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Synthesis, properties and molecular structure of *trans*-hydroxobis(2,2′-bipyridine)nitrosylruthenium(2+): influence of axial ligand on characteristics of nitrosyl moiety in *trans*-$[Ru(NO)XL_4]^{n+}$ (X=OH, Cl; L=py, 1/2(bpy)) type complexes

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Abstract

A new complex, *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$, was prepared and characterized. The *trans* form of the complex was confirmed by NMR spectra (^1H and ^{13}C) and X-ray structure determination: $P2_1/n$; $a=16.365(5)$, $b=11.800(7)$, $c=12.169(1)$ Å, $\beta=90.19(7)°$; $Z=4$; $D_c=1.92$, $D_m=1.92$ g cm^{-3}; formula weight=659.36; $R=0.048$ for 4825 observed reflections. Characteristics of the nitrosyl complex were compared with those of the corresponding complex, *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$, which has a Cl ligand at the *trans* position of nitrosyl.

Introduction

We have reported that the reactivity of the nitrosyl ligand in the *trans*-$[Ru(NO)X(py)_4]^{2+}$ (X=Cl, OH) type of complexes depends strongly on the axial ligand X. With the reaction of NaClO, the nitrosyl complex having a Cl ligand, *trans*-$[Ru(NO)Cl(py)_4]^{2+}$, is oxidized to give an oxo complex of Ru(IV), *trans*-$[Ru(O)Cl(py)_4]^+$, while that having an OH ligand yields *trans*-$[Ru(ONO)(O)(py)_4]^+$ with retention of the original nitrosyl nitrogen [1–4]. Several examples which reflect the effects of different axial ligands have been found. With hydroxylamine, *trans*-$[RuCl(NO)(py)_4]^{2+}$ undergoes one-electron reduction to generate *trans*-$[RuCl(NO)(py)_4]^+$ containing the $(Ru^{II}–NO^0)^{2+}$ moiety [5]. Under the same conditions, *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ did not undergo any reduction [5], whereas both nitrosyl complexes, *trans*-$[RuX(NO)(py)_4]^{2+}$ (X=Cl, OH), are reduced by Sn^{2+} to give six-electron reduction species: $[RuCl(NH_3)(py)_4]^+$ (for X=Cl) and $[Ru(NH_3)(OH_2)(py)_4]^{2+}$ (for X=OH) [6]. In the reaction with N_3^-, SO_3H^-, $(CH_3)_2CO$ or OH^-, the nitrosyl ligand in *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ functions as a good electrophile [6–8], while that of *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ shows very poor electrophilicity [9]. Clearly, the characteristics of the nitrosyl complexes are dominated by which ligand exists at the *trans* position of nitrosyl.

Before we can generalize the findings about the effects of the axial ligands, further studies using another *trans*-$[Ru(NO)XL_4]^n$ type of complex are necessary. Thus, the title complex, *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$, was synthesized and characterized. The complexes are the analogue of *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ whose synthesis, characteristics and structure have recently been investigated [10]. A preparative work of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ has been reported briefly by another researcher [11], but no detailed data are available yet.

Experimental

Materials

cis-$[RuCl_2(bpy)_2]Cl\cdot 2H_2O$, $[Ru(CO_3)(bpy)_2]$ and *trans*-$[Ru(OH_2)_2(bpy)_2](ClO_4)_2$, used as starting materials of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$, were prepared according to known methods [12, 13].

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Synthesis of trans-$[Ru(OH)(NO)(bpy)_2](ClO_4)_2$

To an aqueous solution containing *trans*-$[Ru(OH_2)_2(bpy)_2](ClO_4)_2$ (100 mg/50 cm^3), $NaNO_2$ (200 mg) was added. The mixed solution was warmed at 60 °C for 6 h. When the solution volume was reduced, red crystalline material (*trans*-$[Ru(NO_2)_2(bpy)_2]$) deposited. The red material (100 mg), collected by filtration, was dissolved in $HClO_4$ (6 mol dm^{-3}, 15 cm^3) containing $NaClO_4$ (30 mg), and then the mixed solution was allowed to stand at 60 °C for 3 h. The yellow material obtained was collected by filtration, washed with cold water, EtOH and finally with ether, and dried *in vacuo*. Yield 80%. *Anal.* Found: N, 10.6; C, 36.3; H, 2.4. Calc. for $[Ru(NO)(OH)(bpy)_2](ClO_4)_2$: N, 10.6; C, 36.4; H, 2.6%.

