Electrophilic Nitrosyls: Preparation, Structure, and Reactivity of *cis*-Chloronitrosylbis(pyridine-2-carboxylato)ruthenium† and Related Complexes

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Reaction of $[RuCl_5(NO)]^{2-}$ with pyridine-2-carboxylic acid (Hpyca) at pH 4.5 gave *cis*-$[RuCl(pyca)_2(NO)]$, isomer (**I**), with the acetate groups co-ordinated *trans* to the nitrosyl and chloro-ligands and the pyridine nitrogens *trans* to one another, as proved by an *X*-ray crystallographic investigation. Crystal data: orthorhombic, space group $P2_12_12_1$, a = 15.297(8), b = 11.401(5), and c = 8.224(3) Å; R = 0.072. A second product of the reaction was $[RuCl_3(pyca)(NO)]^-$. At pH 7 the reaction gave a second isomer of *cis*-$[RuCl(pyca)_2(NO)]$, (**II**), with the acetate oxygen *trans* to NO and a pyridine nitrogen *trans* to Cl. Reaction of quinoline-2-carboxylic acid (Hqnca) with $[RuCl_5(NO)]^{2-}$ at pH 4.5 gave *cis*-$[RuCl(qnca)_2(NO)]$, isomer (**II**), and at pH 7 $[Ru(OH)(qnca)_2(NO)]$. With $[OsCl_5(NO)]^{2-}$ and Hpyca only $[OsCl_3(pyca)(NO)]^-$ was obtained. It was not possible to isomerise isomer (**I**) thermally without decomposition by loss of HCl. Reactions of the nitrosyl group in isomers (**I**) and (**II**) with nucleophiles were complicated by ligand-replacement reactions.

In previous publications we have described complexes in which the nitrosyl ligand behaves as an electrophile.[1-3] Although a variety of reactions of nucleophiles at nitrosyls of the Group 8 metals are now known,[3,4] one problem is very apparent. All electrophilic nitrosyls so far known are charged species, mostly cations. These only dissolve in solvents which are themselves potential nucleophiles and/or can be deprotonated to produce powerful nucleophiles. Reactions in inert solvents such as toluene or even diethyl ether are not possible. We have been searching for some years for nitrosyls which are both electrophiles and neutral. Since ruthenium complexes with both pyridine[2] and bipyridine[3-5] are electrophilic we felt that negatively charged bidentate derivatives of pyridine would be suitable ligands for the preparation of neutral, electrophilic, nitrosyls. We have accordingly prepared and investigated the reactivity of ruthenium complexes of pyridine-2-carboxylate (pyca) and quinoline-2-carboxylate (qnca) and the results are presented here.

Experimental

Instruments used in the preparative part of this work were a Hitachi EP1-G2 spectrophotometer for i.r. spectra (samples measured as KBr discs) and a Hitachi 624 spectrophotometer for reflectance electronic spectra. Magnetic moments were measured by the Guoy method. Microanalyses were by the Sophia University analytical facility. Ruthenium trichloride was purchased from Engelhardt and converted into $K_2[RuCl_5(NO)]$ by the literature method;[6] $Cs_2[OsCl_5(NO)]$ was purchased from Johnson Matthey. All other chemicals were reagent grade.

cis-*Chloronitrosylbis(pyridine-2-carboxylato)ruthenium, Isomer* (I), *cis*-$[RuCl(pyca)_2(NO)]$.—To a solution of $K_2[RuCl_5(NO)]$ (0.25 g) in water (10 cm^3) was added a solution of Hpyca (0.25 g) in water (10 cm^3) which had been adjusted to pH 4.5 with aqueous NaOH using a pH meter. The mixture was refluxed for 1 h, transferred to an open beaker, and concentrated to 5 cm^3 on a water-bath. On cooling and setting aside overnight, red crystals of $[RuCl(pyca)_2(NO)]$ deposited. These were collected by filtration, washed with water, acetone, and ether, and air dried. The product was recrystallised from nitromethane in 25% (0.07 g) yield (Found: C, 34.8; H, 2.0; Cl, 8.6; N, 10.2. Calc. for $C_{12}H_8ClN_3O_5Ru$: C, 35.1; H, 2.0; Cl, 8.7; N, 10.2%). The complex was diamagnetic with ν(NO) at 1 892 cm^{-1} in the i.r. spectrum (KBr disc) and $\lambda_{max.}$ 470 nm (ε = 69 dm^3 mol^{-1} cm^{-1}) in the electronic spectrum (CH_3NO_2 solution). For further characterisation see the structural data below.

