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FULL PAPER

Reactions of $[RuCl_2(NO)(terpy)]^+$ (terpy = 2,2′ : 6′,2″-terpyridine) with mono anions such as NO_2^-, Br^- and N_3^-, and structural studies on terpyridineruthenium having a nitrosyl ligand

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$[RuCl_2(NO)(terpy)]PF_6$ ([**1**]PF_6) has been synthesized by the reaction of $K_2[RuCl_5(NO)]$ with terpy and characterized by single-crystal X-ray crystallography. [**1**]PF_6 has a structure in which the two chloro ligands are located *trans* to each other with the nitrosyl ligand on the plane of the terpy ligand. Reactions of [**1**]PF_6 with mono anions such as NO_2^-, Br^- and N_3^- have been investigated. Its reactions with NO_2^- in H_2O and CH_3OH afford nitrosylterpyridineruthenium complexes, $[Ru(OH)(NO_2)(NO)(terpy)]PF_6$ ([**2**]PF_6) and $[RuCl(OCH_3)(NO)(terpy)]PF_6$ ([**3**]PF_6), respectively, whose geometrical configurations differ from that of [**1**]$^+$. The Br^--substituted complex of [**1**]$^+$, $[RuBr_2(NO)(terpy)]PF_6$ ([**4**]PF_6), and two solvated complexes, $[RuCl_2(CH_3CN)(terpy)]$ ([**5**]) and $[RuCl(CH_3CN)_2(terpy)]PF_6$ ([**6**]PF_6), have been formed in its reactions with Br^- and N_3^-. Structures of [**2**]PF_6, [**3**]PF_6 and [**4**]PF_6 have been determined by singal-crystal X-ray crystallography and compared with each other.

Introduction

A number of $\{RuNO\}^6$-type nitrosylruthenium complexes have been synthesized and their structures and chemical, photochemical and electrochemical properties have been widely studied.[1–12] Reactivities of the nitrosyl ligand have been discussed in connection with the electron configuration of the nitrosyl–ruthenium moiety and electronic and/or structural effect(s) of coexisting ligands.[1–3] In our previous investigations on $[Ru(NO)(L^1)(L^2)_4]^{n+}$-type complexes ($L^1 = Cl$, NO_2 or ONO, L^2 = pyridine, 1/2(2,2′-bipyridine) or 1/2(pyridine-2-carboxylate)), we showed that the nitrosyl ligand of these complexes plays an important role in the stability of the complexes and reactions such as a structural rearrangement of the coexisting ligand (L^1) accompanying the reduction of the nitrosyl ligand.[4] In $[Ru(NO)(L^1)(L^2)_4]^{n+}$-type complexes, the L^1 ligand functions as a labile site or regulates the reactivity of the nitrosyl ligand, and pyridyl ligands (L^2) are inert sites, forming strong Ru–N bonds with the ruthenium center. In the present investigation, $[Ru(NO)(L^1)(L^{1\prime})(L^3)]$-type complexes having two labile ligands (L^1 and $L^{1\prime}$ = Cl, Br, NO_2, OH or OCH_3) have been synthesized using tridentate 2,2′ : 6′,2″-terpyridine (terpy; L^3). The terpy ligand is known to show interesting photo- and electro-chemical behavior like the bpy ligand in coordination compounds.[13] This paper describes the synthesis of *trans*(Cl,Cl),-*cis*(Cl,NO)-$[RuCl_2(NO)(terpy)]^+$ ([**1**]$^+$) as a starting complex and its reactions with several mono anions to form new terpyridinenitrosylruthenium complexes, $[Ru(L^1)(L^{1\prime})(NO)(terpy)]^{n+}$.

Experimental

Measurements

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 and ^{13}C NMR spectra were obtained with a JEOL JML-LA500 spectrometer in CD_3CN using $(CH_3)_4Si$ as an internal reference. Cyclic voltammetric measurements were made in acetonitrile solutions containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (Nakarai Tesque. Ltd.) as supporting electrolyte with a platinum disk working electrode (φ =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.

Materials

$RuCl_3 \cdot nH_2O$ was purchased from Furuya Kinzoku Co. 2,2′ : 6′,2″-Terpyridine was purchased from Aldrich Chemical Co. $K_2[RuCl_5(NO)]$ was prepared by the procedure reported in the literature.[5] All other solvents and chemicals were of reagent quality and were used without further purification.

