Comparison of the Reactivity, Electrochemical Behaviour, and Structure of the *trans*-Bis(acido)tetra(pyridine)nitrosylruthenium Cations (Acido = Hydroxo or Chloro)†

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The ion *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ reacts with N_3^- to give $[Ru(OH)(N_3)_2(py)_2(NO)]$ and $[Ru(N_3)_3(py)_2(NO)]$ (py = pyridine). There was no reaction between *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ and NH_2OH, nor with OH^- except at pH $\geqslant 13$ when some replacement of pyridine occurred. The ion *trans*-$[RuCl(py)_4(NO)]^{2+}$ reacted with N_3^- to give $[RuCl(py)_4(N_2)]^{2+}$ and $[RuCl(py)_4(NO)]^+$. Reduction of *trans*-$[RuCl(py)_4(NO)]^{2+}$ by NH_2OH or $SnCl_2$ gave $[RuCl(py)_4(NO)]^+$. The apparent substitution of pyridine in *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ by N_3^- is ascribed to an initial reduction of the complex by N_3^-, substitution of the reduced cation, and subsequent reoxidation. At 25 °C in MeCN, *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ showed an irreversible reduction wave at $E_{\frac{1}{2}} = -0.69$ V, which became reversible at −20 °C. At 25 °C *trans*-$[RuCl(py)_4(NO)]^{2+}$ showed a reversible wave at $E_{\frac{1}{2}} = -0.11$ V corresponding to simple reduction to $[RuCl(py)_4(NO)]^+$. The reactions of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ and *trans*-$[RuCl(py)_4(NO)]^{2+}$ are compared. The structure of *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2 \cdot H_2O$ was determined by *X*-ray diffraction: space group $P2_1/n$, $a = 10.876(1)$, $b = 27.711(4)$, $c = 10.631(1)$ Å, $\beta = 116.05(1)°$, $Z = 4$, final $R = 0.038$ for 469 variables and 5 130 observed reflections. The ruthenium is octahedrally co-ordinated by *cis*-pyridines and *trans*-OH and NO. The Ru–OH distance is very short [1.910(3) Å] and the Ru–NO distance relatively long [1.756(3) Å]. The Ru–py distances average 2.102(3) Å.

Several nitrosyl complexes of ruthenium behave as electrophiles or undergo redox reactions in which the nitrosyl is converted into a new ligand.[1,2] Complexes of type *trans*-$[RuX(py)_4(NO)]^{n+}$ [3–6] and $[RuX(bipy)_2(NO)]^{n+}$ [7–9] are particularly important because the pyridine (py) or 2,2′-bipyridine (bipy) ligands are neither labile nor do they undergo changes within themselves. This is not true of ligands such as NO_2^- [10] or NH_3.[11] Also, reactions of $[RuX(py)_4(NO)]^{n+}$ and $[RuX(bipy)_2(NO)]^{n+}$ are not usually dependent on the nature of X. However, during investigations of the electrophilic behaviour of $[RuX(py)_4(NO)]^{2+}$ we encountered reactions in which the pyridine ligands were labile. We also encountered differences in the reactions which were dependent on X and which were not simply reaction or lack of it. The results are reported here, and are explained in terms of the redox behaviour of the complexes.

Results

Reactions of trans-$[RuX(py)_4(NO)]^{2+}$ (X = OH *or* Cl) *with* N_3^- *and* NH_2OH.—Gentle heating of a solution of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ and N_3^- in water resulted in evolution of N_2 gas and formation of two products: $[Ru(OH)(N_3)_2(py)_2(NO)]$ (20% yield) and $[Ru(N_3)_3(py)_2(NO)]$ (30%). These products were separated by their different solubilities in water. They were characterised by analysis, i.r. and n.m.r. spectroscopies, diamagnetism, and conductivity. Experiments using ^{15}NO-labelled derivatives showed that nitrosyl ligand in the products was carried through from the starting material. As previously reported,[4] the reaction between *trans*-$[RuCl(py)_4(NO)]^{2+}$ and N_3^- gave a mixture of the one-electron reduction product, $[RuCl(py)_4(NO)]^+$, and $[RuCl(py)_4(N_2)]^+$. The latter was formed by nucleophilic attack of N_3^- at the nitrosyl ligand.[4,12–14]

