# Electrophilic Behaviour of Nitrosyls: Preparation and Reactions of Six-co-ordinate Ruthenium Tetra(pyridine) Nitrosyl Complexes †

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Reaction of $NO_2^-$ with $[RuCl_2(py)_4]$ gave $[Ru(NO_2)_2(py)_4]$ which on treatment with HCl gave $[RuCl(py)_4(NO)]^{2+}$, isolated as $ClO_4^-$ or $PF_6^-$ salts. Use of HBr or $HClO_4$ instead of HCl gave $[RuBr(py)_4(NO)]^{2+}$ or $[Ru(OH)(py)_4(NO)]^{2+}$ respectively. The nitrosyl ligand in $[RuX(py)_4(NO)]^{2+}$ behaved as an electrophile [$\nu$(NO) was 1 910 cm$^{-1}$ for X = Cl, 1 901 cm$^{-1}$ for X = Br, and 1 868 cm$^{-1}$ for X = OH]. With $OH^-$ $[RuX(NO_2)(py)_4]$ was formed reversibly. With an excess of $N_3^-$ and $[RuCl(py)_4(NO)][ClO_4]_2$ a mixture of $[RuCl(N_3)(py)_4]$ and $[RuCl(H_2O)(py)_4]^+$ was formed, $N_2$ and $N_2O$ being evolved. The less soluble $[RuCl(py)_4(NO)][PF_6]_2$ reacted with an equimolar amount of $N_3^-$ to give $[RuCl(N_2)(py)_4]PF_6$, which was unstable with respect to $N_2$ loss in solution, and was contaminated with a small quantity of a reduced nitrosyl complex, believed to be $[Ru(H_2O)(py)_4(NO)][PF_6]_2$ or $[Ru(py)_4(NO)][PF_6]_2{\cdot}H_2O$. The formation of $[RuCl(N_2)(py)_4]^+$ indicates that the reaction between $[RuCl(py)_4(NO)]^{2+}$ and $N_3$ proceeds *via* a cyclic Ru–N=N–N=N–O intermediate, as was confirmed by labelling experiments. Electrochemical one-electron reduction of $[RuCl(py)_4(NO)]^{2+}$ gave $[Ru(H_2O)(py)_4(NO)]^{2+}$, isolated as the $PF_6^-$ salt; it is not known how strongly the $H_2O$ molecule is attached to the ruthenium, if at all. Electrochemical six-electron reduction of $[RuCl(py)_4(NO)]^{2+}$ gave $[RuCl(NH_3)(py)_4]^+$; this same product could be isolated as the $PF_6^-$ salt from zinc amalgam reduction of $[RuCl(py)_4(NO)]^{2+}$. Polarographic, coulometric, and cyclic voltammetry experiments showed that $[RuCl(py)_4(NO)]^{2+}$ is reduced in two successive reversible one-electron steps followed by an irreversible four-electron reduction.

We have shown previously that a co-ordinated nitrosyl group manifests electrophilic properties in complexes in which it can be considered formally as an $NO^+$ ligand and in which $\pi$ donation of electrons from the metal to NO is relatively small as judged by physical methods.[1 3] Ruthenium complexes such as $[Ru(NH_3)_5(NO)]^{3+}$,[4–6] $[RuCl(pdma)_2(NO)]^{2+}$ [pdma = *o*-phenylenebis(dimethylarsine)],[7,8] and $[RuCl(bipy)_2(NO)]^{2+}$ (bipy = 2,2′-bipyridine)[9–12] are examples of nitrosyl complexes which behave as electrophiles. In order to extend this type of chemistry and to understand the factors which govern the reactivity we have prepared a series of ruthenium tetra(pyridine) nitrosyls, $[RuX(py)_4(NO)]^{2+}$ (py = pyridine; X = Cl, Br, or OH), and have investigated their reactivity towards nucleophiles and towards reduction.

## Experimental

Ruthenium oxide (Engelhardt) was converted into ruthenium trichloride by standard methods, and the product ' activated ' as follows.