Reaction of trans-$[Ru(OH)(NO)(bpy)_2](ClO_4)_2$ *with NaOH; formation of trans-*$[Ru(NO_2)(OH)(bpy)_2]$

To an aqueous solution of the nitrosyl complex (100 mg/20 cm^3), 5 cm^3 of NaOH (5 mol/dm^3) were added to give a dark brown precipitate. The reactant was stirred for 5 h at room temperature. The dark brown material was collected by filtration, washed with cold water and then with acetone, and dried *in vacuo*. *Anal.* Found: N, 13.9; C, 48.0; H, 3.3. Calc. for $[Ru(NO_2)(OH)(bpy)_2]$: N, 14.2; C, 48.6; H, 3.8%. IR: ν(N–O) and ν(N=O), 1304 and 1285 cm^{-1}. No IR absorption band due to ClO_4^- ion was found. λ (nm) (ϵ(dm^3 mol^{-1} cm^{-1})): 475 (7.8×10^3), 334sh (7.1×10^3), 290 (3.7×10^4) in EtOH.

Conversion of trans-$[Ru(OH)(NO)(bpy)_2]^{2+}$ *into trans-*$[RuCl(NO)(bpy)_2]^{2+}$*, via the formation of trans-*$[RuCl(NO_2)(bpy)_2]$

The hydroxo–nitrosyl complex was converted first into *trans*-$[Ru(NO_2)(OH)(bpy)_2]$ by the method described above. Stirring the suspension of the nitro hydroxo complex (30 mg/H_2O 5 cm^3) containing KCl (100 mg) for 2–3 h at room temperature gives a dark brown product which is believed to be $[Ru(NO_2)Cl(bpy)_2]$. *Anal.* Found: N, 13.7; H, 3.6; C, 46.8. Calc. for $[Ru(NO_2)Cl(bpy)_2]\cdot H_2O$: N, 13.7; H, 3.5; C, 46.8%. The material was dissolved by HCl (1 mol dm^3, 10 cm^3) to give a yellow solution. After the solution was stirred for 1–2 h at room temperature, a yellow material (*trans*-$[Ru(NO)Cl(bpy)_2](PF_6)_2$) was obtained from the yellow solution, using NH_4PF_6 as precipitant. The product was collected by filtration, washed with cold water and with alcohol, and dried *in vacuo*. Yield 55% (15–20 mg). Data of both IR spectra (ν(NO)) and cyclic voltammogram ($E_{1/2}$ and E_{pc}) agreed well with those of the authentic sample [10].

Measurements

Elemental analyses were performed at the Sophia University Analytical Facility. Cyclic voltammetry was carried out using a Husoh model 321 polarograph with a stationary platinum disk electrode. The CH_3CN solvent and relevant material used for the electrochemical measurements are the same as those reported previously [2]. UV spectra were recorded on a Hitachi 200-20 spectrometer. ^1H and ^{13}C NMR spectra were obtained on JEOL FX-200 and GX-270 spectrometers. The magnetic property was measured by the Gouy method. IR spectra were measured on a Hitachi EPI G2 spectrometer. IR data were also taken using a Broker IFS-113v (70 and 298 K) for *trans*-$[Ru(NO)X(py)_4]^{2+}$ (X=Cl, OH) and their ^{15}N-substituted complexes, to calculate the force constants of the (RuNO) moiety using their actual parameters. The calculation was

