4-Cyanopyridine and Amide-N and Amide-O Linkage Isomers of 4-Pyridinecarboxamide on *trans*-Chloro(1,4,8,11-tetraazacyclotetradecane)ruthenium(II/III)†

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The synthesis, UV−vis spectra, and electrochemical behavior of the nitrile-bonded *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$(BF_4)_2$ (4-Ncpy = 4-cyanopyridine; cyclam = 1,4,8,11-tetraazacyclotetradecane) and of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH$^+$)]$^{2+}$ are described. The UV−vis spectrum of the Ru(II) nitrile complex shows a MLCT band at 548 nm at pH 1, which is shifted to 440 nm at pH ∼6, for the unprotonated species. *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$ was electrolytically oxidized (+600 mV vs Ag/AgCl) at pH 1 to Ru(III), followed by hydrolysis ($k = 0.25\ s^{-1}$) of the coordinated nitrile to give *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH$^+$)]$^{2+}$, in which the amide is deprotonated and coordinated through nitrogen. The identity of the species is pH dependent, the nitrogen-bonded amide prevailing at low pH (<7), but the oxygen-bonded amide is formed through linkage isomerization at higher pH (>8). Reduction of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ in acidic media does not result in fast aquation ($k = \sim 2.4 \times 10^{-5}\ s^{-1}$) as for other amides on ruthenium(II) pentaammine, but instead linkage isomerization occurs, resulting in the oxygen-bonded species, with an estimated rate constant of $\sim 2 \times 10^{-2}\ s^{-1}$, smaller than in the pentaammine analogues.

Introduction

The isomerization of monodentate amides coordinated to the $(NH_3)_5Co^{III}$ center is fairly well-known[1−4] and also occurs in Ru complexes.[5] Nonchelated N- or O-bonded amides are substitution labile when coordinated to ammineruthenium(II) but inert in ammineruthenium(III) complexes.[5] Tetraammineruthenium(II) and -(III) complexes of glycinamide and derivatives exhibit linkage isomerism, depending on the coordination mode of the amide, and on the oxidation state of the metal center.[6] Recently, relatively fast N→O amide linkage isomerization on Ru(II) and O→N isomerization in Ru(III) was reported.[5] For $[Ru^{II}(NH_3)_5(isn)]^{2+}$ (isn = isonicotinamide), an amido to pyridinyl linkage isomerization occurs, competitive with aquation and loss of isn,[7,8] while both pyridinyl to amido and amido to pyridinyl linkage isomerizations were reported to occur in $[Ru^{II}(edta)(isn)]^{n+}$.[9] In addition, an isomerization reaction from amide to olefinic η^2-bonded $[Ru^{II}(NH_3)_5(acrylamide)]^{2+}$ complex was reported to occur upon reduction of the amido-bonded $[Ru^{III}(NH_3)_5(acrylamido)]^{2+}$.[10] In these three latter cases, N↔O amide linkage isomerization was not reported to occur.

Ruthenium(III) ammines with N-bonded amides can be easily synthesized from the corresponding nitrile complex. Nitriles can undergo hydrolysis to amides when coordinated to Ru(II) or Ru(III) complexes,[11−19] though it is usually faster on the more electrophilic Ru(III). Oxidation to Ru(III) of the corresponding Ru(II)−nitrile is followed, in aqueous media, by hydrolysis to the N-bonded amide. This Ru(III)−amide complex can then be reduced to give the corresponding N-bonded amide complex of Ru(II). *trans*-Chloro(cyclam)ruthenium(II) (cyclam = 1,4,8,-11-tetraazacyclotetradecane) complexes with pyridine ligands show some similarities to, but also some differences from, the corresponding ruthenium(II) pentaammines.[20−23] These cyclam

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complexes show redox potentials and MLCT spectra similar to those of the corresponding pentaammines, while the chloro ligand is substitution inert and the pyridines are more labile.[20−23] Thus, as a continuation of our investigations on the hydrolysis of coordinated nitriles in ruthenium ammine complexes, we describe in this paper the synthesis and properties of *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$, which, upon oxidation to Ru(III), undergoes hydrolysis to Ru(III)−amide complexes, [Ru^{III}Cl(cyclam)(L)]$^{n+}$ (L = 4-pyridinecarboxamide/amido, bonded through the amide). Upon reduction to the Ru(II) state the resulting relatively long-lived amido-bonded complexes show relatively slow linkage isomerization of N- and O-bonded coordinated amide species.

Experimental Section

Chemicals and Reagents. Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) (Strem) was the starting material for ruthenium complex syntheses. Reagent grade 4-cyanopyridine, 3-cyanopyridine, and isonicotinamide were recrystallized from hot water after treatment with activated charcoal. Acetone and ethanol were purified according to literature procedures.[24] Doubly distilled water was used throughout. All other materials were reagent grade and were used without further purification. Cyclam (Strem) was used as supplied.

Complex Syntheses. $K_3[RuCl_6]$[25] and $[Ru(NH_3)_5Cl]Cl_2$[26,27] were prepared according to the literature procedure. *trans*-[Ru^{III}(cyclam)-Cl_2]Cl was synthesized by modification of described procedures.[21,28,29] Equimolar amounts of cyclam (0.46 g (2.32 mmol)) and $K_3[RuCl_6]$ (1 g (2.32 mmol)) were refluxed in ethanol under argon for 2 days. The greenish-brown solid formed was collected by filtration and discarded. The volume of the filtrate was reduced to dryness by rotoevaporation to give another crop of brown solid (0.980 g). This brown solid was washed with acetone. The first acetone extracts were violet, and the procedure was repeated several times, until the acetone washes were no longer violet, and the solid became brown ($m = 0.940$ g). The brown solid (0.940 g) was purified by ion exchange chromatography on a Dowex AG-50-W-X4 resin column. Elutions were performed first with water and then with HCl solutions of increasing concentration. The complex began to elute with 1.0 M HCl and finished with 1.5 M HCl. The elution was monitored spectrophotometrically. All *trans*-dichlorocyclam complex fractions were evaporated to dryness, giving the solid as orange needles ($m = 0.56$ g; $n = 1.36$ mmol). Elemental analysis, % calcd (found): C, 29.5 (29.46); N, 13.7 (13.67), H, 5.9 (5.79). The UV−vis spectrum of the product shows bands at 358 nm ($\epsilon = 2600$ M·cm^{-1} (2560[21])) and 315 nm ($\epsilon = 1250$ M·cm^{-1}) (1250[21])). Yields average 58%.

***trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)](BF$_4$)$_2$ (I). I** (4-Ncpy = cyanopyridinum nitrile bound) was synthesized by the method described by Walker[20] with slight modifications. *trans*-[Ru^{III}(cylam)Cl_2]Cl (100 mg (0.24 mmol)) was suspended in deaerated 0.1 M HCl solution (15 mL), and argon was bubbled through the mixture. After dissolution, Zn(Hg) was added to the solution, with continuous argon bubbling and protection from light. Then a deaerated 2.4 mmol (250 mg) solution of 4-cyanopyridine dissolved in 0.1 M HCl (5 mL) was added dropwise. After 24 h, the mixture was filtered, the volume of the filtrate was reduced to about 5 mL by rotoevaporation, and a freshly prepared, deaerated, saturated (0.25 g/0.25 mL) aqueous $NaBF_4$ solution was added. The violet solid obtained was collected by filtration, and the crude solid was washed with ethanol and vacuum-dried. The product was recrystallized from 0.1 M HCl. Average yield: $m = 0.110$ g (50%). Redox potentials and UV−vis absorption spectral data of the compound agree with literature values.[20]

***trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH$^+$)]$^{2+}$ (II).** This was prepared from the corresponding Ru(III) nitrile by oxidation with controlled potential electrolysis of the Ru(II) complex (10^{-3} M) in 0.1 M HCl/KCl solution, at +600 mV vs Ag/AgCl.

Electrochemical Measurements. Cyclic voltammetry and constant potential electrolysis measurements were taken with a CV-1B cyclic voltammograph from Bio-Analytical Systems and a Houston Instrument Omnigraph 100 X-Y recorder. A PARC, model 273, potentiostat/galvanostat was also used. All tests were carried out using a conventional three-electrode cell. Glassy carbon and platinum gauze were used as working electrode for cyclic voltammetry and coulometry, respectively. An Ag/AgCl electrode was used as the reference electrode and a platinum wire as the auxiliary electrode. Electrochemical data were obtained in aqueous solutions of 0.1 M KCl/HCl. All solutions were deaerated by bubbling high-purity argon and thermostated using a Haake, model FK, ultracryostat. In the cyclic voltammograms, no anodic or cathodic peaks in the absence of complexes in the potential range studied were observed. The reported $E_{1/2}$ values are the arithmetic mean of E_{pa} and E_{pc} values.

Spectra. Electronic absorption spectra were recorded using a Hewlett-Packard model 8452 A recording spectrophotometer using quartz cells.

Results and Discussion

Syntheses of *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$. The *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$ complex was synthesized using *trans*-[Ru^{III}(cyclam)Cl_2]$^+$ as the starting complex, following basically the procedure described by Walker.[20] This synthesis is similar to those of *trans*-[Ru^{II}Cl(cyclam)L]$^+$ (L = 4-pic (4-picoline), py (pyridine), isn, or 4-acpy (4-acetylpyridine)).[21] For the trans tetraammine analogues the general procedure to prepare *trans*-[$Ru^{II}(NH_3)_4L_2$]$^{2+}$ involves reduction of *trans*-[$Ru^{III}(NH_3)_4Cl_2$]$^+$ to *trans*-[$Ru^{II}(NH_3)_4Cl_2$], which rapidly aquates both chlorides, to form *trans*-[$Ru^{II}(NH_3)_4(OH_2)_2$]$^{2+}$. In the presence of an unsaturated ligand, L, this latter Ru species forms *trans*-[$Ru^{II}(NH_3)_4L_2$]$^{2+}$. Notably, the behavior of the cyclam complex is markedly different. In the reduced form, *trans*-[Ru^{II}(cyclam)Cl] was shown to have an unexpected affinity for chloride, when compared with ruthenium(II) ammine complexes.[20] Earlier studies indicate that chloride aquation from *trans*-[Ru^{II}(cylam)Cl_2] is slower[20] than in [$Ru^{II}(NH_3)_5Cl$]$^+$ [30] and that aquation of the second chloride is even slower. This difference was rationalized using dielectric and solvation effects which cause the affinity of chloride for Ru^{II} to increase from [$Ru^{II}(NH_3)_5(H_2O)$]$^+$ ($K = 1.6$) to *trans*-[Ru^{II}(cyclam)$(H_2O)_2$]$^{2+}$ ($K = 32$).[28] In addition, cyclam sterically restricts the access of other ligands to and from the axial coordination sites. For example, chloride is more rapidly lost from [$Ru^{II}(NH_3)_5Cl$]$^+$ ($k = 5$ s^{-1}) than from *trans*-[Ru^{II}(cyclam)Cl_2] ($k = 2.1 \times 10^{-2}$ s^{-1}), and loss of the second chloride occurs even more slowly.[31] Similar features are observed in the analogous isoelectronic complexes of Co^{3+}.[32] It was assumed, then, that the ligand L does not labilize the remaining trans chloro ligand. Indeed the aquation of chloride from *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$ has been shown to have a half-live of 71 h at 25 °C.[20] In

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Table 1. Electronic Absorption Data of Some Amineruthenium(II) Complexes with Nitriles

	λ_{max}/nm (log ϵ)			
L	LF	MLCT	IL	ref
$[Ru^{II}(NH_3)_5(4\text{-NCpy})]^{2+}$ (nitrile bonded)[a]		425 (3.73)	253 (3.95)	44
		424 (4.00)	253 (4.22); 212 (4.09)	15
		422 (4.05)		37
$[Ru^{II}(NH_3)_5(4\text{-NCpy})]^{2+}$ (pyridyl bonded)[b]		500		44
$[Ru^{II}(NH_3)_5(4\text{-NCpyH})]^{3+}$ (nitrile bonded)[c]		532 (3.91)	260 (3.93)	44
		534 (4.14)		15
$[Ru^{II}(NH_3)_5(4\text{-mcp})]^{3+}$ [d]		545 (4.26)	267 sh; 257 sh; 242 (4.23)	45
$[Ru^{II}(NH_3)_5(4\text{-bzcp})]^{3+}$ [d]		556 (4.31)	240 (4.22); 256 (4.26)	39
t-$[Ru^{II}Cl(cyclam)(4\text{-NCpy})]^{+}$ (nitrile bonded)[a]		436 (4.04)	262 (4.30)	20
		440 (4.01)	262 (4.18); 218 (4.04)	37
t-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH})]^{2+}$ (nitrile bonded)[e]		548 (4.20)	270 (4.22); 212 (4.09)	20
$[Ru^{II}(NH_3)_5(bzn)]^{2+}$		376 (3.93); 347 (3.84) sh	249 (4.21)	44
			226 (4.17)	
$[Ru^{II}(NH_3)_5(1,4\text{-dcb})]^{2+}$		462	262 (4.18)	44
$[Ru^{II}(NH_3)_5(4\text{-tln})]^{2+}$		367 (3.86); 347 (3.8) sh		46
$[Ru^{II}(NH_3)_5(acn)]^{2+}$	350 (2.40)	229 (4.19)		46
$[Ru^{II}(NH_3)_5(prn)]^{2+}$	350 (2.38)	262 (4.18)		46
$[Ru^{II}(NH_3)_5(2\text{-cedp})]^{2+}$	334 sh (2.58)		307 (3.46)	46