Isomer (II), $[RuCl(pyca)_2(NO)]$. To a solution of $K_2[RuCl_5(NO)]$ (0.25 g) in water (10 cm^3) was added a solution of Hpyca (0.25 g) in water (10 cm^3). The solution was neutralised to pH 7 with aqueous NaOH. The mixture was refluxed for 3 h, concentrated to 5 cm^3, then cooled and set aside overnight. Red crystals of $[RuCl(pyca)_2(NO)]$ were deposited, collected by filtration, washed with water, acetone, and ether, and air dried. The crude product (0.14 g, 52%) showed two ν(NO) absorption bands, at 1 892 cm^{-1} [isomer (I)] and 1 864 cm^{-1} [isomer (II)] of approximately equal intensity. After five fractional recrystallisations from nitromethane [in which isomer (II) is less soluble, precipitating slowly on setting the solution aside at room temperature], a material was obtained which showed a single ν(NO) absorption at 1 864 cm^{-1} with a very small shoulder at 1 895 cm^{-1}. This shoulder could not be eliminated by further recrystallisation; it is not known whether isomer (II) of $[RuCl(pyca)_2(NO)]$ has a shoulder on the ν(NO) band due to lattice effects or whether the sample was still contaminated by a small amount of isomer (I) (Found: C, 35.0; H, 2.1; Cl, 8.6; N, 10.0%). The complex was diamagnetic.

Tetraethylammonium Trichloronitrosyl(pyridine-2-carboxylato)ruthenate, $[NEt_4][RuCl_3(pyca)(NO)]$.—To the filtrate

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† *Supplementary data available* (No. SUP 56338, 6 pp.): thermal parameters, H-atom co-ordinates, complete bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

after removal of the red crystals of [RuCl(pyca)$_2$(NO)] {see preparation of [RuCl(pyca)$_2$(NO)] above} was added NEt$_4$Cl (0.3 g) dissolved in water (5 cm^3). The resultant solution was set aside overnight giving brown needles (0.05 g, 16%), which were recrystallised from methanol (Found: C, 34.2; H, 4.8; Cl, 21.3; N, 8.7. Calc. for $C_{14}H_{24}Cl_3N_3O_3Ru$: C, 34.3; H, 5.0; Cl, 21.7; N, 8.6%). The complex was diamagnetic with ν(NO) at 1 844 cm^{-1} in the i.r. spectrum.

Chloronitrosylbis(quinoline-2-carboxylato)ruthenium, [RuCl(qnca)$_2$(NO)].—To a solution of K$_2$[RuCl$_5$(NO)] (0.2 g) in water (10 cm^3) was added a solution of Hqnca (0.25 g) in water (20 cm^3) which had been neutralised to pH 4.5 with aqueous NaOH. The mixture was heated to 70 °C (water-bath) for 15 min, then set aside at room temperature overnight. The light brown crystals of [RuCl(qnca)$_2$(NO)] which precipitated were collected by filtration, washed with water, ethanol, and ether, and air dried. They were recrystallised from acetone as the dihydrate [RuCl(qnca)$_2$(NO)]·2H$_2$O, yield 0.03 g, 11% (Found: C, 44.8; H, 2.9; Cl, 5.3; N, 7.6. Calc. for $C_{20}H_{14}ClN_3O_6Ru$: C, 43.9; H, 2.9; Cl, 6.5; N, 7.7%). The complex was diamagnetic and showed ν(NO) at 1 880 cm^{-1} in the i.r. spectrum, as well as a broad band centred at 3 400 cm^{-1} due to the water of crystallisation. The two molecules of water were quantitatively lost at 50 °C, as determined by thermal analysis.