TABLE 1. Positional parameters ($\times10^4$) for non-hydrogen atoms

Atom	x	y	z	B_{eq} (A^2)
Ru	4260.1(3)	2016.3(3)	4531.7(4)	1.51
N(1)	5542(3)	2117(4)	4563(5)	2.10
C(12)	5873(4)	1833(4)	3590(6)	2.20
C(13)	6694(5)	1580(6)	3467(7)	2.70
C(14)	7190(5)	1676(7)	4417(8)	3.65
C(15)	6873(5)	2037(8)	5375(8)	4.08
C(16)	6026(4)	2266(6)	5464(6)	2.97
N(2)	4560(3)	2305(4)	2893(5)	1.98
C(22)	5317(4)	1963(5)	2632(5)	2.11
C(23)	5571(5)	1886(6)	1552(6)	2.83
C(24)	5051(5)	2295(6)	729(6)	3.03
C(25)	4306(5)	2754(7)	1036(6)	3.35
C(26)	4062(4)	2753(5)	2120(6)	2.75
N(3)	3034(3)	1580(4)	4375(5)	2.07
C(32)	2637(4)	1400(5)	5311(6)	2.03
C(33)	1811(5)	1094(6)	5323(8)	2.92
C(34)	1413(4)	927(6)	4316(8)	3.08
C(35)	1816(5)	1073(6)	3402(7)	3.32
C(36)	2656(4)	1401(5)	3408(6)	2.70
N(4)	3947(3)	1525(4)	6143(4)	1.89
C(42)	3133(4)	1400(5)	6335(6)	2.24
C(43)	2831(5)	1185(6)	7346(7)	2.72
C(44)	3351(7)	1029(6)	8250(7)	3.49
C(45)	4202(6)	1076(6)	8019(6)	3.19
C(46)	4471(5)	1328(5)	6979(6)	2.88
N(O)	4089(4)	3480(4)	4755(5)	2.16
O(N)	3994(5)	4436(4)	4816(6)	4.48
O(H)	4465(3)	427(3)	4221(4)	2.21
Cl(1)	4314(1)	4390(1)	7564(2)	2.60
Cl(2)	3153(2)	−552(2)	1195(2)	4.15
O(11)	3565(4)	3882(5)	7213(7)	4.71
O(12)	4977(4)	3875(5)	6974(6)	3.85
O(13)	4431(5)	4221(7)	8717(6)	6.94
O(14)	4268(5)	5585(5)	7320(7)	5.27
O(21)	2545(8)	−1007(7)	1890(10)	7.48
O(22)	2961(9)	601(6)	969(7)	9.20
O(23)	3072(12)	−1181(8)	219(11)	13.97
O(24)	3842(7)	−641(14)	1781(19)	21.33

performed by a GF matrix method using the computer program written by Schachtshneider [14].

X-ray measurements

The reflections were collected by the ω-scan technique ($2\theta < 60°$) on a Rigaku AFC-6A automated four-circle diffractometer, with graphite Mo Kα radiation (0.7107 Å). The 4825 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure refinement. The intensities were collected for Lorentz and polarization factors, but no correction was made for absorption. All calculations were carried out on a HITAC M200H computer at the Computer Center of the University of Tokyo, using UNICS [15]. The atomic scattering factors were taken from ref. 16. The structure was solved by a heavy-atom method. The positions of Ru and Cl atoms were obtained from a three-dimensional Patterson function, while the positions of all the non-hydrogen atoms were successively located by Fourier synthesis. All hydrogen atoms were found at reasonable positions on the final difference Fourier map. Refinements using UNICS [15], with all atoms except anisotropic H, resulted in $R_F = 0.048$ and $R_{wF} = 0.055$, where $R_F = \Sigma(F_o - F_c)/\Sigma(F_o)$ and $R_{wF} = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o)^2]^{1/2}$, respectively. The final atomic coordinates and temperature factors are listed in Table 1.

Results and discussion

The present complex is diamagnetic, a common feature for the $\{RuNO\}^6$ type of nitrosyl complexes [17]*. The *trans* type of nitrosylruthenium(II) complexes with 2,2′-bipyridine, *either* trans-$[Ru(NO)(OH)(bpy)_2]^{2+}$ or the analogue *trans*-$[RuCl(NO)(bpy)_2]^{2+}$, were less soluble in most solvents than the corresponding *cis* type of complexes [10]. The following data, however, are available in the characterization of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$: the ^1H NMR spectral pattern (in CD_3CN) is essentially the same as that reported for the corresponding *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ (δ=8.89 (d, 4H), 8.56 (d, 4H), 8.46 (dd, 4H), 7.91 (dd, 4H)) [10]. The ^{13}C NMR spectrum also confirms the *trans* configuration, where two bpy molecules exist in positions essentially equivalent to each other (δ=157, 153, 144, 129, 118) [10].