There was immediate reduction of *trans*-$[RuCl(py)_4(NO)]^{2+}$ by NH_2OH to give $[RuCl(py)_4(NO)]^+$ [15] but *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ did not react with NH_2OH. Reduction of *trans*-$[RuCl(py)_4(NO)]^{2+}$ by $SnCl_2$ under mild conditions gave the one-electron reduction product *trans*-$[RuCl(py)_4(NO)]^+$ also, but under forcing conditions some $[RuCl_3(py)_2(NO)]$ was obtained. The product $[RuCl(py)_4(NO)]^+$ was characterised, as the PF_6^- salt, by comparison with the complex prepared as described previously; $[RuCl_3(py)_2(NO)]$ was characterised by analysis and i.r. spectroscopy.

Electrochemistry.—The electrochemical behaviour of *trans*-$[RuX(py)_4(NO)]^{2+}$ (X = OH or Cl) in acetonitrile as solvent is summarised in Figure 1 and Table 1. Two reduction waves were observed for the chloro derivative with $E_{\frac{1}{2}}$ values of −0.11 and −0.99 V. Cyclic voltammograms of the first reduction wave at a scan rate, v, varying from 200 to 50 mV s^{-1} showed that the peak ratio i_{p_c}/i_{p_a} was always unity, the term $i_{p_c}v^{\frac{1}{2}}$ remained essentially constant, and the peak separation ΔE increased only slightly from 70 mV at 50 mV s^{-1} to 80 mV at 200 mV s^{-1}. In normal pulse voltammetry, measured under the same experimental conditions, plots of $\log(i/i_d - i)$ *versus* E were linear with a slope of 27 mV. The height of the reduction wave was comparable to that of the *trans*-$[RuCl_2(py)_4]^+$–$[RuCl_2(py)_4]^0$ couple.

At 25 °C the hydroxo derivative exhibited only an irreversible

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

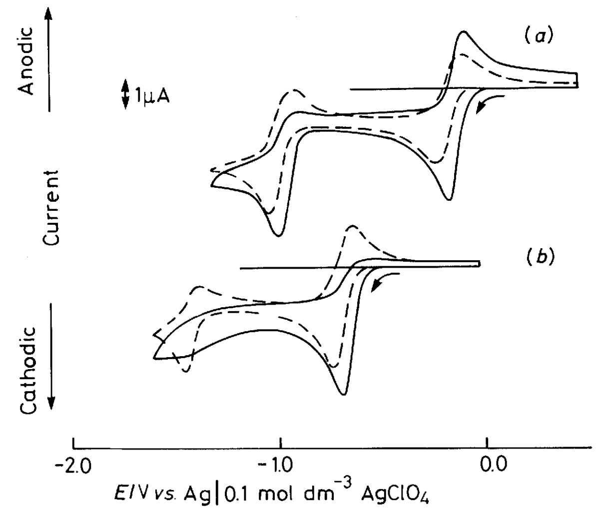

Figure 1. Cyclic voltammograms of *trans*-$[RuCl(py)_4(NO)]^{2+}$ (*a*) and *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ (*b*) in CH_3CN as solvent. The concentration of *trans*-$[RuX(py)_4(NO)]^{2+}$ is 1.00×10^{-3} mol dm^{-3} (as the PF_6^- salt). The continuous line represents an experiment at 297 K, the dotted at 253 K