Hydroxonitrosylbis(quinoline-2-carboxylato)ruthenium, [Ru(OH)(qnca)$_2$(NO)].—To the filtrate after removal of [RuCl(qnca)$_2$(NO)] (see preparation above) was added aqueous NaOH until the pH was 7. The resultant solution was boiled for 15 min, then concentrated to *ca.* 20 cm^3. A yellow-brown powdery precipitate of [Ru(OH)(qnca)$_2$(NO)] formed on cooling. It was collected by filtration, washed with water, acetone, and ether, and air dried. Yield 0.08 g, 31% (Found: C, 48.6; H, 2.6; Cl, 0; N, 8.5. Calc. for $C_{20}H_{13}N_3O_6Ru$: C, 48.8, H, 2.7; N, 8.5%). The complex was diamagnetic and showed ν(NO) at 1 834 cm^{-1} (sharp) and ν(OH) at 3 420br cm^{-1}. The complex was only sparingly soluble in dimethylformamide and nitromethane and insoluble in other common solvents.

Tetraethylammonium Trichloronitrosyl(pyridine-2-carboxylato)osmate, [NEt$_4$][OsCl$_3$(pyca)(NO)].—The salt Cs$_2$[OsCl$_5$(NO)] (0.3 g) in aqueous solution (150 cm^3) was changed to the sodium form using a cation-exchange resin (Dowex 40 X-X8, 50—100 mesh). To the resultant solution was added a solution of Hpyca (0.2 g) in water (10 cm^3) which had been neutralised to pH 6 with aqueous NaOH. The mixture was refluxed for 1 h, then set aside at room temperature overnight. Dark brown crystals formed, which were collected by filtration and recrystallised from methanol. Yield 0.1 g, 40% (Found: C, 29.0; H, 4.0; N, 6.9. Calc. for $C_{14}H_{24}Cl_3N_3O_5Os$: C, 29.0; H, 4.2; N, 7.3%). The complex was diamagnetic and showed ν(NO) at 1 790 cm^{-1} in the i.r. spectrum.

Reaction of cis-[RuCl(pyca)$_2$(NO)] *with Hydroxide Ion: Formation of μ-Hydroxo-bis[nitrosylbis(pyridine-2-carboxylato)ruthenium] Hexafluorophosphate Dihydrate,* [{Ru(pyca)$_2$(NO)}$_2$(μ-OH)]PF$_6$·2H$_2$O.—The complex *cis*-[RuCl(pyca)$_2$(NO)] (0.3 g) was dissolved in aqueous NaOH (0.05 mol dm^{-3}, 40 cm^3) by heating. Dissolution was accompanied by a colour change from orange-red to dark brown. Ammonium hexafluorophosphate (0.1 g) was added, and the solution was concentrated to *ca.* 15 cm^3 and cooled to room temperature. On setting aside for 3 d the solution deposited yellow crystals of [{Ru(pyca)$_2$(NO)}$_2$(μ-OH)]PF$_6$·2H$_2$O. These were collected by filtration, washed with water and acetone, and air dried. Yield 0.17 g, 49% [Found: C, 30.2; H, 2.3; N, 8.7; PF$_6$ (as NPh$_4$AsPF$_6$), 14.9. Calc. for $C_{24}H_{21}F_6N_6O_{13}PRu_2$: C, 30.4; H, 2.2; N, 8.9; PF$_6$, 15.3%]. The complex was diamagnetic and showed ν(NO) at 1 906 cm^{-1} and a broad band with several spikes between 2 800 and 3 600 cm^{-1} in the i.r. spectrum [ν(OH) of H$_2$O and OH, and ν(C–H) of pyca].