Synthesis of $[RuCl_2(NO)(terpy)]PF_6$ ([1]PF_6). $K_2[RuCl_5(NO)]$ (100 mg, 0.26 mmol), terpy (60 mg, 0.26 mmol) and KCl (400 mg, 5.37 mmol) were suspended in C_2H_5OH–H_2O (3 : 1 v/v; 20 cm^3). This mixture was refluxed for an hour to give a reddish-brown solution. This solution was cooled to room temperature. NH_4PF_6 (100 mg) was added to the solution as a precipitating agent. The brown product obtained was collected by filtration, washed with methanol and diethyl ether and then dried *in vacuo* (60 mg, 40%), (Found: C, 30.89; H, 1.75; N, 9.18. Calc. for $[RuCl_2(NO)(terpy)]PF_6$: C, 31.05; H, 1.91; N, 9.66%).

Reaction of [1]PF_6 with NO_2^- in H_2O to form $[Ru(OH)(NO_2)(NO)(terpy)]PF_6$ ([2]PF_6). A suspension of [**1**]PF_6 (100 mg, 0.26 mmol) and $NaNO_2$ (60 mg, 0.87 mmol) in water (20 cm^3) was refluxed for an hour to give a yellow solution. The solution was concentrated on a hot plate to *ca.* 5 cm^3. After the solution was cooled, NH_4PF_6 (100 mg) was added. The yellow product obtained was collected by filtration, washed with cold water, ethanol and diethyl ether and dried *in vacuo* (78 mg, 80%), (Found: C, 31.48; H, 2.12; N, 12.17. Calc. for $[Ru(OH)(NO_2)(NO)(terpy)]PF_6$: C, 31.48; H, 2.11; N, 12.24%).

Reaction of [1]PF_6 with NO_2^- in CH_3OH to form $[RuCl(OCH_3)(NO)(terpy)]PF_6 \cdot 0.5H_2O$ ([3]$PF_6 \cdot 0.5H_2O$). A suspension of [**1**]PF_6 (100 mg, 0.26 mmol) and $NaNO_2$ (60 mg, 0.87 mmol) in methanol (20 cm^3) was refluxed for an hour to give an

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Table 1 Crystallographic data for [RuCl$_2$(NO)(terpy)]PF$_6$ ([**1**]PF$_6$), [Ru(OH)(NO$_2$)(NO)(terpy)]PF$_6$ ([**2**]PF$_6$), [RuCl(OCH$_3$)(NO)(terpy)]PF$_6$ ([**3**]PF$_6$) and [RuBr$_2$(NO)(terpy)]PF$_6$ ([**4**]PF$_6$)

	[**1**]PF$_6$	[**2**]PF$_6$	[**3**]PF$_6$	[**4**]PF$_6$
Formula	$C_{15}H_{11}ON_4Cl_2F_6PRu$	$C_{15}H_{12}O_4N_5F_6PRu$	$C_{16}H_{15}O_{2.5}N_4ClF_6PRu$	$C_{15}H_{11}ON_4Br_2F_6PRu$
FW	580.22	572.33	584.81	669.12
Color	Brown	Orange	Brown	Reddish-brown
Crystal size/mm	0.23 × 0.17 × 0.13	0.40 × 0.30 × 0.20	0.30 × 0.30 × 0.25	0.17 × 0.15 × 0.07
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2/n$	$P2_1/c$
a/Å	9.0749(4)	9.7439(5)	10.254(2)	9.187(1)
b/Å	16.4893(9)	13.9922(8)	8.545(2)	16.638(1)
c/Å	12.8905(6)	14.654(1)	24.593(2)	13.1219(9)
β/°	95.753(2)	106.286(2)	96.93(1)	95.479(5)
V/Å^3	1919.2(2)	1917.7(2)	2139.1(7)	1996.6(3)
Z	4	4	4	4
D_c/g cm^{-3}	2.01	1.98	1.82	2.23
μ(MoKα)/cm^{-1}	12.51	9.94	10.08	49.51
Transmission factor	0.625–0.850	0.546–0.820	0.788–0.998	0.492–0.778
$2\theta_{max}$/°	54.9	55.0	55.0	55.0
No. of total reflections collected	17377	14814	10001	18624
No. of unique reflections	4387	4374	4907	4576
No. of observed reflections ($I > 3\sigma(I)$)	3379	3657	3728	2934
No. of variables	271	289	288	271
R	0.038	0.060	0.045	0.031
R_w	0.047	0.096	0.060	0.039
R_{int}	0.052	0.041	0.030	0.055
GOF	1.28	1.08	1.97	1.00

orange solution. This solution was concentrated using a rotary evaporator to *ca.* 5 cm^3, and NH$_4$PF$_6$ (100 mg) was added. Addition of diethyl ether precipitated an orange crude product. This crude product was purified by column chromatography with alumina as column packing material and acetonitrile as the eluent. The portion of the eluent containing the product was collected and the solvent was removed with a rotary evaporator (25 mg, 24%), (Found: C, 32.62; H, 2.43; N, 9.51. Calc. for [RuCl(OCH$_3$)(NO)(terpy)]PF$_6$·0.5H$_2$O: C, 32.86; H; 2.59, N; 9.58%).