A solution of the ruthenium trichloride (0.2 g) in aqueous HCl (3 mol dm$^{-3}$, 10 cm$^3$) was evaporated to dryness, the residue dissolved in ethanol–water (3 : 1 v/v, 40 cm$^3$) and the resultant solution again evaporated to dryness on a steam-bath. The dissolution in ethanol–water and subsequent evaporation to dryness were repeated four times. The residue was then dissolved in a mixture of aqueous HCl (1 mol dm$^{-3}$, 10 cm$^3$) and formic acid (2 cm$^3$), the solution heated (80—90 °C) in an open beaker on a steam-bath until it became a dark brown-green colour (*ca.* 30—60 min), and then further heated (93—95 °C, *ca.* 30 min, with the beaker covered with a watch glass to prevent concentration of the solution) until a deep blue colour was achieved. This deep blue solution was used for the preparation of the tetra(pyridine)ruthenium complexes. The blue solution is not stable for long periods in air.

trans-*Dichlorotetra(pyridine)ruthenium*, *trans*-$[RuCl_2(py)_4]$.[13,14]—To the blue solution was added pyridine (30 cm$^3$), the resultant mixture heated on a steam-bath for 2 h, and then the volume was reduced on a rotary evaporator until the yellow-brown crystalline product precipitated. The material was used without further purification in the syntheses below. The n.m.r. spectrum (see Table) showed that the $[RuCl_2(py)_4]$ was the *trans* isomer.

trans-*Dinitrotetra(pyridine)ruthenium*, *trans*-$[Ru(NO_2)_2(py)_4]$.—To *trans*-$[RuCl_2(py)_4]$ (1.0 g) dissolved in pyridine (150 cm$^3$) was added a solution of $NaNO_2$ (0.4 g) dissolved in water (40 cm$^3$). The reddish brown mixture was warmed to 70 °C and stirred at this temperature for 4 d, giving a yellow solution. On concentrating the solution by rotary evaporation a yellow powder precipitated, which was removed by filtration, washed with water, ethanol, and diethyl ether, and air dried. Yield 0.85 g, 85%.

trans-*Chloronitrosyltetra(pyridine)ruthenium Diperchlorate Monohydrate and Bis(hexafluorophosphate) Hemihydrate*, *trans*-$[RuCl(py)_4(NO)][ClO_4]_2{\cdot}H_2O$ *and* *trans*-$[RuCl(py)_4(NO)][PF_6]_2{\cdot}0.5H_2O$.—To a suspension of $[Ru(NO_2)_2(py)_4]$ (0.3 g) in ethanol ‡ (5 cm$^3$) was added aqueous HCl (3 mol dm$^{-3}$, 5 cm$^3$). The mixture was gently heated on a water-bath for 10 min, then evaporated to a small volume. The precipitate was redissolved in water (10 cm$^3$), the solution filtered, and to the filtrate was added a solution of $NaClO_4$ (2 g) in water (20 cm$^3$) or $NH_4PF_6$ (2 g) in water (5 cm$^3$). The orange precipitate of $[RuCl(py)_4(NO)][ClO_4]_2$ was recrystallised from

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† *Non-S.I. unit employed:* B.M. ≈ 9.27 × 10$^{-24}$ J T$^{-1}$.

‡ Ethanol is necessary for good yields of $[RuCl(py)_4(NO)]^{2+}$; without it $[Ru(OH)(py)_4(NO)]^{2+}$ is obtained.