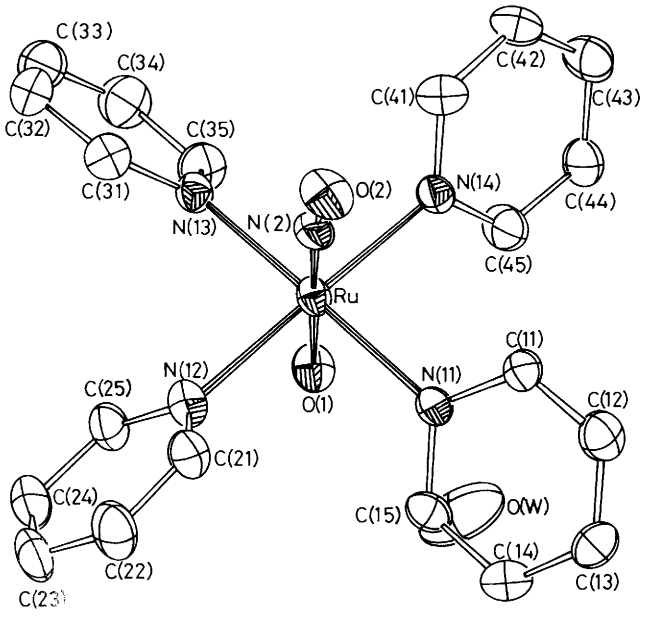

Figure 2. Structure of the *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ cation in *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2{\cdot}H_2O$

one-electron reduction wave with an $E_{\frac{1}{2}}$ of −0.69 V. On reducing the temperature to −20 °C this wave became chemically reversible and a new wave with an $E_{\frac{1}{2}}$ of −1.43 V appeared. The electrochemical behaviour of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ at −20 °C was similar to that of *trans*-$[RuCl(py)_4(NO)]^{2+}$ at 25 °C. In both cases the second reduction wave, observed at the most negative potential, was irreversible even under the fastest attainable scan rates. The behaviour of *trans*-$[Ru(NH_3)(py)_4(NO)]^{3+}$ was similar to that of *trans*-$[RuCl(py)_4(NO)]^{2+}$; reduction occurred at more positive potentials, in part because of the higher charge on the ammine complex.

Table 1. Electrode potentials for reduction of *trans*-$[RuX(py)_4(NO)]^{2+}$ (X = Cl or OH) at 297 and 253 K

Complex[a]	*T*/K	First wave $E_{\frac{1}{2}}$[b,c]/V	Second wave $E_{\frac{1}{2}}$/V
$[Ru(OH)(py)_4(NO)]^{2+}$	297	−0.69[d]	—
	253	−0.68	−1.43
$[RuCl(py)_4(NO)]^{2+}$	297	−0.11	−0.99
	253	−0.14	−0.97
$[Ru(NH_3)(py)_4(NO)]^{3+}$	297	0.08	−0.76
	253	0.03	−0.79

[a] Concentration 1×10^{-3} mol dm^{-3}. [b] Platinum electrode, scan rate 50 mV s^{-1}. [c] $E_{\frac{1}{2}} = (E_{p_a} + E_{p_c})/2$. [d] E_{p_c}.

Table 2. Important distances (Å) and angles (°) in *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2{\cdot}H_2O$ with estimated standard deviations in parentheses

Ru–N(2)	1.756(3)	Ru–N(13)	2.100(3)
Ru–O(1)	1.910(3)	Ru–N(14)	2.104(2)
Ru–N(11)	2.103(3)	N(2)–O(2)	1.145(4)
Ru–N(12)	2.102(3)		
Ru–N(2)–O(2)	172.8(3)	N(2)–Ru–(N13)	94.5(1)
O(1)–Ru–N(2)	179.1(1)	N(2)–Ru–N(14)	91.3(1)
O(1)–Ru–N(11)	89.4(1)	N(11)–Ru–N(12)	90.7(1)
O(1)–Ru–N(12)	86.1(1)	N(11)–Ru–N(13)	175.7(1)
O(1)–Ru–N(13)	86.3(1)	N(11)–Ru–N(14)	90.4(1)
O(1)–Ru–N(14)	88.2(1)	N(12)–Ru–N(13)	89.9(1)
N(2)–Ru–N(11)	89.8(1)	N(12)–Ru–N(14)	173.9(1)
N(2)–Ru–N(12)	94.4(1)	N(13)–Ru–N(14)	88.5(1)

Structure of trans-$[Ru(OH)(py)_4(NO)][PF_6]_2{\cdot}H_2O$.—The cation is octahedrally co-ordinated by four *cis*-pyridine ligands, arranged in a propeller fashion, and *trans*-OH and NO groups (Figure 2). Important distances and angles are given in Table 2. The parameters important for the present work are the short Ru–OH distance of 1.910(3) Å, the Ru–NO distance of 1.756(3) Å, and the average Ru–py distance of 2.102(3) Å.