Reaction of [1]PF$_6$ with Br$^-$ to form [RuBr$_2$(NO)(terpy)]PF$_6$ ([4]PF$_6$). [**1**]PF$_6$ (50 mg, 0.13 mmol) and KBr (120 mg, 1.01 mmol) were suspended in C$_2$H$_5$OH–H$_2$O (3 : 1 v/v 20 cm^3). The suspension was heated under reflux for 6 hours to give a reddish-brown solution. The solution was concentrated on a hot plate to *ca.* 2 cm^3 to form a brown precipitate. The precipitate was collected by filtration, washed with cold water, ethanol and then diethyl ether and dried *in vacuo* (42 mg, 73%), (Found: C, 27.07; H, 1.66; N, 8.30. Calc. for [RuBr$_2$(NO)(terpy)]PF$_6$: C, 26.93; H, 1.66; N, 8.37%).

Reaction of [1]PF$_6$ with N$_3^-$ in CH$_3$CN to form [RuCl$_2$(CH$_3$CN)(terpy)]·CH$_2$Cl$_2$ ([5]·CH$_2$Cl$_2$). A suspension of [**1**]PF$_6$ (50 mg, 0.13 mmol) and NaN$_3$ (8 mg, 0.12 mmol) in acetonitrile (40 cm^3) was stirred for 12 hours to give a dark purple solution. The solution was concentrated using a rotary evaporator to *ca.* 5 cm^3. Diethyl ether was added to the solution to give a dark purple crude product. The crude product was collected by filtration and was recrystallized from CH$_2$Cl$_2$ (20 mg, 44%), (Found: C, 40.12; H, 3.02; N, 11.00. Calc. for [RuCl$_2$(CH$_3$CN)(terpy)]·CH$_2$Cl$_2$: C, 40.70; H, 3.04; N, 10.55%); *m*/*z* 446 (M − CH$_2$Cl$_2$), 405 (M − CH$_2$Cl$_2$ − CH$_3$CN), 370 (M − CH$_2$Cl$_2$ − CH$_3$CN − Cl).

Reaction of [1]PF$_6$ with N$_3^-$ in CH$_3$CN to form [RuCl(CH$_3$CN)$_2$(terpy)]PF$_6$ ([6]PF$_6$). A suspension of [**1**]PF$_6$ (50 mg, 0.13 mmol) and NaN$_3$ (8 mg, 0.12 mmol) in acetonitrile (40 cm^3) was stirred for 8 hours at 60 °C to give a brown solution changed from a dark purple solution. The solution was concentrated using a rotary evaporator to *ca.* 5 cm^3. Diethyl ether was added to give a brown product. The brown product was collected by filtration, washed with methanol and diethyl ether and then dried *in vacuo* (28 mg, 54%), (Found: C, 37.83; H, 2.81; N, 11.38. Calc. for [RuCl(CH$_3$CN)$_2$(terpy)]PF$_6$: C, 38.23; H, 2.87; N, 11.73%); δ_H (CD$_3$CN) 4.34 (3H, s, CH$_3$), 5.43 (3H, s, CH$_3$), 7.66 (2H, t, 3-terpy), 798 (2H, t, 4-terpy), 8.04 (2H, t, 5-terpy), 8.32 (2H, d, 3′-terpy) and 8.34 (1H, d, 2-terpy); δ_C (CD$_3$CN) 2.7 (CH$_3$), 3.5 (CH$_3$), 121.5 (3-terpy), 122.9 (4-terpy), 127.0 (5-terpy), 134.3 (3′-terpy), 137.2 (4′-terpy), 153.5 (2-terpy), 158.5 (6-terpy) and 159.2 (2′-terpy); *m*/*z* 452 (M − PF$_6$), 411 (M − PF$_6$ − CH$_3$CN), 370 (M − PF$_6$ − 2CH$_3$CN).