Conversion of [{Ru(pyca)$_2$(NO)}$_2$(μ-OH)]PF$_6$·2H$_2$O *into Aquanitrosylbis(pyridine-2-carboxylato)ruthenium Perchlorate or Hexafluorophosphate,* [Ru(H$_2$O)(pyca)$_2$(NO)]ClO$_4$ *or* [Ru(H$_2$O)(pyca)$_2$(NO)]PF$_6$.—The complex [{Ru(pyca)$_2$(NO)}$_2$(μ-OH)]PF$_6$·2H$_2$O (0.17 g) was dissolved in water (20 cm^3) with heating. To the solution was added HClO$_4$ (0.7 mol dm^{-3}, two drops) and NaClO$_4$ or NH$_4$PF$_6$ (0.1 g). On concentrating the solution to *ca.* 15 cm^3 and setting it aside for 24 h, orange crystals of [Ru(H$_2$O)(pyca)$_2$(NO)]X (X = ClO$_4$ or PF$_6$) were deposited. These were collected by filtration, washed with cold water and acetone, and air dried. Yield 0.12 g, 68%: ClO$_4$ salt {Found: C, 28.4; H, 2.1; N, 8.3; ClO$_4$, 19.7. Calc. for $C_{12}H_{12}ClN_3O_{11}Ru$, [Ru(H$_2$O)(pyca)$_2$(NO)]ClO$_4$·H$_2$O: C, 28.3; H, 2.4; N, 8.3; ClO$_4$, 20.2%}, diamagnetic, ν(NO) at 1 940s cm^{-1} (sharp) and ν(H$_2$O) as a very broad envelope centred at 3 420 cm^{-1}; PF$_6$ salt (Found: C, 27.0; H, 2.1; N, 7.8. Calc. for $C_{12}H_{10}F_6N_3O_{10}PRu$: C, 26.8; H, 1.9; N, 7.8%), diamagnetic, ν(NO) 1 940 cm^{-1}, ν(H$_2$O) 3 450vbr cm^{-1}.

Reaction of cis-[RuCl(pyca)$_2$(NO)] *with Hydroxide Ion: Formation of Hydroxonitrosylbis(pyridine-2-carboxylato)ruthenium,* [Ru(OH)(pyca)$_2$(NO)].—The complex *cis*-[RuCl(pyca)$_2$(NO)] (0.3 g) was dissolved in aqueous NaOH (0.0375 mol dm^{-3}, 40 cm^3) by heating. Dissolution was accompanied by a colour change from orange-red to dark green. The solution was concentrated to about 15 cm^3, cooled to room temperature, and set aside for 3 d. The solution deposited [Ru(OH)(pyca)$_2$(NO)] as a powder. This was collected by filtration, washed with cold water and acetone, and air dried. Yield: 0.15 g, 50% {Found: C, 35.4; H, 2.5; N, 10.2. Calc. for $C_{12}H_{11}N_3O_7Ru$, [Ru(OH)(pyca)$_2$(NO)]·H$_2$O: C, 35.1; H, 2.4; N, 10.2%}. The complex was diamagnetic and showed ν(NO) at 1 850 cm^{-1} with a shoulder at 1 830 cm^{-1} and ν(OH) at 3 450s, br cm^{-1} in the i.r. spectrum.

Determination of the Crystal Structure of cis-[RuCl(pyca)$_2$(NO)].—Crystals of *cis*-[RuCl(pyca)$_2$(NO)] were obtained as described above. The one used in the diffraction experiment was a hexagon 0.12 × 0.12 × 0.40 mm in size and was visually an excellent specimen. The rather high final *R* value indicates that the mosaicity of the crystal was not optimal.

Crystal data. $C_{12}H_8ClN_3O_5Ru$, $M = 410.7$, orthorhombic, space group $P2_12_12_1$, $a = 15.297(8)$, $b = 11.401(5)$, $c = 8.224(3)$ Å, $Z = 4$, $D_c = 1.90$ Mg m^{-1}, $F(000) = 808$, graphite-monochromated Mo-$K_α$ radiation, $λ = 0.710\,69$ Å, $μ$(Mo-$K_α$) = 4.2 cm^{-1}. Because of the low μ, no absorption correction was applied.

A unique data set was collected by the ω—2θ scan technique on a Syntex $P2_1$ automatic diffractometer. Of 1 754 independent reflections with $2θ \leqslant 55°$, 1 421 had $I > 2σ(I)$ and were used for the structure determination.