Discussion

The products of the reaction between *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ and N_3^- are the azide-substituted derivatives $[Ru(OH)(N_3)_2(py)_2(NO)]$ and $[Ru(N_3)_3(py)_2(NO)]$. However, the evolution of N_2 gas is clear evidence that the reaction is not a simple substitution. Further evidence on this point is that when *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ was treated with a variety of nucleophiles, substitution only occurred with N_3^-. With OH^- at pH $\geqslant 13$ some loss of pyridine did occur,[4] but the product(s) could not be characterised; no substitution occurred at pH < 13. It is concluded that simple substitution of pyridine in *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ does not take place.

An alternative to simple substitution is initial nucleophilic attack of N_3^- at the co-ordinated nitrosyl. Such electrophilic behaviour towards N_3^- has been demonstrated for *trans*-$[RuCl(py)_4(NO)]^{2+}$,[4] and occurs also for *trans*-$[Ru(NH_3)(py)_4(NO)]^{3+}$. Formation of *trans*-$[Ru(OH)(py)_4\{N(O)N_3\}]^+$ would place electron density into a π*(RuNO) orbital.[16] This orbital may contain a significant contribution from the *cis*-pyridine ligand orbitals, and is antibonding with respect to such an interaction. Thus the *cis*-pyridine ligands would be labilised. If this mechanism were operating, N_2 could only be evolved by further reaction of the adduct, with loss of the nitrosyl ligand. However, this ligand is retained throughout the reaction. Also, if this mechanism were operating, any nucleophile would cause substitution. Neither NH_2OH nor OH^- does so under similar conditions to N_3^-. Finally, nucleophilic attack of OH^- at *trans*-$[RuCl(py)_4(NO)]^{2+}$ does not cause substitution of pyridine. We conclude that nucleophilic attack at the nitrosyl of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ does not occur.

A second alternative is initial reduction of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ by N_3^- according to equation (1). The added

Table 3. Comparison of Ru–Cl and Ru–OH distances (Å) in ruthenium compounds

Compound	Ref.	Ru–NO	Ru–Cl	Ru–OH	Ru–*cis*-L	N–O
$[RuCl(py)_4(NO)]^{2+}$	*a*	1.766(8)	2.315(3)		2.105(8)	1.123(1)
$[Ru(OH)(py)_4(NO)]^{2+}$	This work	1.756(3)		1.910(3)	2.102(3)	1.145(4)
$[RuCl(OH)(py)_4]^{+}$	*b*		2.377(3)	1.957(9)	2.088(9)	
$[RuCl_2(py)_4]^{+}$	*c*		2.326(4)		2.09(1)	
$[Ru(OH)(NO_2)_4(NO)]^{2-}$	*d*	1.748(4)		1.950(5)	2.079(3)	1.127(7)
$[Ru(OH)(NO_2)_2(NH_3)_2(NO)]$	*e*	1.76(1)		1.945(10)	2.12(1)[f] 2.06(1)[g]	1.26(2)
$[Ru(OH)(NH_3)_4(NO)]^{2+}$	17	1.735(3)		1.961(3)	2.102(3)	1.159(5)
$[RuCl_5(NO)]^{2-}$	*h*	1.738(2)	2.357(1)		2.376(1)	1.131(3)
$[RuCl_3(PMePh_2)_2(NO)]$	*i*	1.744(6)	2.357(2)		2.398(7)[j]	1.132(6)
$[RuCl_3(PPh_3)_2(NO)]$	*k*	1.737(7)	2.353(2)		2.394(2)[j]	1.142(8)
$[RuCl(py)_4(O)]^{+}$	5		2.419(4)		2.096(10)	
$[RuCl(py)_4\{N(OH)CHC(O)Me\}]^{+}$	*l*		2.442(4)		2.108(10)	