X-Ray crystallography

The crystallographic and intensity data of [**1**]PF$_6$, [**2**]PF$_6$ and [**4**]PF$_6$ were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer and those of [**3**]PF$_6$ on a Rigaku AFC5S automated four-circle diffractometer with graphite monochromated Mo-Kα radiation (0.71069 Å) at 23 °C. All the calculations were carried out on a Silicon Graphics O$_2$ Workstation, using the TEXSAN crystallographic software package of the Molecular Structure Corporation (Houston, TX, 1992). The structures were solved by a direct method, expanded using Fourier techniques and refined using full-matrix least-square techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions, not refined but included in the structure factor calculations. The final cycle of full-matrix least-squares refinements was based on 3379 observations ($I < 3\sigma(I)$) and 271 variable parameters for [**1**]PF$_6$, 3657 and 289 for [**2**]PF$_6$, 3728 and 288 for [**3**]PF$_6$, and 2934 and 271 for [**4**]PF$_6$, respectively. The crystallographic data of [**1**]PF$_6$, [**2**]PF$_6$, [**3**]PF$_6$ and [**4**]PF$_6$ thus obtained are summarized in Table 1.

CCDC reference numbers 165247–165250.

See http://www.rsc.org/suppdata/dt/b1/b101546j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of *trans*(Cl,Cl), *cis*(Cl,NO)-[RuCl$_2$(NO)(terpy)]PF$_6$ ([1]PF$_6$)

The complex [**1**]PF$_6$ has been synthesized by the reaction of K$_2$[RuCl$_5$(NO)] with equimolar amounts of terpy and KCl in C$_2$H$_5$OH–H$_2$O followed by addition of NH$_4$PF$_6$ to precipitate the product. Its infrared data and redox potentials are summar-

Table 2 Infrared data and redox potentials

Complex	ν(NO)/cm^{-1}	$E_{1/2}$ /V	E_{pc}/V
[**1**]PF$_6$	1895	−0.51	−1.12
[**2**]PF$_6$	1860	−0.79	−1.22
[**3**]PF$_6$	1870	−0.90	−1.22
[**4**]PF$_6$	1916	−0.51	−1.04
[**5**]		0.09	
[**6**]PF$_6$		0.63	

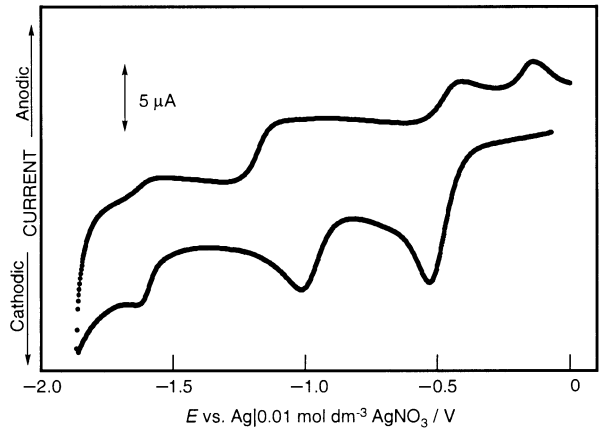

Fig. 1 Cyclic voltammogram of [**1**]PF$_6$ (1 mmol dm^{-3}) in CH_3CN containing $(C_2H_5)_4NClO_4$ (0.1 mol dm^{-3}) as a supporting electrolyte on a Pt working electrode (Scan rate = 200 mV s^{-1}).

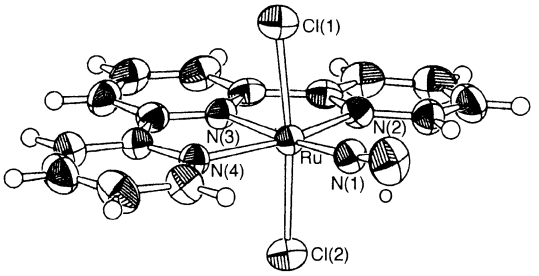

Fig. 2 Structure of [**1**]$^+$ with atom labeling. Carbon atoms of the terpy ligand and all the hydrogen atoms are not labeled for clarity.

ized in Table 2. Nitrosylation of the useful starting complex, [RuCl$_3$(terpy)],[14–16] which is easily synthesized from $RuCl_3\cdot nH_2O$ and terpy, for the synthesis of a nitrosylruthenium complex by NO gas was attempted in vain since [RuCl$_3$(terpy)] is insoluble in all solvents. A characteristic nitrosyl stretching band, ν(NO), of [**1**]PF$_6$ is observed at 1895 cm^{-1} and the cyclic voltammogram (CV) shows a reversible redox couple ($E_{1/2} = -0.51$ V) and two irreversible reduction waves ($E_{pc1} = -1.12$ V, $E_{pc2} = -1.73$ V) (Fig. 1). The reversible and the former irreversible waves are based on reductions of the nitrosyl ligand and the latter irreversible one on a reduction of the terpy ligand.[13–17] As for nitrosyl complexes, the relationship between chemical behavior and physical properties such as ν(NO) and redox potentials has been well studied.[6–9] Nitrosyl complexes having high ν(NO) wavenumbers behave as electrophiles and undergo nucleophilic reactions at the nitrosyl nitrogen. On the other hand, those having low ν(NO) wavenumbers are unreactive to nucleophiles at the nitrosyl nitrogen. Based on its ν(NO) and reduction potentials, the present nitrosyl complex is classified as intermediate between reactive and unreactive nitrosyl complexes.