After the usual Lorentz and polarisation corrections had been applied and the data reduced, the structure was solved using Patterson and Fourier methods and refined using the SHELX 76[7] program package. The scattering factor for Ru was taken from ref. 8 and was corrected for the real and imaginary parts of the anomalous dispersion; scattering factors for other atoms were from ref. 9. The refinement minimised the function $\Sigma w(\Delta F)^2$ with $w = 1.75/[\sigma(F)^2 + 0.01F^2]$ and converged at R $(= \Sigma|\Delta F|/\Sigma|F_o|) = 0.072$, R' $[= (\Sigma w|\Delta F|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}] = 0.083$. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were included with fixed C–H distances of 1.08 Å and sp^2 hybridisation of the C atom, and

Table 1. Positions of the non-hydrogen atoms in *cis*-[RuCl(pyca)$_2$(NO)] with estimated standard deviations (e.s.d.s) in parentheses*

Atom	x	y	z	Atom	x	y	z
Ru	0.003 9(1)	0.441 6(1)	0.632 3(1)	C(2)	0.165 2(11)	0.376 3(15)	0.782 2(24)
Cl	−0.094 2(4)	0.569 1(6)	0.766 7(6)	C(3)	0.231 0(12)	0.351 5(17)	0.891 9(20)
N(1)	−0.058 6(10)	0.321 5(15)	0.672 7(20)	C(4)	0.215 7(14)	0.378 6(21)	1.057 2(20)
N(2)	0.088 9(9)	0.422 3(14)	0.825 8(17)	C(5)	0.135 8(12)	0.423 8(21)	1.095 2(22)
N(3)	−0.062 6(9)	0.483 7(11)	0.925 0(16)	C(6)	0.074 0(11)	0.447 5(19)	0.985 7(21)
O(1)	−0.110 9(12)	0.241 1(16)	0.675 7(25)	C(7)	0.033 5(13)	0.646 1(15)	0.450 9(20)
O(2)	0.103 5(8)	0.357 6(11)	0.521 0(15)	C(8)	−0.041 8(10)	0.592 9(14)	0.369 1(22)
O(3)	0.241 1(9)	0.296 0(13)	0.556 0(22)	C(9)	−0.084 9(14)	0.640 7(18)	0.235 7(21)
O(4)	0.068 7(8)	0.586 5(10)	0.570 4(17)	C(10)	−0.160 1(13)	0.578 0(18)	0.167 2(21)
O(5)	0.060 6(9)	0.745 0(11)	0.410 1(21)	C(11)	−0.176 7(12)	0.472 3(18)	0.266 0(22)
C(1)	0.171 3(11)	0.342 0(14)	0.602 1(22)	C(12)	−0.128 2(12)	0.428 4(17)	0.353 3(21)

* For numbering scheme see Figure 1.

Table 2. Important distances (Å) and angles in *cis*-[RuCl(pyca)$_2$(NO)]*

Ru–Cl	2.363(5)	Ru–O(2)	2.02(1)
Ru–N(1)	1.70(2)	Ru–O(4)	1.99(1)
Ru–N(2)	2.07(1)	N(1)–O(1)	1.22(2)
Ru–N(3)	2.04(7)		
Cl–Ru–N(1)	92.7(7)	N(1)–Ru–O(4)	174.8(6)
Cl–Ru–N(2)	96.0(4)	N(2)–Ru–N(3)	168.9(5)
Cl–Ru–N(3)	86.0(4)	N(2)–Ru–O(2)	79.9(6)
Cl–Ru–O(2)	169.4(4)	N(2)–Ru–O(4)	88.4(6)
Cl–Ru–O(4)	85.7(4)	N(3)–Ru–O(2)	96.2(5)
N(1)–Ru–N(2)	96.7(7)	N(3)–Ru–O(4)	80.8(5)
N(1)–Ru–N(3)	94.1(6)	O(2)–Ru–O(4)	84.4(5)
N(1)–Ru–O(2)	97.5(7)	Ru–N(1)–O(1)	168(2)

* The numbering scheme is shown in Figure 1; e.s.d.s are given in parentheses.