[a] T. Kimura, T. Sakurai, M. Shima, T. Togano, M. Mukaida, and T. Nomura, *Inorg. Chim. Acta,* 1983, **69**, 135. [b] H. Nagao, K. Aoyagi, Y. Yukawa, F. S. Howell, M. Mukaida, and H. Kakihana, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3247. [c] N. S. Al-Zamil, E. H. M. Evans, R. D. Gillard, D. W. James, T. E. Jenkins, R. J. Lancashire, and P. A. Williams, *Polyhedron*, 1982, **1**, 525. [d] S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, 1965, **27**, 309. [e] T. S. Khodashova, V. S. Sergienko, and M. A. Porai-Koshits, *J. Struct. Chem.*, 1971, **12**, 439. [f] *cis*-NH_3. [g] *cis*-NO_2. [h] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1420. [i] A. J. Schultz, R. L. Henry, J. Reed, and R. Eisenberg, *Inorg. Chem.*, 1974, **13**, 732. [j] *cis*-Cl. [k] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060. [l] F. Bottomley, P. S. White, M. Mukaida, K. Shimura, and H. Kakihana, *J. Chem. Soc., Dalton Trans.*, 1988, 2965.

$$[Ru(OH)(py)_4(NO)]^{2+} + N_3^- + 3H_2O \longrightarrow [Ru(OH)(py)_4(NO)]^{+} + NH_3 + 3OH^- + N_2 \quad (1)$$

electron would enter the π^*(RuNO) orbital of $[Ru(OH)(py)_4(NO)]^{2+}$, thus labilising a *cis* ligand as discussed above. Subsequent reoxidation by O_2 would give the observed products. Such a reduction could not occur with OH^-, nor with NH_2OH, which is a much weaker reducing agent than N_3^-. In the reaction between N_3^- and $[RuCl(py)_4(NO)]^{2+}$ reduction (without substitution) and adduct formation were both observed; NH_2OH reduced $[RuCl(py)_4(NO)]^{2+}$, again without substitution. The electrochemical results show that *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ is more difficult to reduce than the chloro derivative, which is in turn more difficult to reduce than *trans*-$[Ru(NH_3)(py)_4(NO)]^{3+}$. The reduction of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ is irreversible under the same conditions as the reaction with N_3^-. The irreversibility must be due to substitution of pyridine on reduction from an $\{RuNO\}^6$ to an $\{RuNO\}^7$ complex. This substitution does not take place at -20 °C, where the reduction of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ is reversible and very similar to *trans*-$[RuCl(py)_4(NO)]^{2+}$, *trans*-$[Ru(NH_3)(py)_4(NO)]^{3+}$, or *cis*-$[RuCl(bipy)_2(NO)]^{2+}$ at 25 °C.[9]

The evidence clearly indicates that the apparent substitution of pyridine in *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ is in fact due to initial reduction and subsequent substitution in the reduced complex. The chloro derivative does not undergo loss of pyridine on reduction; the only substitution reaction observed is slow loss of chloride. Since the chloro and hydroxo complexes have very similar structural parameters (see below), the difference in their behaviour on reduction lies in the nature of the unoccupied π^*(RuNO) orbital of *trans*-$[RuX(py)_4(NO)]^{2+}$ (X = Cl or OH) into which the electron is added. This orbital must contain a significant contribution from *cis*-pyridine ligands in the case of *trans*-$[Ru(OH)(py)_4(NO)]^{2+}$ but not in *trans*-$[RuCl(py)_4(NO)]^{2+}$. The π^*(RuNO) orbital is also of higher energy in the hydroxo derivative, as shown by the $E_{\frac{1}{2}}$ values. One reason for the increased contribution of pyridine orbitals to the unoccupied π^*(RuNO) in the hydroxy case could be the close match in energy between NO, OH, and pyridine π orbitals compared to the chloro case.

Table 3 shows that the Ru–OH and Ru–Cl distances are short, and the Ru–NO distances long, in the *trans*-$[RuX(py)_4(NO)]^{2+}$ (X = OH or Cl) complexes, compared to all other similar compounds. For some reason that is not clear at present, the *trans* effect which mutually reinforces X–M–NO bonds, and produces mutually short distances, is not operating in either of the *trans*-$[RuX(py)_4(NO)]^{2+}$ compounds. The Ru–py distances are the same as the Ru–NH_3 distances in *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$.[17] The π bonding between Ru and pyridine is not manifested in the Ru–N distances. As usual in octahedral complexes containing the strongly π-bonding NO ligand, the ligating nitrogen atoms of the pyridine ligands are displaced 0.1 Å away from NO towards OH.

