}H_{23}N_6O_{14}Ru_2PF_6$	$C_{14}H_{15}O_7N_3Ru$
M	966.58	439.37
Color	Yellow	Orange
Crystal size/mm	0.10 × 0.10 × 0.25	0.17 × 0.25 × 0.30
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.7164(2)	8.120(1)
b/Å	13.5928(2)	15.082(3)
c/Å	21.0368(4)	7.009(1)
α/°	90	91.963(7)
β/°	99.750(1)	103.913(6)
γ/°	90	97.687(10)
V/Å^3	3301.88(9)	823.8(2)
Z	4	2
D_c/g cm^{-1}	1.94	1.77
μ(MoKα)/cm^{-1}	10.74	9.95
T/°C	−150	−100
Trans. factor	0.820–0.936	0.694–0.844
$2\theta_{max}$/°	55.0	55.0
No. of total reflections collected	28439	6734
No. of unique reflections	7559	3510
No. of observed reflections ($I > 3\sigma(I)$)	5535	3374
No. of variables	478	226
R	0.029	0.035
R_w	0.036	0.073
R_{int}	0.042	0.020
GOF	1.04	1.44

Table 2 Infrared and redox potential data

Complex	ν(NO)/cm^{-1}	$E_{1/2}$/V[a]	E_{pc}/V[a]
[**1**]	1890	−0.71[b]	−1.48[b]
[**2**]PF_6·$2H_2O$	1896, 1910		
[**3**]	1838	−1.12[b]	−1.71[b]
[**4**]ClO_4·$0.5H_2O$	1940	−0.53[c]	−1.23[c]
cis-[Ru(NO)(NO_2)(pyca)$_2$]	1907	−0.60[b]	−1.46[b]
cis-[Ru(NO)(H_2O)(pyca)$_2$](ClO_4)	1894	−0.57[c]	−1.34[c]

[a] *vs.* Ag\|0.1 mol dm^{-3} $AgNO_3$ (AN). [b] Measured in CH_3CN containing TEAP. [c] Measured in DMF containing TEAP.

Table 3 Selected bond distances (Å) and angles (°) for [**2**]PF_6·$2H_2O$

Ru1–N1	1.739(3)	Ru1–N2	2.064(3)
Ru1–N3	2.058(3)	Ru1–O2	1.995(2)
Ru1–O3	2.026(2)	Ru1–O5	2.038(2)
Ru2–N4	1.744(3)	Ru2–N5	2.056(3)
Ru2–N6	2.060(3)	Ru2–O8	1.992(2)
Ru2–O9	2.042(2)	Ru2–O11	2.032(2)
N1–O1	1.150(3)	N4–O7	1.153(3)
O2–O8	2.427(3)		
O2–H1	0.88	O2–H2	0.87
O8–H11	1.02		
Ru1–N1–O1	178.0(3)	Ru2–N4–O7	177.1(3)

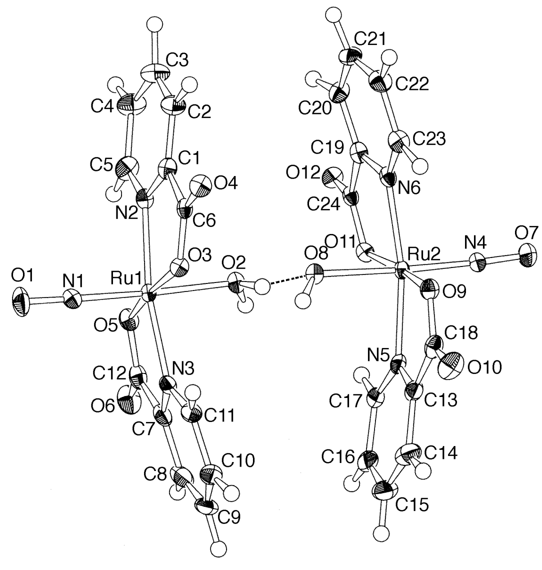


Fig. 1 Structure of [**2**]$^+$ with atom labels. Labels of hydrogen atoms are omitted for clarity.