**Table.** Analysis and physical properties of the complexes

| Complex | Analysis (%)[a] | | | | I.r. ($cm^{-1}$)[b] | $^1H$ N.m.r. (p.p.m.)[c] | $\Lambda$[d]/S $cm^2$ $mol^{-1}$ | Comments |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Other | | | | |
| *trans*-$[RuCl(py)_4(NO)][ClO_4]_2{\cdot}H_2O$ | 34.2<br>(34.3) | 3.3<br>(3.2) | 10.0<br>(10.0) | Cl 5.2, $H_2O$ 2.3[e]<br>(5.1) (2.6) | 1 908vs<br>[ν(NO)] | 8.6 (d, $H^{2,6}$),<br>8.3 (t, $H^4$),<br>7.7 (t, $H^{3,5}$) | 181 | Diamagnetic<br>ν($^{15}NO$) 1 877 $cm^{-1}$ |
| *trans*-$[RuCl(py)_4(NO)][PF_6]_2{\cdot}0.5H_2O$ | 31.2<br>(30.7) | 2.5<br>(2.7) | 9.1<br>(8.95) | Cl 4.6, Ru 13.3<br>(4.5) (12.9) | 1 910vs<br>[ν(NO)] | | 177 | Diamagnetic<br>ν($^{15}NO$) 1 869 $cm^{-1}$ |
| *trans*-$[RuBr(py)_4(NO)][ClO_4]_2{\cdot}H_2O$ | 32.8<br>(32.3) | 3.0<br>(3.0) | 9.5<br>(9.4) | | 1 901vs<br>[ν(NO)] | | 171 | Diamagnetic |
| *trans*-$[Ru(OH)(py)_4(NO)][ClO_4]_2{\cdot}2H_2O$ | 34.1<br>(34.3) | 3.5<br>(3.6) | 10.0<br>(10.0) | $H_2O$ 4.9<br>(5.1) | 1 860vs<br>[ν(NO)] | 8.7 (d, $H^{2,6}$),<br>8.2 (t, $H^4$),<br>7.7 (t, $H^{3,5}$) | 201 | Diamagnetic<br>ν($^{15}NO$) 1 821 $cm^{-1}$ |
| *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2$[f] | 31.6<br>(31.8) | 2.6<br>(2.8) | 9.0<br>(9.3) | Ru 13.8<br>(13.4) | 1 868vs<br>[ν(NO)] | | 177 | Diamagnetic<br>ν($^{15}NO$) 1 833 $cm^{-1}$ |
| $[RuCl(NO_2)(py)_4]{\cdot}H_2O$ | 46.0<br>(46.4) | 3.9<br>(4.3) | 13.1<br>(13.5) | | 1 305vs,<br>1 227m<br>[ν($NO_2$)] | 8.5 (d, $H^{2,6}$),<br>7.5 (t, $H^4$),<br>7.0 (t, $H^{3,5}$) | | Diamagnetic<br>ν($^{15}NO_2$) 1 281,<br>1 210 $cm^{-1}$ |
| *trans*-$[Ru(NO_2)_2(py)_4]$ | | | | | | 8.3 (d, $H^{2,6}$),<br>7.6 (t, $H^4$),<br>7.0 (t, $H^{3,5}$) | 1 | |
| $[RuCl(NH_3)(py)_4]PF_6{\cdot}2H_2O$ | 36.5<br>(36.9) | 4.0<br>(4.15) | 10.6<br>(10.9) | Cl 5.2, Ru 15.4<br>(5.5) (15.5) | 1 314m<br>[$\delta_{sym}$ ($NH_3$)] | | 116 | Diamagnetic<br>$\delta_{sym}$($^{15}NH_3$) 1 309 $cm^{-1}$<br>$\delta_{sym}$($N^2H_3$) 1 010 $cm^{-1}$ |
| $[Ru(H_2O)(NH_3)(py)_4][PF_6]_2$ | 33.2<br>(32.3) | 2.7<br>(3.1) | 9.5<br>(9.4) | Ru 13.3, $PF_6$ 39.7<br>(13.6) (39.1) | | | 183 | Diamagnetic |
| *trans*-$[RuCl_2(py)_4]$ | 48.8<br>(49.2) | 4.2<br>(4.1) | 11.4<br>(11.5) | | | 8.5 (d, $H^{2,6}$),[g]<br>7.5 (t, $H^4$),[g]<br>7.0 (t, $H^{3,5}$)[g] | 3 | Diamagnetic |
| $[RuCl_2(py)_4]ClO_4$ | 39.7<br>(40.8) | 3.5<br>(3.4) | 9.5<br>(9.5) | | | | 98 | Paramagnetic<br>$\mu_{eff.}$ = 1.87 B.M. |
| $[RuCl(N_3)(py)_4]{\cdot}2H_2O$ | 45.3<br>(45.2) | 4.3<br>(4.5) | 17.8<br>(18.5) | | 2 030vs<br>[ν($N_3$)] | | | Diamagnetic |
| $[RuCl(H_2O)(py)_4]PF_6$ | 38.2<br>(39.0) | 3.4<br>(3.6) | 9.0<br>(9.1) | | | | | Diamagnetic |
| $[RuCl(N_2)(py)_4]PF_6$ | 37.9<br>(38.4) | 2.8<br>(3.2) | 12.4<br>(13.4) | Cl 5.2, Ru 16.0<br>(5.7) (16.0) | | | | |

[a] Calculated values are given in parentheses. [b] As KBr pellets. [c] In acetone; d = doublet, t = triplet. Numerals refer to proton positions on pyridine ring. [d] Nitromethane. [e] Water determined by Karl Fischer method. [f] Also occurs with $0.5H_2O$ in lattice. [g] In $CDCl_3$.

methanol–acetone (1 : 1 v/v) containing a few drops of water, and the product washed with water, ethanol, and diethyl ether, and air dried. Yield 0.31 g, 68%. The precipitate of $[RuCl(py)_4(NO)][PF_6]_2$ (also orange) was also recrystallised from methanol–acetone, and washed and dried as for the perchlorate salt. Yield 0.37 g, 84%.

trans-*Bromonitrosyltetra(pyridine)ruthenium Diperchlorate Monohydrate,* *trans*-$[RuBr(py)_4(NO)][ClO_4]_2{\cdot}H_2O$.—This orange-brown complex was obtained in an exactly analogous manner to the chloro-derivative except that aqueous HBr was used instead of aqueous HCl.