Experimental

The starting materials *trans*-$[Ru(OH)(py)_4(NO)]A_2$ and *trans*-$[RuCl(py)_4(NO)]A_2$ (A = ClO_4 or PF_6) were prepared by the literature methods.[4] The salt *trans*-$[Ru(NH_3)(py)_4(NO)][PF_6]_3 \cdot H_2O$ was prepared by warming a suspension of *trans*-$[RuCl(py)_4(NO)][PF_6]_2$ in aqueous ammonia and collecting the precipitate which deposited on slow cooling. The brown, diamagnetic, product was characterised by i.r. [ν(NO) 1 940, $\delta(NH_3)$ 1 380 cm^{-1}], ^1H n.m.r. [$(CD_3)_2CO$ solution] δ 8.3 (d, 2 H, py $H^{2,6}$), 7.8 (t, 1 H, py H^4), and 7.3 (t, 2 H, py $H^{3,5}$), and analysis (Found: C, 26.3; H, 2.6; N, 9.0. Calc.: C, 26.2; H, 2.75; N, 9.2%). All other chemicals were reagent grade. Infrared spectra were measured on a Hitachi EPIG2 instrument, u.v.–visible on a Hitachi 200-20, n.m.r. on a Hitachi R22, and conductivities, in MeOH or $MeNO_2$, on a Metrohm Konduktskop E356. The electrochemical experiments used a Fuso 312 polarograph with a stationary platinum disk electrode. All potentials were measured against a Ag–$AgClO_4$ (0.1 mol dm^{-3}) electrode in acetonitrile. Elemental analyses were performed by the Sophia University analytical facility or the Institute of Chemical and Physical Research, Wako, Saitama, Japan.

Reaction of trans-$[Ru(OH)(py)_4(NO)][ClO_4]_2$ *with* NaN_3: *Formation of* $[Ru(OH)(N_3)_2(py)_2(NO)]$ *and* $[Ru(N_3)_3(py)_2(NO)]$.—To a solution of *trans*-$[Ru(OH)(py)_4(NO)][ClO_4]_2$ (0.3 g) in water (50 cm^3) was added NaN_3 (0.25 g). The solution was slowly warmed, while stirring, until the colour turned brown. During the reaction there was evolution of N_2 gas. On setting the solution aside at room temperature, dark green $[Ru(N_3)_3(py)_2(NO)]$ precipitated. This was removed by filtration, washed with water, water–methanol, and ether, and air dried. It was recrystallised from acetone–ether. Yield 0.035 g, 20% (Found: C, 29.0; H, 2.3; N, 40.3. Calc. for $C_{10}H_{10}N_{12}ORu$: C, 28.9; H, 2.45; N, 40.5%). The compound was diamagnetic, had a conductivity of 3 s cm^2 mol^{-1} in $MeNO_2$ and 5 s cm^2 mol^{-1} in MeOH. I.r.: ν(NO) 1 863vs; $\nu(N_3)$ 2 050vs cm^{-1}.

The filtrate, after removal of $[Ru(N_3)_3(py)_2(NO)]$, was concentrated by warming until the first red-brown crystals appeared, then filtered, and the filtrate set aside at room temperature for 2 d. The red-brown crystals of $[Ru(OH)(N_3)_2(py)_2(NO)]$ which deposited were collected by filtration, washed with cold water, water–methanol, and ether. Yield 0.05 g, 30% (Found: C, 30.5; H, 2.9; N, 32.3. Calc. for $C_{10}H_{11}N_9O_2Ru$: C, 30.8; H, 2.8; N, 32.3%). The complex was diamagnetic and had a conductivity of 4 s cm^2 mol^{-1} in $MeNO_2$ or MeOH. I.r. (Nujol mull): ν(NO) 1 812vs; $\nu(N_3)$ 2 010vs; ν(OH) 3 520s; δ(RuOH) 900w cm^{-1}. On deuteriation the absorption at 3 520 shifted to 3 350 cm^{-1}; that at 900 cm^{-1} was no longer observed. ^1H N.m.r. ($CDCl_3$ solution): δ 8.8 (d, 2 H, py $H^{2,6}$), 7.9 (t, 1 H, py H^4), and 7.6 (t, 2 H, py $H^{3,5}$). Electronic spectrum (MeCN solution): 288 (log ε = 4.4), 410 (sh), and 520 (sh) nm.