The structure of [**1**]PF$_6$ was determined by single-crystal X-ray structural analysis and is shown in Fig. 2. The geometry around the ruthenium ion is a distorted octahedron, with the two chloride ions located *trans* to each other and the nitrosyl ligand on the tridentate terpy plane. Therefore, [**1**]PF$_6$ is identified as *trans*(Cl,Cl),*cis*(Cl,NO)-[RuCl$_2$(NO)(terpy)]PF$_6$. The geometrical configuration of [**1**]PF$_6$ is reasonable, since the Cl$^-$ ligand *trans* to the nitrosyl ligand in [RuCl$_5$(NO)]$^{2-}$ is easily substituted by a solvent molecule.[18] The structural parameters of the Ru–NO moiety indicate that the nitrosyl ligand of [**1**]PF$_6$ is linearly coordinated to the ruthenium center and [**1**]PF$_6$ is a {RuNO}^{6}-type of nitrosylruthenium complex.[10,11]

Although the synthesis of [**1**]PF$_6$ was carried out under various different conditions, the yields of [**1**]PF$_6$ were all around 40%. After isolating [**1**]PF$_6$, the filtrate was evaporated to dryness under reduced pressure using an evaporator. The evaporation residue was dissolved in CH_3CN and addition of diethyl ether precipitated a solid mixture after filtration of the insoluble materials. The CV of this mixture shows an oxidation wave at 0.96 V in the oxidative scan, and three reduction waves at −0.49, −0.72 and −1.01 V in the reductive scan. The wave at 0.96 V is assigned to the Ru^{II}/Ru^{III} couple of [Ru(terpy)$_2$](PF$_6$)$_2$ as compared with the potential of the authentic sample.[19–22] Although the waves at −0.49 and −1.01 V are assigned to the (RuNO)$^{3+/2+}$ couple and (RuNO)$^{2+/+}$ reduction of [**1**]PF$_6$, respectively, a differential-pulse voltammetric measurement reveals another wave which overlaps that of [**1**]PF$_6$ at −0.49 V. The IR spectrum of the mixture shows strong bands at 1895 and 1920 cm^{-1} and the band at 1895 cm^{-1} is assigned to the NO stretching vibrational mode of [**1**]PF$_6$. The waves at around −0.49 and −0.72 V in the CV and the strong IR band at 1920 cm^{-1} may indicate the existence of another nitrosylruthenium complex. Attempts to isolate the unidentified nitrosyl complex by recrystallization or column chromatography were unsuccessful. The reaction of K$_2$[RuCl$_5$(NO)] with terpy in the absence of KCl also affords a mixture of [**1**]PF$_6$ and the unidentified nitrosyl complex, but the yield of [**1**]PF$_6$ is increased by the presence of KCl. Thus, the addition of KCl prevents the formation of the unidentified nitrosyl complex. The results of IR analysis and the reduction potential of the mixture suggest that the unidentified nitrosylruthenium complex is a geometrical isomer of [**1**]$^+$ or a nitrosyl complex, containing OH$^-$(H$_2$O) instead of Cl$^-$.