The molecular structure of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ is shown in Fig. 1. Crystallographic data are the following: $P2_1/n$; $a = 16.365(5)$, $b = 11.800(7)$, $c = 12.169(1)$ Å, $\beta = 90.19(7)°$; $Z = 4$; $R = 0.048$; $D_c = 1.92$, $D_m = 1.92$ g cm^{-3}; formula weight = 659.36. The cation has the expected *trans*-octahedral coordination geometry, with two bpy ligands in equatorial positions and with both nitrosyl and hydroxo oxygen in the axial positions.

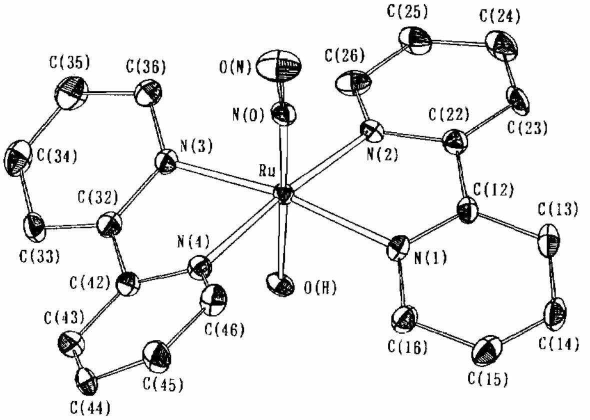

Fig. 1. Molecular structure of the $[Ru(NO)(OH)(bpy)_2]^{2+}$ complex cation.

TABLE 2. Important bond distances (Å) and bond angles (°) of *trans*-$[Ru(OH)(NO)(bpy)_2](ClO_4)_2$

Distances			
Ru–O(H)	1.942(5)	Ru–N(3)	2.079(6)
Ru–N(0)	1.771(6)	Ru–N(4)	2.110(5)
Ru–N(1)	2.101(5)	N(0)–O(N)	1.140(9)
Ru–N(2)	2.083(5)		
Angles			
Ru–N(0)–O(N)	174.7(6)	O(H)–Ru–N(2)	86.1(2)
O(H)–Ru–N(0)	177.4(2)	O(H)–Ru–N(3)	84.9(2)
N(1)–Ru–N(2)	76.7(2)	O(H)–Ru–N(4)	87.6(2)
N(2)–Ru–N(3)	100.6(2)	N(O)–Ru–N(1)	95.8(2)
N(3)–Ru–N(4)	77.3(2)	N(O)–Ru–N(2)	91.4(2)
N(4)–Ru–N(1)	104.1(2)	N(O)–Ru–N(3)	95.9(2)
O(H)–Ru–N(1)	83.4(2)	N(O)–Ru–N(4)	95.0(2)

The important bond distances and angles in the coordination sphere are given in Table 2. The Ru–N(nitrosyl) and N–O bond distances (1.751(6) and 1.132(9) Å, respectively) were comparable to those in *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ [10] (Table 3). The RuNO angle is approximately linear. The Ru–N(bpy) bond distances of 2.080–2.109 Å are also very similar to those of other *trans*-bis(2,2′-bipyridine)ruthenium complexes [20–23], including *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ [10]. Table 3 shows that in the *trans*-$[Ru(NO)XL_4]^{2+}$ (X = OH or Cl, L = 1/2(bpy) or py) type of complexes, the Ru–*trans*-L distances (L = OH and Cl) are short and the Ru–NO distances are long, compared to all other similar compounds [9 and refs. therein]. The Ru–*cis*-L (L = N atom) distances, however, are almost the same as that of *trans*-$[Ru(NO)(OH)(NH_3)_4]^{2+}$ [23]. A 'bowed' type of distortion is found in the bpy ligands; this structural feature is similar to that of *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$

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*Mononitrosyl complexes are conveniently described as $\{RuNO\}^n$, where n is the number of the d electrons on the metal when the NO group is formally bound as NO^+.

TABLE 3. *trans*-$[Ru(NO)XL_4]^{2+}$ type of complexes; some of their properties and significant structural parameters