trans-*Hydroxynitrosyltetra(pyridine)ruthenium Diperchlorate Dihydrate and Bis(hexafluorophosphate),* *trans*-$[Ru(OH)(py)_4(NO)][ClO_4]_2{\cdot}2H_2O$ *and* *trans*-$[Ru(OH)(py)_4(NO)][PF_6]_2$.—A solution of $[Ru(NO_2)_2(py)_4]$ (0.3 g) in aqueous $HClO_4$ (1.75 mol $dm^{-3}$, 40 $cm^3$) was filtered and to the filtrate was added either a solution of $NaClO_4$ (1.5 g) in water (10 $cm^3$) or of $NH_4PF_6$ (1.5 g) in water (20 $cm^3$). The yellow products were recrystallised from methanol–acetone (1 : 1 v/v). Yields: 0.32 g ($ClO_4$ salt), 0.37 g ($PF_6$ salt); 85% in both cases.

trans-*Amminechlorotetra(pyridine)ruthenium Hexafluorophosphate Dihydrate,* *trans*-$[RuCl(NH_3)(py)_4]PF_6{\cdot}2H_2O$.—A solution of $[RuCl(py)_4(NO)][ClO_4]_2{\cdot}H_2O$ (0.15 g) in aqueous HCl (2 mol $dm^{-3}$, 25 $cm^3$) was added to zinc amalgam (5 $cm^3$) under argon. The mixture was shaken for 15 min, filtered, and a solution of $NH_4PF_6$ (1.5 g) in water (5 $cm^3$) added to the filtrate. On setting aside overnight in a refrigerator, pale yellow crystals of $[RuCl(NH_3)(py)_4]PF_6$ formed. These were collected by filtration, washed with cold water, ethanol, and diethyl ether, and air dried. Yield 0.063 g, 45%.

trans-*Ammineaquatetra(pyridine)ruthenium Bis(hexafluorophosphate),* *trans*-$[Ru(H_2O)(NH_3)(py)_4][PF_6]_2$.—This was prepared in 30% yield exactly analogously to $[RuCl(NH_3)(py)_4]PF_6$ except that a mixture of concentrated $H_2SO_4$ (0.3 $cm^3$) and water (20 $cm^3$) was used instead of HCl.

trans-*Chloronitrotetra(pyridine)ruthenium,* *trans*-$[RuCl(NO_2)(py)_4]$.—To a suspension of $[RuCl(py)_4(NO)][ClO_4]_2$ (0.1 g) in water (10 $cm^3$) was added a solution of NaOH (1 mol $dm^{-3}$) to bring the pH to between 9 and 10 (pH meter). The mixture was stirred for 30 min and the product removed by filtration, washed with water, and a small quantity of methanol and diethyl ether. Yield 0.05 g, 75%.

*Reaction of* trans-*Chloronitrotetra(pyridine)ruthenium with Acid.*—To a solution of $[RuCl(NO_2)(py)_4]$ (0.05 g) in ethanol (10 $cm^3$) was added water (3 $cm^3$) and then the solution was made acid with aqueous HCl (1 mol $dm^{-3}$). The resultant solution was concentrated to 5 $cm^3$ on a steam-bath, filtered, and $NH_4PF_6$ (0.5 g) dissolved in water (5 $cm^3$) added, giving an orange precipitate of $[RuCl(py)_4(NO)][PF_6]_2$ (0.055 g, 70%). The product was identical with the $[RuCl(py)_4(NO)][PF_6]_2$ prepared as described above.

*Reaction of* trans-*Chloronitrosyltetra(pyridine)ruthenium Diperchlorate Monohydrate with Azide Ion. Formation of Aquachlorotetra(pyridine)ruthenium Hexafluorophosphate,* $[RuCl(H_2O)(py)_4]PF_6$, *and Azidochlorotetra(pyridine)ruthenium Dihydrate,* $[RuCl(N_3)(py)_4]\cdot 2H_2O$.—To a suspension of $[RuCl(py)_4(NO)][ClO_4]_2\cdot H_2O$ (0.1 g) in ethanol (5 cm$^3$) was added a solution of $NaN_3$ (0.1 g) in water (5 cm$^3$). The mixture was set aside for 4 h at room temperature, during which time an orange precipitate of $[RuCl(N_3)(py)_4]$ formed in low yield. This was collected by filtration and washed with water.