[a] In dilute aqueous solution. [b] Spectrum from reaction solution of $[Ru(NH_3)_5(OH_2)]^{2+}$ (pH = 6) with excess 4-NCpy. [c] 1 M HCl solution. [d] In acetonitrile solution. [e] 0.1 M HCl solution. 4-mcp = 1-methyl-4-cyanopyridinium. 4-bzcp = 1-benzyl-4-cyanopyridinium. 1,4-dcb = 4-dicyanobenzene. 4-tln = 4-toluenenitrile. acn = acetonitrile. prn = propionitrile. 2-cedp = 2-cyanoethyldiphenylphosphine.

addition, in the *trans*-$[Ru^{II}Cl(cyclam)(L)]^{+}$(L = 4-pic, py, isn, or 4-acpy) complexes, L loss occurs both thermally and photochemically without observable chloride loss.[21,23] This difference in chloride affinities allowed us to devise a synthetic procedure to obtain *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$.

The stereoretentive behavior in substitution reactions of ruthenium(II) ammines[33] and Ru(II) (macrocyclic amines)[20,21] was assumed to hold for the present cyclam complexes, and trans geometry was assigned for *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$ by analogy to *trans*-$[Ru^{II}Cl(cyclam)(4\text{-acpy})]^{+}$.[22]

Spectra in Aqueous Solutions of *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$ and *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpy})]^{+}$. Table 1 shows electronic absorption data of *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$ and related nitrile complexes. The spectra of *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpy})]^{+}$ and *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$ are essentially identical to those previously reported,[20] and the assignments here reported follow basically the same reasoning. The strong absorption bands in the UV region can be assigned as intraligand (IL) $\pi-\pi^*$ in character. The electronic spectra of *trans*-$[Ru^{II}Cl(cyclam)L]^{n+}$ (L = 4-NCpy or 4-$NCpyH^{+}$) are dominated in the visible range by one intense absorption band as occurs for *trans*-$[Ru^{II}Cl(cyclam)L]^{+}$ (L = 4-pic, py, isn, or 4-acpy).[21] This is assigned as a metal-to-ligand charge-transfer (MLCT) transition, by analogy to spectral assignments for similar absorptions in the analogous $[Ru^{II}(NH_3)_5L]^{2+}$.[33−36] The MLCT band energy of each *trans*-$[Ru^{II}Cl(cyclam)L]^{+}$ complex is similar to that of the respective pentaammine analogue $[Ru^{II}(NH_3)_5L]^{2+}$ (Table 1).[20,21,37]

For *trans*-$[Ru^{II}Cl(cyclam)L]^{+}$ (L = isn or 4-acpy) there is a third band, assigned as a ligand field (LF) band, with an energy intermediate to those of the IL and MLCT. This band is not seen in the py and 4-pic complexes probably because it is buried under the MLCT band, which is higher in energy in these two latter complexes.[21] It is interesting to note that the aqua complex *trans*-$[Ru^{II}Cl(cyclam)(H_2O)]^{+}$, which does not have MLCT bands in the visible region, displays an absorption band at 330 nm ($\epsilon \approx 400$).[38] The spectra of the cyclam complexes of 4-NCpy and 4-$NCpyH^{+}$, which have the MLCT bands at lower energies (440 and 550 nm, respectively) than the py and 4-pic complexes (405 nm and 390, respectively), show a weak broad shoulder in the 300−400 nm region (centered around ≈360 nm), as occurs for the isn (345 nm) and 4-acpy (350 nm) complexes. In addition, some pentaammineruthenium(II) complexes with nitriles (acn, 2-cedp, prn, Table 1) have a LF band in their spectra near 350 nm.

Electrochemistry of *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$. The cyclic voltammogram of *trans*-$[Ru^{II}Cl(cyclam)(4\text{-NCpyH}^{+})]^{2+}$ (**I**), at pH 1, is basically similar to that of other ruthenium(II) nitrile complexes, $[Ru^{II}(NH_3)_5L]^{n+}$ (L = *x*-cyanopyridine (*x* = 3, 4, or 2))[15,39] or cyanopyridinium.[15,16] There is an anodic peak (1a) at +538 mV vs Ag/AgCl, with the corresponding cathodic (1c) peak at +462 mV vs Ag/AgCl, which correspond, respectively, to the oxidation and reduction of the metal center. The $E_{1/2}$ value for $Ru^{III/II}$ in *trans*-$[RuCl(cyclam)(4\text{-NCpyH}^{+})]^{3+/2+}$ is +500 mV vs Ag/AgCl, and the diffusion coefficient D_r for the reduced species is 2.0×10^{-6} $cm^2\ s^{-1}$ (obtained from the $I_{pa}v^{-1/2}$ plots and the Randles Sevcick equation[40]).The oxidation of the metal center is followed by hydrolysis of the coordinated nitrile to amide. The cathodic peak (2c) at −310 mV corresponds to the reduction of the metal center in the Ru(III)−amide complex formed. The cathodic peaks at −850 mV (3c) and −1000 mV (4c) correspond, respectively to the reduction of the coordinated carboxamide and nitrile. The formed coordinated amide can be deprotonated depending on the medium pH to give the amido form.[5,8] Scheme 1 shows the reactions involved in the electrochemical processes.