moieties. The hydrogen atoms of the $H_3O_2^-$ moiety have been located in the difference Fourier map. Both Ru units have the expected octahedral coordination geometry around the ruthenium atoms. Two pyca ligands in each unit coordinate to the ruthenium center in the *trans*-form with the pyridyl nitrogen atoms and the carboxylic oxygen atoms being in the *trans* position to each other (*trans*(N,N), *trans*(O,O)-configuration). The Ru–N(nitrosyl) bond distances are 1.739(3) (Ru1–N1) and 1.744(3) Å (Ru2–N4), and the N–O bond distances of the nitrosyl ligand are 1.150(3) (N1–O1) and 1.153(3) Å (N4–O7). The Ru–N–O angles of the nitrosylruthenium moieties are 178.0(3) (Ru1–N1–O1) and 177.1(3)° (Ru2–N4–O7); the Ru–N–O moieties are thus essentially linear as expected for the $\{RuNO\}^6$ configuration.[2] The Ru–N(pyca) and Ru–O bond distances of two pyca ligands are similar to those of previously reported ruthenium complexes containing the pyca ligand.[13,15] No remarkable difference is found in the structural parameters between Ru1 and Ru2 units. The oxygen atoms of the aqua and hydroxo ligands in the bridging unit exist at the *trans* positions to the nitrosyl ligands. Although the central hydrogen atom of the $H_3O_2^-$ moiety can be found near the O2 atom in the Ru1 unit, 0.88 Å (O2–H1), the two Ru–O bond distances of the present complex are nearly the same as each other (1.995(2) (Ru1–O2) and 1.992(2) Å (Ru2–O8)). The values of the Ru–O bond are longer than those of reported ruthenium–hydroxo moieties (*ca.* 1.87–1.99 Å), and shorter than those of reported ruthenium–aqua moieties (*ca.* 2.04–2.08 Å) in $\{RuNO\}^6$-type complexes.[9,16–22] They are in analogy with the Ru–O bond distances of the previously reported ruthenium complexes having the $H_3O_2^-$ bridging unit.[23–25] Although metal–oxygen bond distances are distinctly different from each other between metal–aqua and metal–hydroxo moieties in the cases of Fe and Zn complexes containing the $H_3O_2^-$ bridging unit,[26–29] it is difficult to distinguish between the aqua and hydroxo complexes from the comparison of their structural parameters in the present complex. The short O2–O8 bond distance, 2.427(3) Å, of the $H_3O_2^-$ bridging unit indicates the existence of a strong hydrogen bond between O2 and O8 atoms. The strong interaction between two ruthenium centers or ruthenium–nitrosyl moieties should be predictable from this short distance compared with those of similar ruthenium complexes containing the $H_3O_2^-$ bridging unit. The two oxygen atoms (O13 and O14) of the two free water molecules bond to each other by a hydrogen bond, 2.747(6) Å (O13–O14). The O14 atom is sited near the nitrosyl ligand of the Ru1 unit, 3.223(6) Å (O1–O14). The IR spectrum shows two strong bands at 1896 and 1910 cm^{-1} assigned to ν(NO) and $[\mathbf{2}]^+$ is thus classified into $\{RuNO\}^6$-type. The present dimer complex is insoluble in solvents usually used for electrochemical and spectrochemical measurements, except DMSO and DMF. The CV in DMF shows two reduction waves at the same potentials and the same wave profiles as those of $[\mathbf{4}]^+$ described below. It is difficult to investigate the chemistry of the complex further in solution.

This *cis*–*trans* geometrical isomerization from the *trans*-(N,N), *cis*(O,O)-configuration in [**1**] to the *trans*(N,N), *trans*(O,O)-configuration in $[\mathbf{2}]^+$ is rare in the sense that the change in conformation of co-existing ligands occurs in the reaction of the $\{RuNO\}^6$-type nitrosylruthenium complex with the hydroxide anion. Contrary to this, the *trans*-form nitrosylruthenium cannot be obtained by the reaction of *cis*-$[Ru(NO)(X)(pyca)_2]^{n+}$ (X = Cl^- [**1**], NO_2^-, H_2O) (*trans*(N,N), *cis*(O,O)-configuration) either in acidic (*ca.* pH 3) or neutral (*ca.* pH 7) conditions. Although the reaction of *cis*-$[Ru(NO)(NO_2)(pyca)_2]$ (*trans*(N,N), *cis*(O,O)-configuration) in the acidic conditions gives *cis*-$[Ru(NO)(H_2O)(pyca)_2]^+$, no *trans*-form complex is obtained; only starting complexes are recovered during the reactions of *cis*-$[Ru(NO)(X)(pyca)_2]^{n+}$ (X = Cl^-, H_2O) complexes in acidic and neutral conditions. These results indicate that the hydroxide anion contributes to the *cis*–*trans* isomerization.