Complexes	IR[a] ν (NO)	Reduction potential[b]		Structural parameter				Reference
		1st wave $E_{1/2}$	2nd wave E_{pc}	N–O[c]	Ru–N(O)[c]	∠RuNO[d]	Ru–Cl[c] or Ru–O(H)[c]	
trans-$[Ru(NO)Cl(bpy)_2]^{2+}$	1912	−0.20	−0.82	1.132(9)	1.751(6)	170.4(5)	2.306(2)	10
trans-$[Ru(NO)(OH)(bpy)_2]^{2+}$	1890	−0.72[e]		1.140(9)	1.771(5)	174.7(6)	1.942(5)	this work
		(−0.74)[e]	(−1.26)					
trans-$[Ru(NO)Cl(py)_4]^{2+}$	1910	−0.11	−0.99	1.123(1)	1.766(8)	172.9(8)	2.315(3)	2,6,19
		(−0.14)	(−0.97)[f]					
trans-$[Ru(NO)(OH)(py)_4]^{2+}$	1868	−0.69[e,g]		1.145(4)	1.756(3)	172.8(3)	1.910(3)	6,9
		(−0.68)[g]	(−1.43)[f,g]					
trans-$[Ru(NO)NH_3(py)_4]^{3+}$	1935	0.08	−0.76					9

[a]In cm^{-1} (KBr). [b]In CV; V vs. Ag|$AgClO_4$ (0.1 mol dm^{-3} in CH_3CN) at 25 °C. Values given in parentheses were obtained at −40 °C. [c]In Å. [d]In deg. [e]E_{pc}. [f]$E_{1/2}$. [g]ClO_4 salt.

[10]. Generally, either a 'bowed' or a 'twisted' distortion is expected in the complexes with bpy ligands, so as to minimize steric interaction due to 6,6′-hydrogen atoms of the ligands.

IR absorption bands due to ν(NO) of *trans*-$[Ru(NO)(OH)L_4]^{2+}$ (L = py, 1/2(bpy)) appeared at a lower frequency region than those of the corresponding chloro complexes, *trans*-$[Ru(NO)ClL_4]^{2+}$ (Table 3). This trend can be observed notably in *trans*-$[Ru(NO)X(py)_4]^{2+}$, where the pyridines exist as the co-ligand L; 1867.2 cm^{-1} is for X = OH and 1910.4 for X = Cl. IR spectra of the pair complex, *trans*-$[Ru(NO)X(py)_4]^{2+}$ (X = OH, Cl), were therefore investigated in detail.

To calculate the force constants of the (RuNO) moiety, IR spectra of the complexes and their ^{15}N-substitution complexes were measured. The results are summarized in Table 4. The $\{MNO\}^6$ type of nitrosyl complexes are known to show two more absorption bands due to ν(Ru–N) and δ(Ru–N–O), within a very close frequency region around 600 cm^{-1}, in addition to the ν(NO) band at the 1800 ~ 1900 cm^{-1} region [24]. These two bands have been assigned so that ν(Ru–N) is observed at a higher region than δ(Ru–N–O) [24]. Thus, the bands observed at 622.0 and 595.7 cm^{-1} in *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ (and also 608.8 and 603.2 cm^{-1} in *trans*-$[Ru(NO)Cl(py)_4]^{2+}$) correspond to ν(Ru–N) and δ(Ru–N–O), respectively, in their frequency region. Since we were unable to assign them correctly by means of a calculation*, these two bands were abbreviated as ν_1 and ν_2 in Table 4.

The force constants calculated for the Ru–N–O three atom system [14], using data of both IR and structural parameters (Table 4), are listed in Table 5. (The calculation was also applied to the O–N–Ru–X (X = OH, Cl) four atom system; the data are given in Table 6.) The values obtained here are a bit higher than those of other nitrosyl complexes that were calculated for other $\{MNO\}^6$ type of complexes, without using the practical data of structural parameters [26, 27].

Addition of NaOH to the aqueous solution of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ gave *trans*-$[Ru(NO_2)(OH)(bpy)_2]$ (see 'Experimental') as a main product, indicating that the following conversion reaction occurs at the basic condition [28]:

$$[Ru(NO)(OH)(bpy)_2]^{2+} + OH^- \rightleftarrows [Ru(NO_2H)(OH)(bpy)_2]^+ \quad (1)$$

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*We calculated the contribution ratio of both vibration modes (ν(Ru–N) and δ(Ru–N–O)) to the absorption bands through a calculation of the force constant of the Ru–N–O three-body model. The result showed that each absorption band was contributed to by each vibration mode nearly equally, indicating the difficulty in assigning those bands independently.