The estimated value of the rate constant for the hydrolysis reaction of the oxidized species formed in the potential range of the peak 1a, k_f, calculated following the procedure described by Nicholson and Shain[41] is 0.245 s^{-1}. This value is similar to

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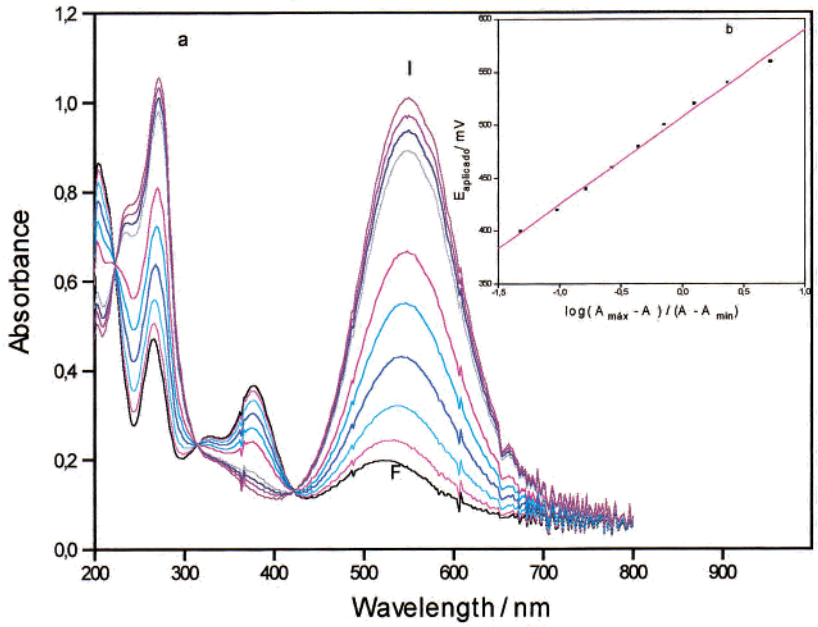
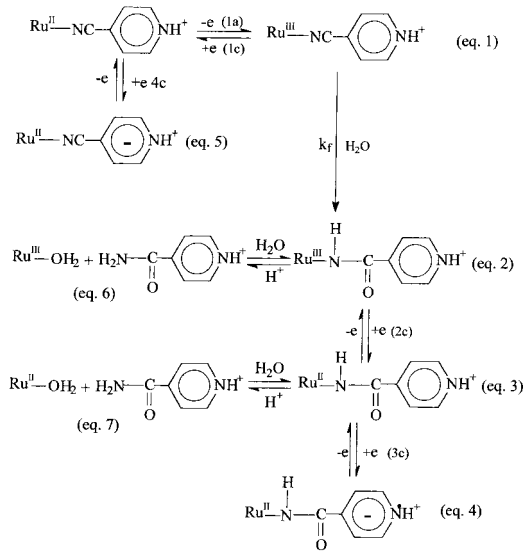


Figure 1. Spectral changes of 1.82×10^{-3} M *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH)]$^{2+}$ (**I**), at pH 1 and 25 °C, upon applied potential (+380 mV to +600 mV). Potentials applied: 0 (**I**), 400, 420, 440, 460, 480, 500, 520, 540, 560, and 600 mV. Reference electrode: Ag/AgCl.

the rate constant of hydrolysis of 0.193 ± 0.001 s^{-1} for [Ru^{III}-$(NH_3)_5$(4-NcpyCH$_3$)]$^{3+}$ at pH 1, obtained from chemical oxidation of the corresponding nitrile.[15] For the more similar [$Ru^{III}(NH_3)_5$(4-NCpyH$^+$)]$^{3+}$ complex, the reported rate constant is $(10.4 \pm 0.1) \times 10^{-3}$ s^{-1} in 1.0 M $HClO_4$.[15] However, this low value for this latter pentaammine complex, when compared with 0.245 s^{-1} for *trans*-[Ru^{III}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$ at pH 1.0, is not unexpected, since the rate of hydrolysis should decrease with decreasing pH of the medium.

Scheme 1



Electrolyses of *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH$^+$)]$^{2+}$, in 0.1 mol·L^{-1} HCl at 25 °C, in the +380 to +600 mV range, were monitored spectrophotometrically in the UV−visible range (Figure 1). At these potentials, Ru(II) is oxidized to Ru(III) and the coordinated nitrile is hydrolyzed to amide (see above), forming *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**). Concomitant with the Ru(II) oxidation, the MLCT band (λ_{max} = 548 nm) decreases as expected for this process.

Spectra of the 4-Pyridinecarboxamide Complexes. Table 2 presents spectral data for *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ and related complexes. Amide-bonded Ru(III) ammine complexes display absorption bands in the 300−400 nm range assigned as ligand to metal charge transfer (LMCT) transitions,[5,8,12,42] and *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ **(II)** shows pH dependent absorption bands in this range. There are several different modes of bonding of the amide in these complexes, including N and O linkage isomers. In addition, in this range also appear Cl−Ru(III) LMCT absorption bands.[21−23,28,43] These features make the unequivocal interpretation of these spectra difficult. Despite that, a likely interpretation is offered, which is based on the assumption that the spectral and electrochemical properties of the cyclam complexes are similar to those of the ammines. With that assumption the linkage isomerism proposed ahead is opposite to that observed in the ammines. One alternative explanation assuming that the linkage isomerism should be similar in both the ammine and cyclam complexes will result in opposite spectral properties. Structures **1**−**9** (Chart 1) depict possible protonated and deprotonated forms for the *trans*-[Ru^{III}Cl(cyclam)(L)]$^{n+}$ species and include possible linkage isomers, bonded through the amide N or the amide O.

The bands at 375 and 391 nm, in acidic medium, are consistent with an amide N coordinated to Ru(III).[5,8,12,42] Oxygen-bonded Ru(III)−amides show such absorption below 350 nm.[42] Thus, strucutures **8** and **9** can be ruled out in acidic medium. The Ru(III)−cyclam complex is formed by oxidation of the nitrile-bonded cyanopyridine ruthenium(II) complex, followed by hydrolysis. Immediately after hydrolysis at pH = 1, the N-bonded amide is formed. The presence of a long-lasting absorption around 380 nm is indicative that isomerization to the oxygen-bonded complex should be very slow at this pH. In addition, no spectral changes are observed to indicate that there is a fast amide aquation. Such fast aquation would result in *trans*-[Ru^{III}Cl(cyclam)(H_2O)]$^{n+}$ and isnH$^+$, which do not absorb at 375−391 nm,[20,38] and would result in decrease of the absorbance around these wavelengths. Thus, these spectral features indicate that the amide is rather substitution inert.