Reactions of [1]PF$_6$ with mono anions

The nitrite ion is a well-known ambidentate ligand functioning as an N- (nitro form) or O-bonded (nitrito form) monodentate ligand.[4,23–25] The coordination mode of the nitrite ion strongly depends on the natures of the central metal and the adjacent ligands. In our previous investigations, it has become possible to isolate nitrito-form complexes in the reactions of polypyridineruthenium complexes containing the nitrosyl ligand, [Ru(NO)(L^1)(L^2)$_4$]$^{n+}$ (L^2 = pyridine, 1/2(2,2′-bipyridine) or 1/2(pyridine-2-carboxylate)), with the nitrite ion, in addition to nitro-form complexes owing to the strong electron-withdrawing character of the nitrosyl ligand.[4] The reaction of [**1**]PF$_6$ with NO_2^- in H_2O affords [Ru(OH)(NO$_2$)(NO)(terpy)]PF$_6$ ([**2**]PF$_6$), and that in CH_3OH, [RuCl(OCH$_3$)(NO)(terpy)]PF$_6$ ([**3**]PF$_6$). IR spectra show a strong stretching band ν(NO) at 1860 cm^{-1} and ν_{as}(NO$_2$) and ν_s(NO$_2$) at 1408 and 1336 cm^{-1}, respectively, for [**2**]PF$_6$ and a ν(NO) band at 1870 cm^{-1} for [**3**]PF$_6$. The CV of [**2**]PF$_6$ in CH_3CN exhibits a reversible wave at $E_{1/2} = -0.79$ V and an irreversible one at $E_{pc} = -1.22$ V, and that of [**3**]PF$_6$ reveals $E_{1/2} = -0.90$ and $E_{pc} = -1.22$ V. Structures of [**2**]PF$_6$ and [**3**]PF$_6$ have been determined by single crystal X-ray crystallography and are shown in Figs. 3 and 4, respectively. Geometries of both [**2**]$^+$ and [**3**]$^+$ are distorted octahedral like that of the starting material [**1**]$^+$ and both [**2**]PF$_6$ and [**3**]PF$_6$ belong to typical {RuNO}^{6}-type nitrosylruthenium complexes. Geometrical configurations of [**2**]$^+$ and [**3**]$^+$ have been determined as *trans*(NO,OH),*cis*(NO,NO$_2$)-[Ru(OH)(NO$_2$)(NO)(terpy)]$^+$ and *trans*(NO,OCH$_3$), *cis*(NO,Cl)-[RuCl(OCH$_3$)(NO)(terpy)]$^+$. It is worth noting that geometrical isomerizations take place during reactions of [**1**]$^+$ with NO_2^- instead of simple substitution reactions by the NO_2^- ion. Reac-

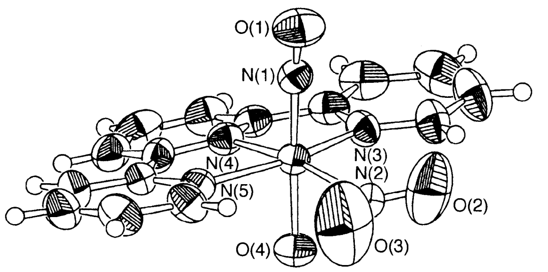

Fig. 3 Structure of $[\mathbf{2}]^+$ with atom labeling. Carbon atoms of the terpy ligand and all the hydrogen atoms are not labeled for clarity.

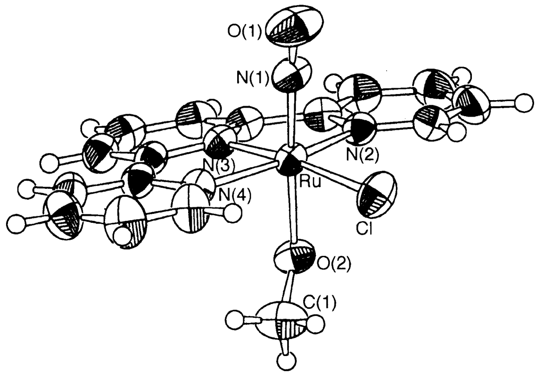

Fig. 4 Structure of $[\mathbf{3}]^+$ with atom labeling. Carbon atoms of the terpy ligand and all the hydrogen atoms are not labeled for clarity.

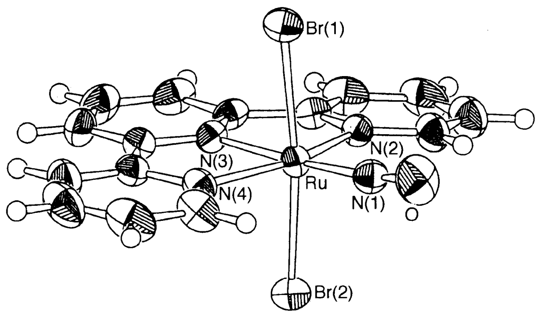

Fig. 5 Structure of $[\mathbf{4}]^+$ with atom labeling. Carbon atoms of the terpy ligand and all the hydrogen atoms are not labeled for clarity.

tions of $\{RuNO\}^6$-type nitrosylruthenium complexes with nucleophiles (Lewis base) have been classified into two types: (i) an addition reaction at the nitrosyl nitrogen followed by some chemical reactions such as deprotonation and bond cleavage, that is, a characteristic reaction of the nitrosyl ligand and (ii) a substitution reaction at the coexisting ligands. The present reaction with NO_2^- seems to be a new type of reaction, *i.e.*, a type (ii) reaction accompanying geometrical isomerization.