The reaction of $\{RuNO\}^6$-type nitrosyl complexes with the azide ion is well known to form the corresponding solvated complexes by the reactions at the nitrosyl nitrogen.[30] Contrary to this general observation, the reaction of [**1**] (*cis*-form) with an excess of N_3^- in water (*ca.* pH 7) gives the product of [**2**]PF_6 (*trans*-form), identified by the IR measurement and the elemental analysis, like the reaction of [**1**] with OH^- (Scheme 1). The reactivity of [**1**] toward nucleophiles such as OH^- and N_3^- is thus relatively low, which is supported by the results of measurements of IR and redox properties. It seems that OH^- and N_3^- contribute to the *cis*–*trans* isomerization, although the detailed reaction mechanism is not clarified yet.

Reaction of [1] with $NaOCH_3$ in methanol

The reaction of [**1**] with equimolar $NaOCH_3$ in methanol gives *trans*-$[Ru(NO)(OCH_3)(pyca)_2]\cdot CH_3OH$ ([**3**]$\cdot CH_3OH$) (Scheme 1). Therefore, the *cis*–*trans* geometrical isomerization also occurs by the reaction of [**1**] with CH_3O^- in methanol. A strong ν(NO) of [**3**] is observed at 1838 cm^{-1}, similar to that of *trans*-$[Ru(OCH_3)(pdma)(py)_2(NO)](PF_6)_2$ (pdma = 1,2-phenylenebis(dimethylarsine)).[31] The ^1H NMR spectrum of [**3**] shows four signals assigned to hydrogen atoms of the pyridyl moieties and the ^{13}C NMR spectrum five signals of carbon atoms of pyridyl moieties and a signal of the carboxyl carbon. These results are consistent with the result of the X-ray structural analysis shown in Fig. 2 and Table 4. The nitrogen atom of the nitrosyl ligand is located at the *trans* position to the oxygen atom of the methoxo ligand, and two pyca ligands coordinate to Ru in the *trans*-form with the pyridyl nitrogen atoms and carboxylic oxygen atoms being at the *trans* position to each other (*trans*(N, N), *trans*(O, O)-configuration). The bond distances of Ru–N(pyridyl), 2.076(3) and 2.073(3) Å, and those of Ru–O(carboxyl), 2.035(2) and 2.036(2) Å, are, respectively, approximately equivalent to each other (Table 4). These values are similar to those of previously reported ruthenium complexes containing pyca ligands.[13,15] The nitrosyl ligand with Ru–N(nitrosyl) 1.760(3), N(nitrosyl)–O(nitrosyl) 1.143(4) Å, and Ru–N(nitrosyl)–O(nitrosyl) 173.3(3)°, is essentially linearly coordinated to the ruthenium center as expected for the $\{RuNO\}^6$ configuration.[2] The bond distance of Ru–O(methoxo), 1.964(2) Å, is almost the same as those of previously reported complexes.[32]

Table 4 Selected bond distances (Å) and angles (°) for [**3**]$\cdot CH_3OH$

Ru–N1	1.760(3)	Ru–N2	2.076(3)
Ru–N3	2.073(3)	Ru–O2	1.964(2)
Ru–O3	2.035(2)	Ru–O5	2.036(2)
N1–O1	1.143(4)		
Ru–N1–O1	173.3(3)	Ru–O2–C1	123.6(2)

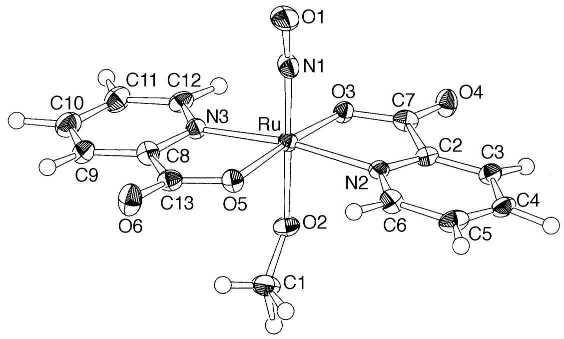


Fig. 2 Structure of [**3**] with atom labels. Labels of hydrogen atoms are omitted for clarity.