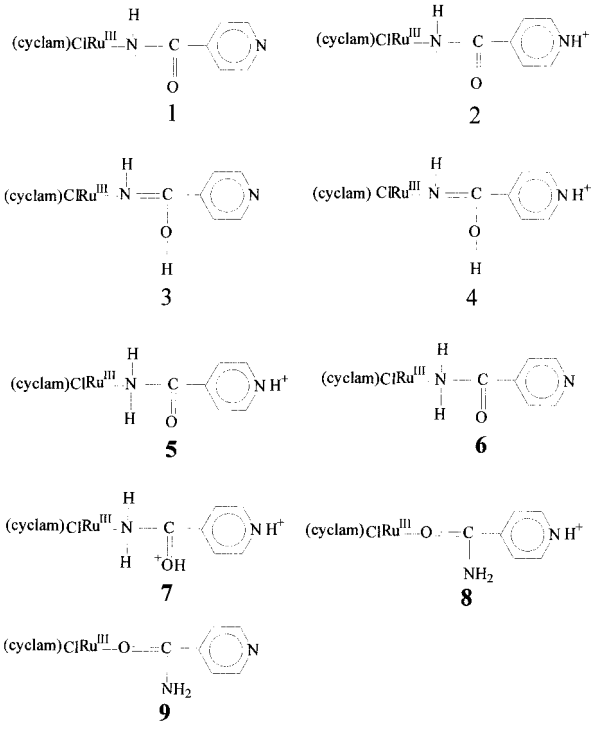
(42) Fairlie, D. P.; Taube, H. *Inorg. Chem.* **1985**, *24*, 3199.

Table 2. Electronic Absorption Data of Some Ru(III)−Amide Complexes

complexes	λ_{max}/nm (log ϵ)	ref
trans-$[Ru^{III}Cl(cyclam)(NHCO\text{-}4pyH)]^{2+}$	494 (2.73); 376 (3.56); 320 (3.37), 260, 212[b]	*a*
trans-$[Ru^{III}Cl(cyclam)(NHCO\text{-}4py)]^{+}$	391 (3.42); 306 (3.44)[c]	*a*
trans-$[Ru^{III}Cl(cyclam)(OCNH_2\text{-}4py)]^{+}$	345 (3.52), sh 299 (3.49)[d]	*a*
$[Ru^{III}(NH_3)_5(NHCOCH_3)]^{2+}$	383 (3.54); 249 (3.36)[e]	12
$[Ru^{III}(NH_3)_5(NHCHO)]^{2+}$	383 (3.58)[f]	42
$[Ru^{III}(NH_3)_5(NH_2COCH_3)]^{3+}$	322 (3.19)[g]	12
$[Ru^{III}(NH_3)_5(NHCO\text{-}4\text{-}py)]^{2+}$	386 (3.51); 306 (3.49); 270 (3.57)[h]	8
	386[i]	15
	384 (3.57); 262 (3.71); 228 (3.61)[c]	37
$[Ru^{III}(NH_3)_5(NHCO\text{-}4\text{-}pyH)]^{3+}$	358 (3.67), 264 (3.67)[j]	8
	358 (3.48)[g]	15
$[Ru^{III}(NH_3)_5(NHCO\text{-}4\text{-}pyCH_3)]^{3+}$	358 (3.70), 268 (3.67), 220 (3.86)[h]	8
	350[k]	16
$[Ru^{III}(NH_3)_5(NHCO\text{-}3\text{-}py)]^{2+}$	386 (3.56); 306 (3.54); 262 (3.65)[c]	37
	387 (3.57)[i]	15
$[Ru^{III}(NH_3)_5(NHCO\text{-}3\text{-}pyH)]^{3+}$	357 (3.45)[g]	15
$[Ru^{III}(NH_3)_5(NHCO\text{-}3\text{-}pyCH_3)]^{3+}$	360 (3.46); 314 (3.43); 266 (3.66)[c]	37
$[Ru^{III}(NH_3)_5(OH_2)]^{3+}$	320 (2.00); 268 (2.87); 210 (2.96)[l]	42
$[Ru^{III}(NH_3)_5(OC(NH_2)_2)]^{3+}$	287 (3.32); 248 (2.95)[m]	42
$[Ru^{III}(NH_3)_5(OCHNH_2)]^{3+}$	294 (3.00); 224 (3.26)[n]	42
$[Ru^{III}(NH_3)_5(OCHN(CH_3)_2)]^{3+}$	335 (3.15); 280 sh (2.97); 240 sh (3.39)[o]	42
$[Ru^{III}(NH_3)_5(OC(CH_3)N(CH_3)_2)]^{3+}$	348 (3.20); 293 (3.24); 205 sh (3.03)[o]	42

[a] This work. [b] 0.1 M HCl solution, pH = 1. [c] 0.1 M CH_3CO_2H/CH_3CO_2Na, pH = 4.65 solution. [d] pH 8.7 with NaOH. [e] 1.0 M $NaClO_4$. [f] $HCONH_2$. [g] 1 M $HClO_4$. [h] In aqueous pH 6.8 phosphate buffer. [i] 0.1 M $LiClO_4$. [j] In 0.1 M triflic acid. [k] In 0.1 M CF_3CO_2H/CF_3CO_2Na. [l] 0.01 M CF_3SO_3H. [m] 0.1 M CF_3SO_3H. [n] 1.0 M HCl. [o] 1.0 M CF_3SO_3H.