The reaction of [**1**]PF_6 with bromide ion affords $[RuBr_2(NO)(terpy)]PF_6$, [**4**]PF_6 by simple substitution of the chloride ions of $[\mathbf{1}]^+$ with bromide ions. A strong NO stretching vibrational mode is observed at 1916 cm^{-1}, and the CV shows a reversible couple at $E_{1/2} = -0.51$ V and an irreversible wave at $E_{pc} = -1.04$ V assignable to $(RuNO)^{3+/2+}$ and $(RuNO)^{2+/+}$, respectively. The single crystal X-ray structural analysis of [**4**]PF_6 reveals that [**4**]PF_6 shows a distorted octahedral geometry similar to that of [**1**]PF_6 (see Fig. 5). In the reaction of [**1**]PF_6 with Br^-, no isomerization reaction is observed and the product has been identified as *trans*(Br,Br),*cis*(Br,NO)-$[RuBr_2(NO)(terpy)]^+$. This reaction is classified in the type (ii) reaction of the $\{RuNO\}^6$-type nitrosylruthenium complexes.

It is well-known that the reaction of the $\{RuNO\}^6$-type nitrosyl complex with N_3^- gives a solvate complex with evolutions of N_2 and N_2O *via* a nucleophilic attack of N_3^- at the nitrosyl nitrogen (eqn. 1):[12]

$$(RuNO)^{3+} + N_3^- + solv \rightarrow [Ru(solv)]^{2+} + N_2 + N_2O \quad (1)$$

In CH_3CN, the reaction of [**1**]PF_6 with N_3^- leads to two solvate complexes, $[RuCl_2(CH_3CN)(terpy)]$, [**5**], and $[RuCl(CH_3CN)_2(terpy)]PF_6$, [**6**]$PF_6$, depending upon the reaction time. The signals in the ^1H and ^{13}C NMR spectra assigned to terpy and CH_3CN ligands and the redox couples of Ru^{II}/Ru^{III} of [**5**] and [**6**]PF_6 indicate that [**5**] and [**6**]PF_6 are diamagnetic ruthenium(II) complexes. ^1H and ^{13}C NMR spectra of [**6**]PF_6 show two signals assigned to CH_3CN ligands, and indicate two CH_3CN ligands located *cis* to each other. Thus, [**6**]PF_6 is identified as *trans*-(Cl,CH_3CN),*cis*(CH_3CN,CH_3CN)-$[RuCl(CH_3CN)_2(terpy)]PF_6$. On the other hand, an experiment to convert [**5**] to $[\mathbf{6}]^+$ under heating at 60 °C in CH_3CN suggests that the steric configuration of [**5**] may be characterized as *trans*(Cl,Cl),*cis*(Cl,-CH_3CN)-$[RuCl_2(CH_3CN)(terpy)]$. Therefore, the formation of [**5**] by the reaction of [**1**]PF_6 with N_3^- has been classified as the characteristic reaction of the coordinated nitrosyl ligand (type (i) reaction), and geometrical isomerization does not take place during this reaction.

Structural comparison of nitrosylterpyridineruthenium complexes

The structural parameters of [**1**]PF_6, [**2**]PF_6, [**3**]PF_6 and [**4**]PF_6 are summarized in Table 3. The structures of these complexes are all of distorted octahedral geometry. Geometrical distortions around the central Ru ion are caused by the constraint of the tridentate terpy ligand coordinated with three nitrogen atoms in the *mer* configuration. The N(terminal)–Ru–N(terminal) angle is around 157–160°, the bond distance of Ru–N(terminal) is longer than those of Ru–N(center), and all the atoms of the terpy ligand lie on almost the same plane. [**1**]PF_6 and [**4**]PF_6 have long Ru–N(center) bond distances compared to terpyridineruthenium complexes so far reported. This feature is similar to that of terpyridineruthenium complexes having a carbonyl ligand *trans* to the central pyridine nitrogen atom.[25]

The bond distances of Ru–N(nitrosyl) and N(nitrosyl)–O(nitrosyl), and the angle of Ru–N(nitrosyl)–O(nitrosyl) are similar to those of well-characterized linearly coordinated nitrosyl moieties as shown in Table 3. Thus, the four synthesized complexes are grouped as the $\{RuNO\}^6$-type nitrosylruthenium complexes.[10,11] The structural configuration and parameters around the Ru ion of *trans*(X, X),*cis*(X, NO)-$[RuX_2(NO)(terpy)]PF_6$ (X = Cl, Br), [**1**]PF_6 and [**4**]PF_6, are almost the same except for the distances of Ru–halide bond, and the bond distances of Ru–N are within the range of previously reported similar ruthenium complexes.[26,27] In [**2**]PF_6 and [**3**]PF_6, the nitrosyl ligand is perpendicular to the terpy plane and the hydroxo or methoxo ligand lies *trans* to the nitrosyl ligand. Bond distances of Ru–O(hydroxo or methoxo) and Ru–N(nitrosyl) of these two complexes and that of Ru–Cl in [**3**]PF_6 are comparable to those of previously reported complexes.