To the filtrate was added $NH_4PF_6$ (0.3 g) and the mixture set aside at room temperature overnight. The brown crystals of $[RuCl(H_2O)(py)_4]PF_6$ which formed (also in low yield) were collected by filtration and washed quickly with water.

*Reaction of* trans-*Chloronitrosyltetra(pyridine)ruthenium Bis(hexafluorophosphate) Hemihydrate with Azide Ion. Formation of Chloro(dinitrogen)tetra(pyridine)ruthenium Hexafluorophosphate,* $[RuCl(N_2)(py)_4]PF_6$.—To a suspension of $[RuCl(py)_4(NO)][PF_6]_2\cdot 0.5H_2O$ (0.1 g) in ethanol (5 cm$^3$) was added $NaN_3$ (0.01 g) in water (5 cm$^3$). The mixture was set aside for 3 h at 20 °C giving a moss-green precipitate. This was removed by filtration and washed quickly with water, ethanol, and diethyl ether. The product (yield 0.02 g) is mainly $[RuCl(N_2)(py)_4]PF_6$, but contains some reduced nitrosyl complex (see Results and Discussion section). Attempts to recrystallise the dinitrogen complex were not successful because it loses $N_2$ in solution, and even in the solid state its colour changes from pale yellow to dark blue-green over a period of 1 week.

*Aquanitrosyltetra(pyridine)ruthenium Bis(hexafluorophosphate),* $Ru(py)_4(NO)(PF_6)_2\cdot H_2O$.—A solution of $[RuCl(py)_4(NO)][ClO_4]_2$ (0.1 g) in an aqueous acetate buffer (pH 4.5) containing a small quantity of KCl was placed in an electrolysis cell. Polarographic measurements showed the presence of three reduction waves, at +0.10, −0.24, and −0.45 V. The solution was then electrolysed at −0.20 V until the first wave of the d.c. polarogram had disappeared. Addition of $NH_4PF_6$ (0.3 g) precipitated a small yield of $Ru(py)_4(NO)(PF_6)_2\cdot H_2O$.

*Dichlorotetra(pyridine)ruthenium Hydrogendinitrate,* $[RuCl_2(py)_4]HN_2O_6$.—To $[RuCl_2(py)_4]$ (1 g) was added a mixture of concentrated $HNO_3$ (1 cm$^3$) and water (100 cm$^3$). The mixture was warmed to 55 °C and $NaNO_2$ (0.5 g) added in small portions. The mixture was stirred until everything had dissolved, then filtered and concentrated by evaporation until the orange crystalline product appeared. After setting aside at room temperature overnight this was collected by filtration, washed with water, acetone, and diethyl ether, and air dried. Yield 0.9 g, 70%.

Instruments used in this work were an Hitachi EP1 G2 i.r. spectrometer, spectra being measured as KBr discs, an Hitachi R22 n.m.r. spectrometer, and a TOA Electronics ' Conduct Meter ' for conductivities. Magnetic moments were by the Gouy method and microanalyses by the Institute of Chemical and Physical Research, Wako, Saitoma 351, Japan.

## Results and Discussion

The new nitrosyl complexes $[RuX(py)_4(NO)]^{2+}$ (X = Cl, Br, or OH) were readily synthesised by the decomposition of $[Ru(NO_2)_2(py)_4]$. The logical direct synthesis, the reaction between $[RuX_2(py)_4]^+$[15] and NO, cannot be used because of the inertness of the ruthenium(III) complex towards substitution by NO. This inertness towards substitution by NO appears to be a general feature of ruthenium(III) and osmium(III) complexes containing $\pi$-acceptor ligands; $[RuCl(bipy)_2(NO)]^{2+}$,[16] $[MCl(pdma)_2(NO)]^{2+}$ (M = Ru [8] or Os [17]), and $[RuX(py)_4(NO)]^{2+}$ all must be prepared by an indirect route. On the other hand $[M(NH_3)_5(NO)]^{3+}$ (M = Ru [18] or Os [19]) can be obtained by direct bimolecular substitution of one of the non-$\pi$-acceptor $NH_3$ ligands in $[M(NH_3)_6]^{3+}$.