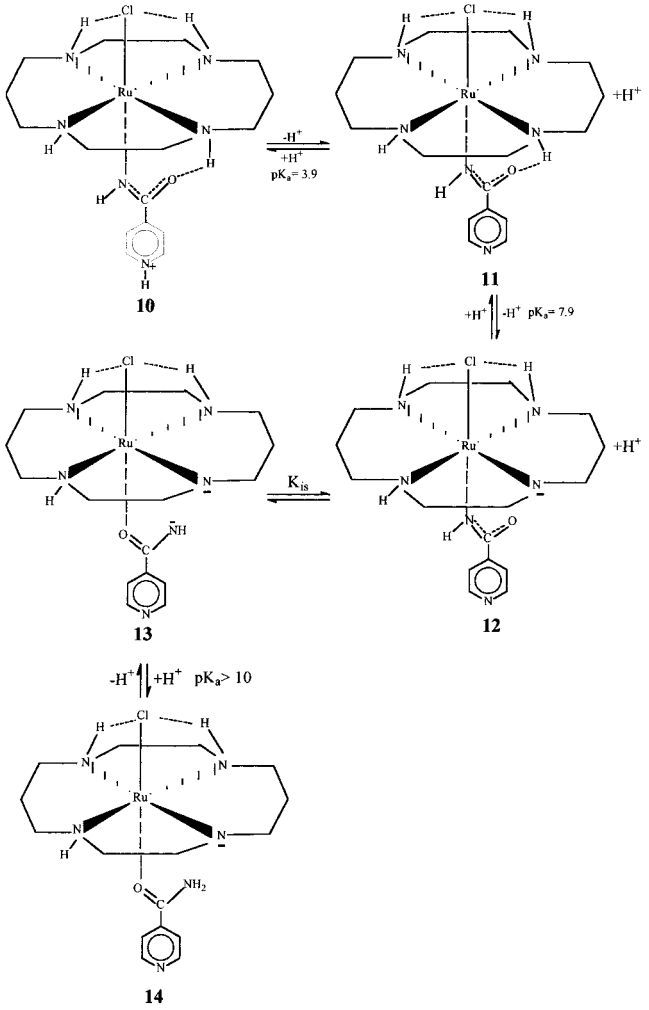
Chart 1



The neutral amide bonded species of coordinated carboxamide complexes with pentaammineruthenium(III), $[Ru^{III}(NH_3)_5(NH_2-C(O)R)]^{n+}$,[5] are not expected to have absorptions above 300 nm, and thus structures **5**, **6**, and **7** can be ruled out. In fact, structure **7** would require very high acid concentrations. The bands at 391 nm (pH 4.5) and 375 nm (pH 1) for *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$ can be assigned to a carboxamido nitrogen bonded carboxamide−Ru(III) (structures **1**−**4**) LMCT transition, as occurs for other similar species,[5,8,11,12,42] the spectra of which display absorption bands around these wavelengths, characteristic of the nitrogen-bonded, deprotonated, amide species. Nevertheless, in some instances, some carboxamide−Ru(III) complexes also display a second absorption band at higher energy, around 320 nm. In addition, recently,[5] bands around this wavelength were assigned to the iminol tautomer of deprotonated amides, $[Ru^{III}(NH_3)_5(NH{=}C(OH)R)]^{3+}$, in acidic medium ($[H^+] > 1$ M), with the absence of the band around 380 nm, which is characteristic of the amido form of the nitrogen-bonded species; addition of base results in absorbance decrease of the higher energy band and increase of absorbance ~380 nm. The iminol form exists in strong acidic medium and the amido form in less acidic or basic medium.[5] The iminol forms of the cyclam complexes discussed here correspond to strucutres **3** and **4**. In the present case, for *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$, consideration only of the presence of both bands (at 306−320 nm and 375−391 nm) at different pH's below pH 4.5 does not allow ruling out any of the structures **1**−**4**. In order to analyze the possible structures, it should be noted that there are some distintictive features between the tetraammines and the cyclam complexes of ruthenium(III/II). In the *trans*-$[Ru^{III}(cyclam)Cl_2]^+$ complex, for instance, the Cl−H(N) distance is smaller than the sum of the van der Waals radii, indicating an intramolecular hydrogen bonding between the chloro ligands and the cyclam nitrogen hydrogens (two in each side of the ring pseudo plane); also, the rate of loss of chloride, upon reduction, is smaller than expected due solely to the chelate effect when compared with the *trans*-dichlorotetraammineruthenium complex, *trans*-$[Ru^{III}(NH_3)_4Cl_2]^+$.[20,28] Furthermore, the pK_a of 1.1 of *trans*-$[Ru^{III}(cyclam)(H_2O)_2]^{2+}$ is smaller than that of *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+}$ (pK_a = 2.6[20]) and $[Ru(NH_3)_5(H_2O)]^{3+}$ (pK_a = 4.2[47,48]), indicating that cyclam turns Ru(III) more acidic than ammines. In addition, we estimated the pK_a value of ~7.9 for *trans*-$[Ru^{III}(cyclam)Cl_2]^+$ by cyclic voltammetry. This pK_a

(43) Boggs, S. E.; Clarke, R. S.; Ford, P. C. *Inorg. Chim. Acta* **1996**, *24*, 129.
(44) Clarke, R. E.; Ford, P. F. *Inorg. Chem.* **1970**, *9*, 495.
(45) Rocha, Z, N.; Tfouni, E. *Polyhedron.* **1992**, *11*, 2375.
(46) Caetano, W.; Alves, J. J. F.; Lima, N. B. S.; Franco, D. W. *Polyhedron* **1995**, *14*, 1245.
(47) Kuhen, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689 and references therein.
(48) Broomhead, J. A.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 826.

Scheme 2



would refer to the cyclam nitrogen hydrogen and is about 5 orders of magnitude smaller than that of $Ru(NH_3)_6^{3+}$ (pK_a = 13.1[49]). Thus, considering that the preferential protonation site is the oxygen in the carboxamide rather than the nitrogen, it is possible that a similar interaction, although smaller, due to the larger distances in the present case, may be occurring between the one (or two) cyclam nitrogen hydrogen and the carboxamide oxygen, forming a six-membered ring, and imparting some iminol character to the carboxamide (structure **10**, Scheme 2).

Such an interaction was already observed in the molecular structure of $[Ru^{III}(NH_3)_5(NHC(O)py)]^{2+}$, as determined by X-ray diffraction, which shows a strong interaction between the amide oxygen and two hydrogens of two cis ammines.[8] Considering that in the Ru(III) complexes the cyclam species are more acidic than the ammines, the cyclam nitrogen hydrogen would be favored to hydrogen bond to the amide oxygen, imparting some iminol character. Accordingly, the estimated oxygen hydrogen interatomic distance in the cyclam complex[50] is 2.4 Å, smaller than the 2.6 Å for the pentaammine. As a consequence, the bands in the 300−400 nm range would then have an energy higher than expected. Protonation/deprotonation of the pyridinyl nitrogen would have only a small effect on the extent of interaction. The above reasoning suggests that the bands at 306−320 nm would have contribution from some iminol character. The $[Ru^{III}(NH_3)_5(NH{=}C(OH)pyCH_3^+)]^{3+}$ (iminol tautomer, analogous to structure **4**) complex deprotonates, forming $[Ru^{III}(NH_3)_5(NH{-}C(O)pyCH_3^+)]^{3+}$ (amido form, analogous to structure **2**) with a pK_a of −0.3.[8] By the same above reasoning, it should be expected, then, that *trans*-$[Ru^{III}Cl(cyclam)(NH{=}C(OH)\text{-}4\text{-}pyH^+)]^{2+}$ (structure **4**) would have a pK_a near −0.3. But, as already noted, no unequivocal spectral changes indicative of an iminol−amido equilibrium were observed from 6 M HCl up to pH 9. However, the bands at 306−320 nm appear in the whole pH range studied, even at pH 8, strongly indicating that these bands may not be due to an iminol tautomer, at least as pure iminol bands. The 300−360 nm range is also the range for Cl−Ru(III)amine LMCT absorption bands.[21−23,28,43] For instance, *trans*-$[Ru^{III}(cyclam)Cl_2]^+$ displays two absorption bands at 358 and 315 nm at pH 1[28] and only one band at pH 9, at 312 nm, and *trans*-$[Ru^{III}Cl(cyclam)(H_2O)]^{2+}$ shows pH dependent absorptions in the 300−350 nm range.[20] Thus, the persistence of these bands in this wide pH range is consistent with Cl−Ru(III)amine LMCT assignment for them, although not completely ruling out some possible contribution from some iminol character. However, these features are consistent with the presence of the iminol character, imparted by the cyclam nitrogen hydrogen.