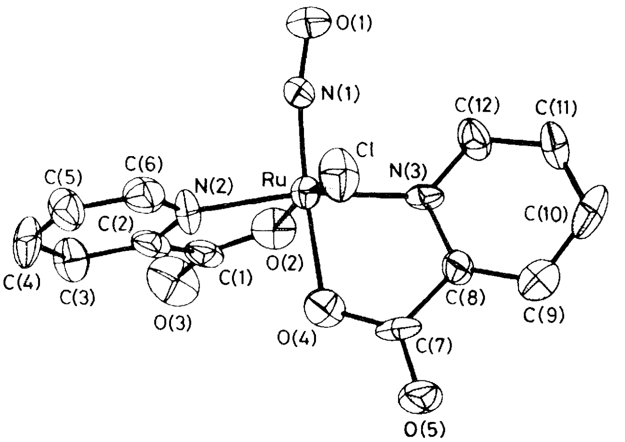

Figure 1. The molecular structure of *cis*-[RuCl(pyca)$_2$(NO)]

with fixed isotropic thermal parameters. The total number of variables was 200, no extinction correction being applied. A final Fourier difference map had as its maximum a peak of + 0.79 e Å^{-3} approximately 0.1 Å from the Ru atom and as its minimum a peak of −0.97 e Å^{-3}. Table 1 gives the positional parameters of the non-hydrogen atoms, Table 2 the important derived distances and angles. The numbering scheme is shown in Figure 1.

Since $P2_12_12_1$ is a polar space group the orientation of the molecule is in question. The structure was therefore refined in parallel using the other enantiomer. This refinement converged at a significantly higher R value (0.085).

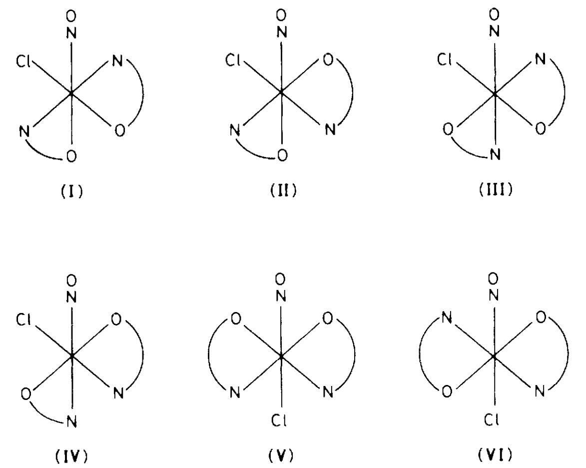

Figure 2. The six possible isomers of formula [RuCl(pyca)$_2$(NO)]; pyca is represented by N⁀O

Results and Discussion

Refluxing an aqueous solution of Hpyca and [RuCl$_5$(NO)]$^{2-}$ which had been buffered to pH 4.5 gave a mixture of [RuCl(pyca)$_2$(NO)] and [RuCl$_3$(pyca)(NO)]$^-$. The analogous reaction between [RuCl$_5$(NO)]$^{2-}$ and Hqnca gave only [RuX(qnca)$_2$(NO)] (X = Cl or OH), whereas the reaction between [OsCl$_5$(NO)]$^{2-}$ and Hpyca at pH 6 gave only [OsCl$_3$(pyca)(NO)]$^-$, there being no evidence for formation of the bis complex.

There are six geometrical isomers of the formula [RuCl(pyca)$_2$(NO)] (Figure 2) of which the four *cis* isomers (**I**)—(**IV**) also have optical isomers. The *trans* isomer (**V**) is unlikely to occur because of the same steric hindrance between the β-hydrogen atoms of the pyridine rings which prevents formation of *trans* bipyridine complexes. The actual isomer formed is (**I**) (Figure 2) as proved by the X-ray crystal structure determination described above. However, by adjusting the mixture of Hpyca and [RuCl$_5$(NO)]$^{2-}$ to pH 7 instead of 4.5 a second isomer, believed to be (**II**), was obtained on refluxing.