During attempts at a direct synthesis, $[RuCl_2(py)_4]$ was treated with $NO_2^-$ in $HNO_3$ instead of in water (thus giving a source of NO). The product was the same as that obtained by reacting pure NO with $[RuCl_2(py)_4]$ in pyridine as solvent, and had the empirical formula $RuCl_2(py)_4(HN_2O_6)$ (Found: C, 38.7; H, 3.6; N, 13.7. Calc. for $C_{20}H_{21}Cl_2N_6O_6Ru$: C, 39.1; H, 3.4; N, 13.7%). We believe this complex is the hydrogendinitrate salt $[RuCl_2(py)_4]HN_2O_6$. The magnetic moment (2.07 B.M. at 16 °C), the conductivity (98 S cm$^2$ mol$^{-1}$ in nitromethane and 210 S cm$^2$ mol$^{-1}$ in water), and the i.r. spectrum (bands at 1 510, 1 330, 980, and 810 cm$^{-1}$, all unshifted when $^{15}NO_2^-$ in $H^{14}NO_3$ was used as reactant) are in agreement with this formulation. In addition $[RuCl_2(py)_4]PF_6$ was obtained after dissolution of $[RuCl_2(py)_4]HN_2O_6$ in water and reprecipitation with $NH_4PF_6$. Hydrogendinitrate salts of platinum-metal complexes containing pyridine have been described previously.[20–22]

The starting material $[RuCl_2(py)_4]$ is known to have the *trans* geometry from the n.m.r. spectra analysed by Raichart and Taube.[14] A crystal-structure determination confirmed the *trans* geometry for $[RuCl(py)_4(NO)][PF_6]_2\cdot 0.5H_2O$.[23] We therefore assume all the other complexes discussed in this work are *trans* also. The four pyridine ligands are arranged in a propeller fashion with a pitch of 46°. This means that the 2 and 6, and 3 and 5, protons of the pyridine rings should be inequivalent in the n.m.r. spectrum of $[RuX(py)_4(NO)]^{2+}$. However at least down to −57 °C only single resonances for the 2,6 or 3,5 protons were observed for both $[RuCl(py)_4(NO)]^{2+}$ and $[RuCl_2(py)_4]$ (where only single resonances would be expected). Hence rapid cog-wheel rotation of the pyridine rings about the Ru–N axis is occurring down to this temperature.

The $\nu$(NO) frequencies are very high (1 860—1 910 cm$^{-1}$) indicating a linear RuNO group and formally $NO^+$ coordinated to $Ru^{II}$. The RuNO angle in $[RuCl(py)_4(NO)][PF_6]_2\cdot 0.5H_2O$ is 174.8°.[23] These high $\nu$(NO) frequencies suggested that the nitrosyl complexes should behave as electrophiles,[3] and this was borne out by experiment. A reversible reaction (1) occurred between $[RuCl(py)_4(NO)]^{2+}$ and $OH^-$.

$$[RuCl(py)_4(NO)]^{2+} + 2OH^- \rightleftharpoons [RuCl(NO_2)(py)_4] + H_2O \quad (1)$$

This reaction went completely to the right at a pH of between 9 and 10. Because of the insolubility of $[RuCl(NO_2)(py)_4]$ in water, and because substitution of $OH^-$ for $Cl^-$ in $[RuCl(py)_4(NO)]^{2+}$ slowly occurred as a side reaction, we were unable to obtain an equilibrium constant for reaction (1). Reversibility was demonstrated by treating $[RuCl(NO_2)(py)_4]$ with acid to regenerate $[RuCl(py)_4(NO)]^{2+}$. A similar reaction to (1) occurred with $[RuBr(py)_4(NO)]^{2+}$. On the other hand $[Ru(OH)(py)_4(NO)]^{2+}$, which has a $\nu$(NO) frequency some 50 cm$^{-1}$ lower than that of $[RuCl(py)_4(NO)]^{2+}$, only reacted with $OH^-$ at very high pH (*ca.* 13). Pure $[Ru(OH)(NO_2)(py)_4]$ could not be obtained from the reaction; it appeared that substitution of $NO_2$ or py by $OH^-$ occurred under the severely alkaline conditions. The $\nu$(NO) frequency of $[Ru(OH)(py)_4(NO)]^{2+}$ (1 860 cm$^{-1}$) is the lowest yet observed for a nitrosyl which behaves as an electrophile, although it is comparable to $[OsCl(pdma)_2(NO)]^{2+}$.[17]

It is known that reactions between $N_3^-$ and electrophilic nitrosyls occur by initial attack of the nucleophile $N_3^-$ at the {MNO} group,[7,24,25] ultimately giving $N_2$, $N_2O$, and a metal complex with a solvent molecule co-ordinated in place of NO. When the soluble perchlorate salt of $[RuCl(py)_4(NO)]^{2+}$ was treated with $N_3^-$ a mixture of $[RuCl(N_3)(py)_4]$ and $[RuCl(H_2O)(py)_4]^+$ was formed. This mixture was readily separable because $[RuCl(N_3)(py)_4]$ precipitated directly from the reaction mixture and $[RuCl(H_2O)(py)_4]^+$ could be obtained from the filtrate by adding $PF_6^-$ as a precipitating anion, although yields were low in both cases. The occurrence of two products can be explained by the consecutive reactions (2) and (3).