The spectral changes of *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$ in the 0.4−4.5 pH range showed an isosbestic point at ∼384 nm, along with other possible paths, allowing the calculation of one pK_a (3.9). In more acidic solutions (pH < 3.5), the band around 380 nm appears at 375 nm. At higher pH's (4.0 < pH < 4.5) there is an absorption band at 391 nm. At pH 1, the band at ≈320 nm is lower in intensity than the 376 nm band, and at pH 4.5 it is blue shifted to 306 nm with a slight intensity increase and lower intensity than the 391 nm band. At higher pH's the band at 306−320 nm is less defined and still is lower in intensity than the bands at 391 or 345 nm (the band at 345 nm appears in basic media (see below)). These spectral changes are regenerated by adding acid or base and occur within mixing time. The *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$ complex can be compared with the pentaammine analogue[8] $[Ru^{III}(NH_3)_5(NHC(O)\text{-}4\text{-}pyH)]^{3+}$, which is reported to have a pK_a of 4.3, close to that of the free isnH^+ (3.61). Thus, it is reasonable to assign for *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$, which would correspond to structure **10**, the pK_a of 3.9, which is close to the value of 4.3 for the pentaammine analogue. The slightly smaller pK_a value of the cyclam complex is consistent with the *trans*-$[Ru^{III}Cl(cyclam)]^{2+}$ core being more acidic, even though the site of protonation is not close to Ru. The absorption band at 375 nm corresponds to the protonated form (structure **10**), whereas that of 391 nm corresponds to the unprotonated form (structure **11**). These energy shift directions upon protonation/deprotonation are similar to those of the pentaammine analogue[8] $[Ru^{III}(NH_3)_5(NHC(O)\text{-}4\text{-}pyH)]^{3+}$.

Increase of the pH from 4.5 to 11 results in a decrease of the band at 391 nm and the appearance of one band at 345 nm, with a more defined isosbestic point at 365 nm. The spectral changes of *trans*-$[Ru^{III}Cl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$ in the 4.5−11 pH range allowed the calculation of another pK_a (∼7.9). The bands at 345 nm above pH 4.5 are more consistent with oxygen-bonded amides, as for $[Ru^{III}(NH_3)_5(OC(NH_2)_2)]^{3+}$, which undergoes relatively fast linkage isomerization to the N-bonded isomer at high pH (pH > pK_a), competitive with urea aquation.[42] If one assumes that this band at 345 nm is indicative of the oxygen-bonded amide in *trans*-$[Ru^{III}Cl(cyclam)(OC-$

(49) Waysbort, D.; Navon, G. *Inorg. Chem.* **1979**, *18*, 9 and references therein.

(50) There is no X-ray diffraction data for the cyclam complex. Thus, comparison was made by calculating interatomic distances using the Spartan program and using the X-ray data for the pentaammine complex.

(NH_2)-4-py)]$^{2+}$ (structure **12** in Scheme 2), then this would mean that a relatively fast linkage isomerization occurred. This isomerization is in contrast with the behavior of other ruthenium(III) amides which at high pH undergo isomerization to the nitrogen-bonded species. In addition to the spectral evidence, cyclic voltammetry experiments at pH 8.7 indicate that the reduction of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-py)]$^{+}$ results in the oxygen-bonded Ru(II) species (see below). Furthermore, the regeneration of the bands with pH changes indicates that, like the nitrogen-bonded isomer, the oxygen-bonded isomer is also relatively inert with respect to substitution. Scheme 2 shows the equations of the reactions consistent with the observed behavior.

In basic medium *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (structure **10**), with a pK_a of 3.9, is deprotonated on the pyridine nitrogen and can be represented by structure **11**. This last species (**11**, *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-py)]$^{+}$) can be further deprotonated at the cyclam nitrogen, with a pK_a of 7.9, resulting in structure **12**, which undergoes a linkage isomerization to an oxygen-bonded species with a deprotonated amide (structure **13**). The pK_a of coordinated amides in pentaammines is estimated to be ≥ 10,[42] and, thus, at pH below 10, they are expected to be protonated. Despite the cyclam Ru(III) complex being more acidic than the pentammines, this increased acidity resides more likely in the cyclam nitrogen, rather than in the amide, as judged by the pK_a of *trans*-[Ru^{III}(cyclam)Cl_2]$^{+}$ as aforementioned. As a result, in basic medium the predominant species would be the deprotanated cyclam nitrogen, oxygen-bonded isomer of the neutral amide (structure **14**). This is consistent with the energy of the band (at 345 nm), since the deprotonated *trans*-[Ru^{III}(cyclam)Cl_2]$^{+}$ (at pH 9) has an absorption band at 312 nm. Although conceivably the nitrogen-bonded amide with deprotonated cyclam (structure **12**) could be the species present, the energy of the band is higher than expected for a nitrogen-bonded amide. The linkage isomerization would be slow due to the ring formed, but deprotonation of the cyclam nitrogen eliminates the ring rigidity, which would impose smaller rates of isomerization.

Reactions following Reduction of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH^{+})]$^{2+}$. The *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH^{+})]$^{2+}$ complex showed a behavior different from that of the corresponding pentaammines upon reduction of the metal center. In the case of pentaammines, reduction of [$Ru^{III}(NH_3)_5$(NHC(O)-4-py)]$^{2+}$ to [$Ru^{II}(NH_3)_5$(NHC(O)-4-py)]$^{+}$ is followed by an amido to pyridinyl linkage isomerization competitive with amide aquation, forming [$Ru^{II}(NH_3)_5$(isn)]$^{2+}$, [$Ru^{II}(NH_3)_5(H_2O)$]$^{2+}$, and free isonicotinamide.[11,51] The reactions are pH dependent, and, accordingly, no linkage isomerization occurs at low pH, with the exclusive formation of [$Ru^{II}(NH_3)_5(H_2O)$]$^{2+}$and free isonicotinamide,[11,51] bearing in mind that protonation in the Ru(II) is on the amide oxygen, and in Ru(III) in the pyridinyl nitrogen.[42,51]