Reaction of trans-$[Ru(NH_3)(py)_4(NO)][PF_6]_3\cdot H_2O$ *with* OH^-: *Formation of trans*-$[Ru(NO_2)(NH_3)(py)_4]PF_6\cdot H_2O$.—To a solution of *trans*-$[Ru(NH_3)(py)_4(NO)][PF_6]_3\cdot H_2O$ (0.05 g) in a mixture of MeCN (5 cm^3) and water (5 cm^3) was added concentrated hydrochloric acid in order to bring the pH to 2.5. The resultant solution was set aside for 3 h. The orange crystals of *trans*-$[Ru(NO_2)(NH_3)(py)_4]PF_6\cdot H_2O$ which formed were collected by filtration, washed with water, water–ethanol, and ether, and air dried. Yield 0.033 g, 95% (Found: C, 37.6; H, 3.7; N, 13.0. Calc. for $C_{20}H_{25}F_6N_6O_3PRu$: C, 37.3; H, 3.9; N, 13.1%). I.r. 1 380 [$\delta(NH_3)$]; 1 308, 1 276 cm^{-1} [$\delta(NO_2)$]. ^1H N.m.r. [$(CD_3)_2CO$ solution]: δ 7.9 (d, 2 H, py $H^{2,6}$), 7.5 (t, 1 H, py H^4), and 7.0 (t, 2 H, py $H^{3,5}$). The compound was diamagnetic and reconverted into $[Ru(NH_3)(py)_4(NO)]^{3+}$ in acid solution.

Synthesis of $[RuCl_3(py)_2(NO)]\cdot H_2O$.—To a solution of *trans*-$[RuCl(py)_4(NO)][ClO_4]_2$ (0.1 g) in acidified [concentrated HCl (2 cm^3)] water (12 cm^3) was added, under argon, a solution of $SnCl_2\cdot 2H_2O$ (0.04 g) in concentrated hydrochloric acid (3 cm^3). The resultant solution was set aside at 25 °C for 6 h, during which time its colour changed from orange to pale green, and pink crystalline $[RuCl_3(py)_2(NO)]\cdot H_2O$ deposited. The crystals were collected by filtration, washed with water, ethanol, and ether, and air dried. Yield 0.02 g, 30% (Found: C, 28.4; H, 3.05; N, 9.8. Calc. for $C_{10}H_{12}Cl_3N_3O_2Ru$: C, 28.45; H, 3.3; N, 10.0%). I.r. ν(NO) 1 852 cm^{-1}. The complex was diamagnetic.

Determination of the Structure of trans-$[Ru(OH)(py)_4(NO)][PF_6]_2\cdot H_2O$ *by X-Ray Diffraction*.—Crystals were obtained from aqueous solution as described previously.[4] A crystal of dimensions 0.15 × 0.15 × 0.40 mm was mounted on a Rigaku-Denki AFC-6A diffractometer. Cell dimensions were determined at 20° by accurate centring of 16 reflections with $30 < 2\theta < 40°$. Space-group symmetry was determined on the diffractometer.

Crystal data. $C_{20}H_{23}F_{12}N_5O_3P_2Ru$, $M_r = 772.4$, monoclinic, space group $P2_1/n$, $a = 10.876(1)$, $b = 27.711(4)$, $c = 10.631(1)$ Å, $\beta = 116.05(1)°$, $U = 2\,878.5(7)$ Å^3, $Z = 4$; $D_c = 1.78$ Mg m^{-3}, $D_m = 1.76$ Mg m^{-3}, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 7.66 cm^{-1}, $F(000) = 1\,536$.