Since both *cis*-[RuCl(pyca)$_2$(NO)] and [RuCl$_3$(pyca)(NO)]$^-$ were formed in the reaction between [RuCl$_5$(NO)]$^{2-}$ and Hpyca, we assume the latter complex is an intermediate on the way to the former. The [RuCl$_3$(pyca)(NO)]$^-$ could in fact be converted into isomer (**I**) of [RuCl(pyca)$_2$(NO)] on treatment with a further mol of Hpyca. We have no direct evidence for which of the three possible isomers of [RuCl$_3$(pyca)(NO)]$^-$ (**VII**)—(**IX**) (Figure 3) is formed but indirect evidence points strongly to (**VIII**). Further reaction of Hpyca

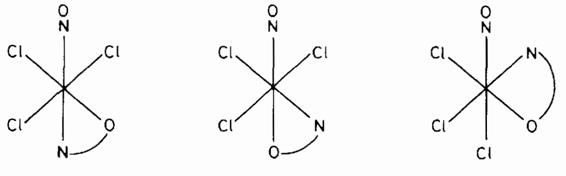

Figure 3. The three possible isomers of formula [$RuCl_3(pyca)(NO)$]$^-$; pyca is represented by N⌒O

with this isomer can produce only isomer (**I**) or (**II**) of [$RuCl(pyca)_2(NO)$] without a complicated intramolecular rearrangement taking place. Isomer (**I**) of [$RuCl(pyca)_2(NO)$] was the sole isomer actually obtained at pH 4.5, and a mixture of isomers (**I**) and (**II**) was obtained at pH 7. Isomer (**VII**) of [$RuCl_3(pyca)(NO)$]$^-$ could only give isomer (**I**) or (**II**) of [$RuCl(pyca)_2(NO)$] when an intramolecular rearrangement takes place during the reaction. From isomer (**IX**) of [$RuCl_3(pyca)(NO)$]$^-$ all six isomers of [$RuCl(pyca)_2(NO)$] could be obtained without rearrangement. We see no reason why the *cis*-isomers (**III**) and (**IV**) should be so much less stable with respect to (**I**) and (**II**) that they would be unobtainable, and a mixture of products should be observed readily by i.r. spectroscopy. [In the ν(NO) region the isomers within the three pairs (**I**)/(**II**), (**III**)/(**IV**), and (**V**)/(**VI**) would be expected to have similar spectra, but the spectra would differ between each pair; the values for isomers (**I**) and (**II**) in fact differ by 28 cm^{-1}.] We therefore conclude that isomer (**VIII**) of [$RuCl_3(pyca)(NO)$]$^-$ is formed exclusively on reaction of [$RuCl_5(NO)$]$^{2-}$ with Hpyca.

The similarity of their i.r. spectra suggests that [$RuCl(pyca)_2(NO)$] [ν(NO) 1 892 cm^{-1}] and [$RuCl(qnca)_2(NO)$] [ν(NO) 1 880 cm^{-1}] have the same *cis*-structure (**I**). No [$RuCl_3(qnca)(NO)$]$^-$ was observed in the reaction between [$RuCl_5(NO)$]$^{2-}$ and Hqnca at pH 4.5. On refluxing a solution of [$RuCl(qnca)_2(NO)$] in neutral solution it was converted into [$Ru(OH)(qnca)_2(NO)$] [ν(NO) 1 834, ν(OH) *ca.* 3 400 cm^{-1}]. The shift in ν(NO) from 1 880 cm^{-1} in the chloro-derivative to 1 834 cm^{-1} in the hydroxo is larger than would be expected for simple replacement of a *cis*-Cl by a *cis*-OH ligand, and is comparable to the shift of 42 cm^{-1} observed on going from *cis*-[$RuCl(NH_3)_4(NO)$]$^{2+}$ to *trans*-[$Ru(OH)(NH_3)_4(NO)$]$^{2+}$.[10] It is therefore possible that a stereochemical rearrangement has taken place during the substitution to give the hydroxo-derivative of the *trans* isomer (**VI**). However we note that the *trans*-chloro-isomer (**VI**) is unstable compared to the *cis*-isomer (**I**). In an attempt thermally to isomerise (**I**) it was found (using d.t.a. and t.g.a.) that this isomer remained unchanged to 350 °C at which point an endothermic change with no weight loss occurred. We ascribe this change to the transformation of (**I**) into (**VI**). Beginning at almost the same temperature (357 °C) there was an exothermic loss of 1 mol of HCl. This process was complete by 370 °C, but the product [$Ru(pyca)(pyca - H)(NO)$], was only stable over a small temperature range and at 400 °C general decomposition occurred. Because of the narrow ranges of thermal stability all attempts to isolate isomer (**VI**) or [$RuCl(pyca)(pyca - H)(NO)$] failed. It is surprising that the *trans* isomer (**VI**) loses Cl so readily, and we have no explanation for this behaviour.