TABLE 4. Important IR data (cm^{-1}) observed for the analogous nitrosyl complexes and their ^{15}N-substitution complexes

Complexes	ν (NO)	ν_1[a]	ν_2[a]	ν(Ru–X)[b]
trans-$[Ru(OH)(NO)(py)_4](PF_6)_2$	1867.2	622.0	595.7	566.8
trans-$[Ru(OH)(^{15}NO)(py)_4](PF_6)$	1832.3	607.8	583.7	566.8
trans-$[RuCl(NO)(py)_4](ClO_4)_2$	1910.4	608.8	603.2	348.6
trans-$[RuCl(^{15}NO)(py)_4](ClO_4)_2$	1873.0	594.0	587.3	348.6

[a]$\nu_1 = \nu$(Ru–N) or δ(Ru–N–O); $\nu_2 = \nu$(Ru–N) or δ(Ru–N–O). [b]X = O(H) or Cl.

TABLE 5. Force constants ($\times 10^2$ N m^{-1}) of *trans*-$[RuX(NO)(py)_4]^{2+}$ type of complexes, and their bond distances and angles used for the calculations

Complexes	Ru–N (Å)	N–O (Å)	∠RuNO (°)	$F(Ru–N_{str})$	$F(N–O_{str})$	$F(Ru–N–O_{bend})$
trans-$[Ru(OH)(NO)(py)_4](PF_6)_2$	1.753	1.141	172.5	5.016	16.298	0.845
trans-$[RuCl(NO)(py)_4](ClO_4)_2$ (**1**)[a]	1.762	1.129	175.8	4.969	16.620	0.863
trans-$[RuCl(NO)(py)_4](ClO_4)_2$ (**2**)[a]	1.758	1.134	172.1	4.980	16.702	0.846

[a] The crystal structure determination of *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ has revealed that the complex ion has two structurally different forms in the unit cell: **1** and **2** [25].

TABLE 6. Force constants ($\times 10^2$ N m^{-1}) calculated for the four atom system

Complexes	$F(Ru–N_{str})$	$F(N–O_{str})$	$F(Ru–N–O_{bend})$	$F(Ru–X_{str})$
trans-$[Ru(OH)(NO)(py)_4](PF_6)_2$	5.05	16.40	0.34	2.86
trans-$[RuCl(NO)(py)_4](ClO_4)_2$ (**1**)[a]	4.79	16.78	0.29	2.05
trans-$[RuCl(NO)(py)_4](ClO_4)_2$ (**2**)[a]	4.79	16.78	0.29	2.05

[a] See footnote to Table 5.

$$[Ru(NO_2H)(OH)(bpy)_2]^+ + OH^- \rightleftharpoons [Ru(NO_2)(OH)(bpy)_2] + H_2O \quad (2)$$

The pK value of the first equilibrium (eqn. (1), pK_1 = 8.8) was estimated roughly for *trans*-$[Ru(NO)OH(bpy)_2]^{2+}$ by the previous method [10]*. The value is higher than that of *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ (pK_1 = 6.1) measured under the same conditions, indicating that *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ is less electrophilic than *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$. In fact, the former did not react with acetone as a nucleophile, while the latter did [10].

The cyclic voltammogram of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$, measured at 25 °C, shows only an irreversible one-electron reduction wave with an E_{pc} of -0.72 V, whilc two one-electron reduction waves were observed in the corresponding chloro complex, *trans*-$[RuCl(NO)(bpy)_2]^{2+}$, at -0.20 V ($E_{1/2}$) and -0.82 V (E_{pc}) [10]. On reducing the temperature to -40 °C, however, a new wave that corresponds to the second reduction wave of *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ appeared at -1.26 V (Table 3). The electrochemical behavior of both complexes appears to be essentially the same, except that *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ is less electrophilic than *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$. Attempts to isolate the one-electron reduction species of both *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ and *trans*-$[RuCl(NO)(bpy)_2]^{2+}$ have been carried out with the aim of obtaining a complex having a ($Ru^{2+}NO^0$) moiety, *trans*-$[RuX(NO)(bpy)_2]^+$, but the experiments have been unsuccessful so far.