The intensities of 6 797 reflections with $2\theta < 55°$ were measured using the ω-2θ scan method. These yielded 5 130 observed reflections for which $I > 3\sigma(I)$. No correction was made for absorption. The structure was solved by the heavy-atom method. Refinement using UNICS[18] (H isotropic, all other atoms anisotropic) resulted in R $[=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] = 0.038$, R' $\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma|wF_o|^2]^{\frac{1}{2}}\} = 0.055$, and a goodness of fit $\{= [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}\}$ of 0.803 (m = number of observations, n = number of variables). A weighting scheme of the form $w = 1/\{[\sigma(|F_o|)]^2 + 0.05|F_o|\}$, where σ was determined from counting statistics, was used in the refinement. All hydrogen atoms, except for the OH group, were observed in difference Fourier syntheses. Atomic scattering factors for the neutral atoms were taken from the literature.[19] The maximum value of the shift-to-error ratio in the final cycle was 0.3 for a hydrogen and 0.1 for a fluorine of a PF_6 group. A final difference synthesis had a maximum of 0.58 e Å^{-3} and a deepest hole of − 0.26 e Å^{-3}. Table 4 gives the co-ordinates of the non- hydrogen atoms.

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Table 4. Positional parameters (× 10^4) for non-hydrogen atoms of *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2\cdot H_2O$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	1 680.8(2)	1 230.2(1)	8 188.6(2)	C(31)	2 506(4)	1 781(1)	10 857(4)
N(2)	101.8(25)	935.5(9)	7 664.4(26)	C(41)	3 971(4)	611(1)	10 229(4)
O(2)	−868.4(25)	704.5(10)	7 276.0(30)	C(42)	4 630(4)	290(2)	11 300(4)
O(1)	3 410.2(22)	1 541.1(8)	8 754.9(24)	C(43)	3 934(5)	74(2)	11 953(4)
N(11)	2 099.0(25)	799.6(9)	6 793.4(25)	C(44)	2 592(4)	191(2)	11 510(4)
N(12)	887.5(27)	1 778.3(9)	6 675.0(28)	C(45)	1 990(4)	516(1)	10 448(3)
N(13)	1 420.5(29)	1 676.6(9)	9 649.6(27)	P(1)	−1 056(1)	865(0)	11 515(1)
N(14)	2 657.4(25)	724.2(9)	9 798.0(25)	F(11)	−347(3)	352(1)	11 668(3)
C(11)	2 602(3)	903(1)	5 947(3)	F(12)	−1 787(3)	1 375(1)	11 332(4)
C(12)	2 880(4)	705(1)	5 045(4)	F(13)	−1 281(3)	896(1)	9 928(3)
C(13)	2 669(4)	217(1)	5 014(4)	F(14)	−826(3)	833(1)	13 086(3)
C(14)	2 136(4)	23(1)	5 854(4)	F(15)	380(3)	1 121(1)	12 002(3)
C(15)	1 873(4)	322(1)	6 724(4)	F(16)	−2 492(3)	605(1)	11 016(3)
C(21)	1 320(4)	2 235(1)	7 030(4)	P(2)	1 123(1)	3 601(0)	9 850(1)
C(22)	939(5)	2 600(1)	6 058(5)	F(21)	2 190(4)	3 845(1)	9 427(4)
C(23)	71(5)	2 494(2)	4 690(4)	F(22)	1 104(3)	4 076(1)	10 683(4)
C(24)	−380(4)	2 026(2)	4 333(4)	F(23)	54(3)	3 367(1)	10 323(3)
C(25)	35(4)	1 682(1)	5 346(4)	F(24)	−131(4)	3 810(1)	8 524(3)
C(35)	211(4)	1 869(1)	9 409(4)	F(25)	1 122(4)	3 122(1)	9 066(4)
C(34)	58(5)	2 168(2)	10 348(5)	F(26)	2 342(3)	3 401(1)	11 217(3)
C(33)	1 172(6)	2 274(2)	11 577(5)	O(W)	5 661(4)	1 288(2)	8 319(4)
C(32)	2 406(5)	2 080(2)	11 836(4)				

tallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Acknowledgements

We thank Professors A. Ouchi (Tokyo University), H. Shimoi (Tohoku University), and Y. Yukama (Nigata University) for assistance with the *X*-ray determination, M. Shiozaki and Y. Hirano for technical assistance, and K. Shimizu and H. Nagao for some of the electrochemical experiments.

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Received 7th March 1989; *Paper* 9/00991D