Attempts to prepare [$OsCl(pyca)_2(NO)$] from Hpyca and [$OsCl_5(NO)$]$^{2-}$ at pH 6 gave only [$OsCl_3(pyca)(NO)$]$^-$ [ν(NO) 1 790 cm^{-1}], assumed also to be isomer (**VIII**).

The very high ν(NO) wavenumber of [$RuCl(pyca)_2(NO)$] (1 892 cm^{-1}) suggests that the co-ordinated nitrosyl group should behave as an electrophile.[3,10] Investigation of this property was hampered by solubility problems (which also prevented the determination of isomers by n.m.r. methods). The complex was only soluble in warm dimethylformamide or nitromethane; [$RuCl(qnca)_2(NO)$] was soluble only in hot acetone or ethanol. Two products could be obtained on warming [$RuCl(pyca)_2(NO)$] with aqueous hydroxide ion. One was the substitution product [$Ru(OH)(pyca)_2(NO)$], the other the hydroxo-bridged dimer [$\{Ru(pyca)_2(NO)\}_2(\mu\text{-}OH)$]$^+$. Whether loss of the *cis*-Cl ligand of [$RuCl(pyca)_2(NO)$] occurs directly or *via* an intermediate nitro-complex as has been proposed previously[11] is not known. Despite the high wavenumber of ν(NO) (1 906 cm^{-1}), the dimer [$\{Ru(pyca)_2(NO)\}_2(\mu\text{-}OH)$]$^+$ is inert to attack of OH^- at the nitrosyl ligands. This is probably because the dimer can be cleaved by OH^- to give [$Ru(OH)(pyca)_2(NO)$], which, with ν(NO) at 1 850 cm^{-1}, would be inert to nucleophilic attack at the nitrosyl group.[10] Both [$\{Ru(pyca)_2(NO)\}_2(\mu\text{-}OH)$]$^+$ and [$Ru(OH)(pyca)_2(NO)$] form [$Ru(H_2O)(pyca)_2(NO)$]$^+$ on reaction with perchloric acid. On reaction of [$RuCl(pyca)_2(NO)$] with both aniline and acetylacetone, products were obtained in which the co-ordinated nitrosyl had been attacked, but in which condensation reactions at the pyca ligand had occurred also. These materials were intractable.

Structure of [$RuCl(pyca)_2(NO)$].—The bond distances and angles for *cis*-[$RuCl(pyca)_2(NO)$] are given in Table 2 and the numbering scheme and geometry are shown in Figure 1. The final *R* is rather high (0.072) and the parameters are not well defined. Therefore discussion will be restricted to the overall structure. The distances and angles in the complex are within the ranges commonly observed in ruthenium nitrosyls with an $\{RuNO\}^6$ group.[12] The primary purpose of the *X*-ray investigation was the assignment of the stereochemistry of the complex. This has been achieved and is shown in Figure 1. As usual in octahedrally co-ordinated mononitrosyls, the ligands *cis* to the NO ligand are bent away from it [average N(1)–Ru–*cis*-L angle 95.2 ± 2.5°] and towards the *trans* ligand [average O(4)–Ru–*cis*-L angle 84.8 ± 4.0°]. The *trans* Ru–O(4) distance [1.99(1) Å] is not significantly different from *cis* Ru–O(2) [2.02(1) Å]. The RuNO group is essentially linear [168(2)°] as expected for an $\{RuNO\}^6$ configuration. The 12° deviation from linearity can be regarded as a minor deviation allowed by the low symmetry of the complex.[13]

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