Compared with the nitro ligands in nitronitrosylruthenium[4] and nitroterpyridineruthenium complexes,[28] the nitro ligand on the terpy plane in [**2**]PF_6 exhibits a characteristic coordination Although the IR stretching bands of the nitro ligand of [**2**]PF_6 are observed in the usual region $\nu_{as} = 1408$ and $\nu_s = 1336$ cm^{-1}), the bond distance between Ru and the nitro nitrogen atoms, 2.241(4) Å, is significantly longer and that between the nitrogen and oxygen atoms of the nitro ligand is shorter than those of corresponding bond distances (2.04–2.09 Å for Ru–N(nitro) and 1.21–1.26 Å for N(nitro)–O(nitro)) of previously reported complexes.[4] In addition, the present O(nitro)–N(nitro)–O(nitro) angle of 131.2(7)° is larger than the previous ones (117–123°) and the distance of Ru–N(center) of the terpy ring is slightly longer. These results indicate that the electron density of the present nitro ligand of [**2**]PF_6 is high enough to lead to a double bond character of the two N–O bonds of the nitro ligand and the coordination bond between the Ru center and the NO_2^- ligand is weak. Therefore, this nitro ligand can be regarded as a π-acceptor ligand.

Table 3 Selected bond distances (Å) and angles (°)

Complex	[**1**]PF_6	[**2**]PF_6	[**3**]PF_6	[**4**]PF_6
N–O(nitrosyl)	1.129(4)	1.134(7)	1.129(5)	1.083(5)
Ru–N(nitrosyl)	1.765(3)	1.771(5)	1.753(4)	1.786(4)
Ru–N(terminal terpy)	2.083(3)	2.104(4)	2.087(4)	2.086(4)
	2.073(3)	2.102(4)	2.075(4)	2.081(4)
Ru–N(central terpy)	2.015(3)	2.005(5)	1.982(4)	2.015(4)
Ru–X	2.375(1) (X = Cl)	2.241(4) (X = NO_2)	2.387(1) (X = Cl)	2.5222(6) (X = Br)
	2.353(1) (X = Cl)	1.941(4) (X = OH)	1.940(3) (X = OCH_3)	2.4986(6) (X = Br)
Ru–N–O(nitrosyl)	174.6(3)	172.8(5)	168.3(4)	174.3(4)
N–Ru–N(terminal terpy)	157.4(1)	158.9(2)	159.8(1)	157.1(2)

Isomerization reactions

The single crystal X-ray structural analysis of [**1**]PF_6, [**2**]PF_6 and [**3**]PF_6 reveals that geometrical isomerizations around the ruthenium ion occur during the reaction of [**1**]PF_6 with NO_2^-. While some photo-induced isomerization reactions have been reported,[29,30] the present isomerization is rare for reactions of nitrosylruthenium complexes, since it occurs even in the dark. Hubbard *et al.* reported that formal isomerization of the nitrosyl complex, in which a nitro or nitrito ligand lies *cis* to the nitrosyl ligand, occurred *via* oxygen transfer from the nitrite ion to the nitrosyl ligand.[24] Although the isomerization from [**1**]$^+$ to [**2**]$^+$ can be explained by Hubbard's mechanism, that from [**1**]$^+$ to [**3**]$^+$ can not. In fact, experiments using ^{15}N-labeled compounds, $Na^{15}NO_2$ and $[RuCl_2(^{15}NO)(terpy)]PF_6$, reveal the following: 1) the reaction in H_2O gives [**2**]PF_6 with both nitrosyl and nitro ligands labeled with ^{15}N atoms, 2) the reaction in CH_3OH gives [**3**]PF_6 with the nitrosyl ligand not labeled, and 3) the reaction of $[Ru(OH)(NO_2)(^{14}NO)(terpy)]PF_6$ ([**2**]$PF_6(^{14}N)$) with $Na^{15}NO_2$ in H_2O gives [**2**]PF_6 with both nitrosyl and nitro ligands labeled. It is worth noting that $[Ru(OH)(^{15}NO_2)(NO)(terpy)]PF_6$ and $[Ru(OH)(NO_2)(^{15}NO)(terpy)]PF_6$ are formed in the reaction of [**2**]$PF_6(^{14}N)$ with $^{15}NO_2^-$ in H_2O, which indicates that not only oxygen transfer but also nitrogen transfer occurs between the nitrosyl and the nitro ligand located *cis* to each other.

We believe that the present isomerization reactions are a characteristic of the $\{RuNO\}^6$-type nitrosyl complexes which is induced by the specific electronic structure of the nitrosyl–ruthenium moiety.

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