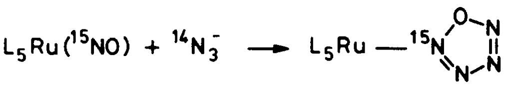
$$[RuCl(py)_4(NO)]^{2+} + N_3^- + H_2O \longrightarrow [RuCl(H_2O)(py)_4]^+ + N_2 + N_2O \quad (2)$$

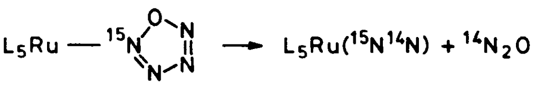
$$[RuCl(H_2O)(py)_4]^+ + N_3^- \rightleftharpoons [RuCl(N_3)(py)_4] + H_2O \quad (3)$$

When the less soluble $[RuCl(py)_4(NO)][PF_6]_2$ was treated with an equimolar amount of $N_3^-$ the intermediate complex $[RuCl(N_2)(py)_4]PF_6$ was trapped because of its insolubility. This dinitrogen complex, which lost $N_2$ rather readily in solution, showed a $\nu(N_2)$ absorption at 2 125 $cm^{-1}$ in the i.r. spectrum, shifted to 2 088 $cm^{-1}$ when $[RuCl(py)_4(^{15}NO)]^{2+}$ was treated with $^{14}N_3^-$. The dinitrogen complex could not be obtained completely pure, but was always contaminated by a complex having a weak absorption at 1 618 $cm^{-1}$ (shoulder on the pyridine absorption at 1 600 $cm^{-1}$) which shifted to 1 579 $cm^{-1}$ when $[RuCl(py)_4(^{15}NO)][PF_6]_2$ was treated with $^{14}N_3^-$. Weak bands in the 3 400 $cm^{-1}$ region indicated the presence of $H_2O$.

The nature of the complex which was formed alongside $[RuCl(N_2)(py)_4]^+$ is not completely clear. However one-electron electrochemical reduction of $[RuCl(py)_4(NO)]^{2+}$ gave a material which also absorbed at 1 618 $cm^{-1}$ in the i.r. spectrum, shifted to 1 582 $cm^{-1}$ when $[RuCl(py)_4(^{15}NO)]^{2+}$ was reduced. This material analysed as $Ru(py)_4(NO)(PF_6)_2 \cdot H_2O$ and was paramagnetic ($\mu_{eff.}$ = 1.73 B.M. at 20 °C). We are unable to say whether the $H_2O$ is co-ordinated to the Ru or not. One-electron reduction of the related $\{RuNO\}^6$ complex $[RuCl(bipy)_2(NO)]^{2+}$ gave six-co-ordinate $[RuCl(bipy)_2(NO)]^+$,[26] whereas the $\{FeNO\}^6$ complex $[Fe(CN)_5(NO)]^{2-}$ gave the five-co-ordinate $[Fe(CN)_4(NO)]^{2-}$.[27–29] It is possible that $Ru(py)_4(NO)(PF_6)_2 \cdot H_2O$ is an intermediate case with a weakly co-ordinated $H_2O$. It is in any event an $\{RuNO\}^7$ complex.

It is certain that $[RuCl(N_2)(py)_4]^+$ is an intermediate in the reaction between $[RuCl(py)_4(NO)]^{2+}$ and $N_3^-$. This fact, coupled with that of the retention of $^{15}N$ in the $N_2$ complex when $[RuCl(py)_4(^{15}NO)]^{2+}$ was treated with $^{14}N_3^-$, indicates that a cyclic $N_4O$ intermediate was formed in the reaction, as proposed by Douglas and Feltham [7] for the reaction between $[RuCl(pdma)_2(NO)]^{2+}$ and $N_3^-$ [equations (4)—(6), $L_5$ = $Cl(py)_4$, S = solvent].