The OH ligand which exists at the *trans* position of $[Ru(NO)XL_4]^n$ type of nitrosyl complexes has been believed to be inert [6]. We found in the present work, however, that the substitution occurred easily in the analogous nitrosyl complex, *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$; when the tetrakis(pyridine)hydroxo nitrosyl complex was heated at 80 °C for 2 h in aqueous HCl solution (6 mol/dm^3), *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ can be obtained quantitatively. This was confirmed by the authentic sample. The same procedure was applied to the present hydroxo nitrosyl complex, *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$, but the experiment did not give *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$, while its isomerized species, *cis*-$[Ru(NO)Cl(bpy)_2]^{2+}$, was isolated. A direct substitution of the OH ligand in *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ by the Cl ligand was difficult, and finally we succeeded in obtaining *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ by the procedure using *trans*-$[Ru(NO_2)(OH)(bpy)_2]^+$ as a starting material (see 'Experimental'). The preparative interrelation of these complexes, including that of the relevant complexes, is shown in Scheme 1.

Conclusions

When the axial ligand Cl in the *trans*-$[Ru(NO)XL_4]^{2+}$ (L = py, 1/2(bpy)) type of complexes is altered by an OH ligand, which is known as a relatively strong π-donor in its ligand character, a drastic decrease in IR (ν(NO)) data and a potential shifting (to the negative potential side) of E_{pc} data were found; both data have been regarded as tools for diagnosis for the reactivity of the nitrosyl ligand [26, 19]. However, structural data of the distances of Ru–N(O) and N–O, including that

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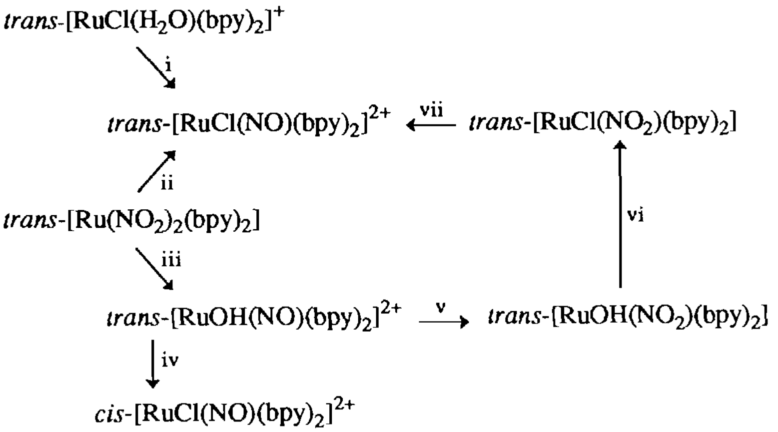
*Measurement of pK_2 value in eqn. (2) was hampered by the precipitation of a brown material, probably *trans*-$[Ru(NO_2)(OH)(bpy)_2]$.



Scheme 1. i, Reacted with NO gas [10]; ii, decomposed by HCl, a mixture of *trans*-$[RuCl(NO)(bpy)_2]^{2+}$ and *trans*-$[RuOH(NO)(bpy)_2]^{2+}$ was obtained [10]; iii, decomposed by $HClO_4$; iv, heated (at 90 °C) in HCl aq. solution for 3 h; v, treated with OH^-; vi, reacted with Cl^-; vii, dissolved in HCl.

of Ru–O(H) were very similar to those of *trans*-$[RuCl(NO)(py)_4]^{2+}$, *trans*-$[RuCl(NO)(bpy)_2]^{2+}$ and *trans*-$[Ru(OH)(NO)(py)_4]^{2+}$ (Table 3). The *trans* influence, which is the effect that is observable for the structural parameters of the nitrosyl moiety when the axial ligands are changed (from Cl to OH), appears to be small. In *trans*-$[Ru(NO)(NH_3)(Py)_4]^{3+}$, the existence of the NH_3 ligand, which acts purely as a σ-donor, results in increasing those data (ν(NO), E_{pc}) remarkably [9]. Studies to prepare *trans*-$[Ru(NO)(NH_3)(bpy)_2]^{3+}$, to determine its structure, and to compare the characteristics of the ammine–nitrosyl complex and those of analogous *trans*-$[Ru(NO)X(bpy)_2]^{2+}$ (X = Cl, OH) are essential for our further investigation. Attempts to prepare *trans*-$[Ru(NO)(NH_3)(bpy)_2]^{3+}$ have so far failed. Some X-ray structural work for *trans*-$[Ru(NO)(NH_3)(py)_4]^{3+}$ prepared earlier was also hampered, owing to the difficulty of making single crystals.

Supplementary material

Observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom coordinates, and the deviations of atoms from least-squares planes are available from the authors on request.

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