Reaction of $[\{Ru(NO)(pyca)_2\}_2(\mu\text{-}H_3O_2)]^+$ ($[\mathbf{2}]^+$) in acidic conditions

Heating of the complex $[\mathbf{2}]^+$ in acidic conditions yields *trans*-$[Ru(NO)(H_2O)(pyca)_2]^+$, $[\mathbf{4}]^+$ (Scheme 1). This result is in agreement with Bottomley's report on the reaction of the nitrosylruthenium dimer with $HClO_4$.[13] The ^{13}C NMR spectrum of $[\mathbf{4}]^+$ in d_6-DMSO shows six signals assigned to carbon atoms of the pyridyl and carboxyl moieties and the ^1H NMR spectrum four signals assigned to hydrogen atoms of the pyridyl moieties, indicating $[\mathbf{4}]^+$ has the *trans*(N,N), *trans*(O,O)-configuration (*trans*-form). The IR spectrum of [**4**]$ClO_4\cdot 0.5H_2O$ shows a strong band at 1940 cm^{-1} assigned to NO stretching, and the CV in DMF shows a reversible redox couple at −0.53 V and an irreversible reduction wave at −1.23 V. The results of IR and CV measurements indicate $[\mathbf{4}]^+$ belongs to $\{RuNO\}^6$-type nitrosylruthenium.[4–9] The change of $[\mathbf{2}]^+$ into $[\mathbf{4}]^+$ thus occurs *via* protonation at the bridging ligand, $H_3O_2^-$, of $[\mathbf{2}]^+$. A characteristics comparison of ν(NO) absorption band between *cis*- and *trans*-isomers of $[Ru(NO)(H_2O)(pyca)_2]^+$ indicates the *trans*-isomer $[\mathbf{4}]^+$ is a better electrophile than the *cis*-isomer, *cis*-$[Ru(NO)(H_2O)(pyca)_2]ClO_4$ (*trans*(N,N), *cis*-(O,O)-configuration) (1894 cm^{-1}). The value of ν(NO) of [**4**]ClO_4 is comparable to that of reported *cis*-$[Ru(NO)(NH_3)(bpy)_2]^{3+}$, which indicates that $[\mathbf{4}]^+$ can be regarded as a typical complex exhibiting a nitrosyl ligand reaction such as a nitrosyl–nitro acid–base reaction and an electrophilic reaction at the nitrosyl nitrogen.[10] However, any chemical reactivity of $[\mathbf{4}]^+$ toward nucleophiles cannot be examined due to its insolubility in any solvent commonly used except DMSO and DMF.

Conclusion

Some of the $\{RuNO\}^6$-type complexes undergo nucleophilic attack at the nitrogen of the nitrosyl ligand by nucleophiles such as OH^-, OR^- and N_3^-. Although thermally- and photochemically-induced geometrical isomerization reactions of $\{RuNO\}^6$-type nitrosylruthenium complexes[33–35] and redox-induced structural isomerization of a coexisting ligand such as a nitrite ion[11,12] have been reported, the present *cis–trans* isomerization reaction is rare in the reaction of nitrosylruthenium complexes with nucleophiles. The reactivity of $[Ru(NO)(X)(pyca)_2]^{n+}$ (X = Cl^- ([**1**]), NO_2^- and H_2O) toward nucleophilic reagents can be classified as at the boundary of being reactive and unreactive. The characteristic feature of [**1**] and the *cis–trans* geometrical isomerization observed in the present study stem from the existence of a nitrosyl ligand and the σ and π electrostatic interactions between the nitrosyl and co-existing ligands through the ruthenium ion such as a *trans*-effect to stabilize a specific configuration.[36]

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