(4)


(5)

$$L_5Ru(^{15}N^{14}N) + S \longrightarrow L_5RuS + {}^{15}N^{14}N \quad (6)$$

The formation of small amounts of $Ru(py)_4(NO)(PF_6)_2 \cdot H_2O$ in the reaction between $[RuCl(py)_4(NO)]^{2+}$ and $N_3^-$ indicates that an intermediate other than the cyclic $Ru(N_4O)$ is present. The most reasonable one is the non-cyclic $[RuCl(py)_4\{N(O)N_3\}]^+$ of the type observed in the reaction between $[Fe(CN)_5(NO)]^{2-}$ and $N_3^-$.[30] If $[RuCl(py)_4\{N(O)N_3\}]^+$ dimerised and subsequently lost $N_2$ the overall reactions would be (7) and (8).

$$2[RuCl(py)_4(NO)]^{2+} + 2N_3^- \longrightarrow 2[RuCl(py)_4(NO)]^+ + 3N_2 \quad (7)$$

$$[RuCl(py)_4(NO)]^+ + H_2O \longrightarrow [Ru(H_2O)(py)_4(NO)]^{2+} + Cl^- \quad (8)$$

The complex $[RuCl(N_3)(py)_4]$ was unusual in that in addition to an intense absorption at 2 030 $cm^{-1}$ in the i.r. spectrum (assigned to the asymmetric vibration of the $N_3$ ligand) only two sharp medium-intensity absorptions of equal intensity at 1 440 and 1 475 $cm^{-1}$ were observed in the py region (1 400—1 600 $cm^{-1}$). A very similar two-band spectrum was observed for the likewise uncharged complex $[RuCl_2(py)_4]$, whereas all charged $[RuXY(py)_4]^{n+}$ complexes showed four bands (two weak, two medium intensity) as is observed for other pyridine complexes.[31,32] It is not clear why the uncharged complexes have anomalous spectra. The n.m.r. spectra were normal.

The reduction of $[RuCl(py)_4(NO)]^{2+}$ by $N_3^-$ is rather surprising, since $N_3^-$ is not normally a powerful enough reductant for an $\{RuNO\}^6$ complex. The $E_{\frac{1}{2}}$ value for electrochemical reduction, +0.1 V, shows that $[RuCl(py)_4(NO)]^{2+}$ is readily reduced, as is $[RuCl(bipy)_2(NO)]^{2+}$ for which the analogous value is 0.20 V.[26] Further chemical reduction of $[RuX(py)_4(NO)]^{2+}$ occurred readily with zinc amalgam; when X = Cl the product was $[RuCl(NH_3)(py)_4]^+$ and when X = OH, $[Ru(H_2O)(NH_3)(py)_4]^{2+}$ was obtained. The products showed the usual i.r. absorptions due to co-ordinated $NH_3$, and the one clearly discernible sharp absorption at 1 314 $cm^{-1}$ [$\delta_{sym}(NH_3)$] shifted to 1 309 $cm^{-1}$ when $[RuCl(py)_4(^{15}NO)]^{2+}$ was reduced, and to 1 010 $cm^{-1}$ when the reduction was performed in $D_2O$. The six-electron reduction of (formally) $NO^+$ to $NH_3$ by zinc which occurred for $[RuX(py)_4(NO)]^{2+}$ parallels the reduction of $[Ru(NH_3)_5(NO)]^{3+}$ by $Cr^{2+}$;[33] reduction of $[RuCl_5(NO)]^{2-}$ by $Sn^{2+}$ on the other hand gave $[Ru_2(N)Cl_8(H_2O)_2]^{3-}$ containing a nitrido-ligand.[34,35] Since all the ruthenum nitrosyls have similar $\nu(NO)$ frequencies and are six-co-ordinate the different products obtained must be a function of the reducing agent.

On electrochemical reduction both $[RuCl(py)_4(NO)]^{2+}$ and $[Ru(OH)(py)_4(NO)]^{2+}$ exhibited three polarographic reduction waves, the $E_{\frac{1}{2}}$ values for $[RuCl(py)_4(NO)]^{2+}$ being +0.10, −0.24, and −0.45 V. The first two waves were reversible, both by direct-current polarography and cyclic voltammetry; the last wave was irreversible. Exhaustive electrolysis at the voltages of the diffusion plateau for the first and third waves gave coulometric values of one and six respectively, and the complexes $Ru(py)_4(NO)(PF_6)_2 \cdot H_2O$ and $[RuCl(NH_3)(py)_4]PF_6$ were isolated from these exhaustive reductions. If it is assumed that reduction can only take place at the {RuNO} moiety, the reactions occurring must be (9)—(11).

$$[RuCl(py)_4(NO)]^{2+} + 1e \rightleftharpoons [RuCl(py)_4(NO)]^+ \quad (9)$$

$$[RuCl(py)_4(NO)]^+ + 1e \rightleftharpoons [RuCl(py)_4(NO)] \quad (10)$$

$$[RuCl(py)_4(NO)] + 5H^+ + 4e \longrightarrow [RuCl(NH_3)(py)_4]^+ + H_2O \quad (11)$$

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