The cyclic voltammograms of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**) formed by controlled potential electrolysis at +600 mV vs Ag/AgCl of *trans*-[Ru^{II}Cl(4-NCpyH)(cyclam)]$^{2+}$ in the −600 to +800 mV range, starting at 0 V and going toward negative potentials, at scan rates higher than 100 mV s^{-1}, show one pair of peaks, with the anodic peak, 1a, at −250 mV, and the cathodic peak, 1c, at −330 mV (ΔE_p = 80 mV; 0.79 < ip_a/ip_c < 0.85; 50 mV s^{-1} < υ < 400 mV s^{-1}). At smaller scan rates other peaks start to appear (Figure 2). The successive cyclic voltammograms at 10 mV s^{-1} are shown in Figure 3. These CVs were recorded in the −500 mV to 0 V range, starting at 0 V and going toward negative potentials. In the first scan, the cathodic peak at −295 mV (1c) appears, and a barely discernible shoulder appears at −400 mV; one anodic peak appears at −220 mV, with also a barely discernible shoulder at −340 mV. In the second scan, the peak at −295 mV decreases in intensity, while the shoulder at −400 mV now becomes a peak with height similar to that of the peak at −295 mV; the anodic shoulder at −340 mV becomes more prominent, and the peak at −220 mV has a small decrease in intensity. Successive scans result in a CV with the cathodic peak at −295 mV with lower intensity than the cathodic peak at −400 mV which becomes more prominent; in their turn, the anodic shoulder at −340 mV becomes more prominent, while the anodic peak at −220 mV shows a small decrease. The presence of two pairs of peaks suggests the existence of two linkage isomers, N-bonded amide and O-bonded amide, as for related pentaamines.[5] In this case,

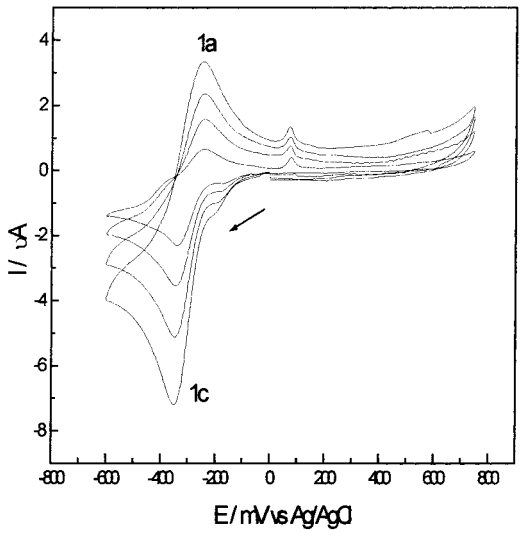


Figure 2. Cyclic voltammograms of 1 × 10^{-3} M *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**) in 0.1 M KCl and 0.1 M HCl, at 25 °C. υ = 50, 100, 150, and 250 mV·s^{-1}.

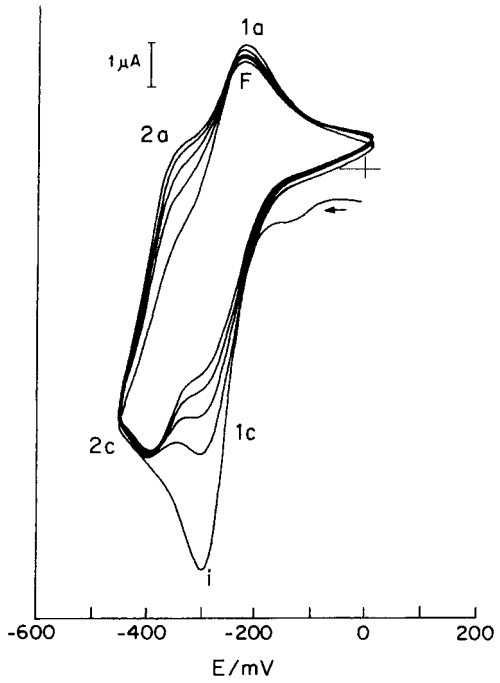


Figure 3. Cyclic voltammograms of 1.87 × 10^{-3} M *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**) in 0.1 M HCl/KCl at 25 °C. υ = 10 mV·s^{-1}. i = first scan. F = fifth scan. Reference electrode: Ag/AgCl.

(51) Chou, M. H.; Brunschwig, B. S.; Creutz, C.; Sutin, N.; Yeh, A.; Chang, C. R.; Lin, C. T. *Inorg. Chem.* **1992**, *31*, 5347.

reduction of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ forms the corresponding Ru(II) N-bonded amide isomer, which isomerizes to the O-bonded amide species. Accordingly, the pairs of peaks 1a/1c and 2a/2c can be assigned to the N-bonded and O-bonded amide species, respectively. The cyclic voltammogram at pH 8.7 shows only one anodic peak and one cathodic peak, at −360 and −450 mV, respectively. The cathodic peak potential is consistent with the reduction of the deprotonated oxygen bonded isomer by the following reasoning. The pK_a corresponding to the cyclam N−H of *trans*-[Ru^{III}Cl(cyclam)-(ONH_2C-4-py)]$^{2+}$ is 7.9, and, thus, cyclam should be deprotonated at pH 8.7, resulting in *trans*-[Ru^{III}Cl(cyclam$^-$)(ONH_2C-4-py)]$^+$, and a lower reduction potential (−450 mV) is consistent with the more negative charge of this latter species when compared with *trans*-[Ru^{III}Cl(cyclam)(ONH_2C-4-pyH)]$^{3+}$, which has a reduction potential of −400 mV. Once reduced to *trans*-[Ru^{II}Cl(cyclam$^-$)(ONH_2C-4-py)] it is readily protonated, resulting in *trans*-[Ru^{II}Cl(cyclam)(ONH_2C-4-py)]$^+$, which is oxidized to *trans*-[Ru^{III}Cl(cyclam)(ONH_2C-4-py)]$^{2+}$ at −360 mV. This lower oxidation potential is slightly smaller than the oxidation potential of *trans*-[Ru^{II}Cl(cyclam)(ONH_2C-4-pyH)]$^{2+}$ (−340 mV), and, although slightly lower, it is again consistent with the lower positive charge of *trans*-[Ru^{II}Cl(cyclam)(ONH_2C-4-py)]$^+$. The cyclic voltammetric and spectral results are self-consistent, giving further support to the O-bonded linkage isomer in basic media. Evidence described below further supported the above assignments.

Chemical reduction of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**) by Zn/Hg resulted in a color change from orange (**II**) to blue (**III**) (absorption changes from 494 nm (ϵ = 540 M·cm^{-1}) and 376 nm (ϵ = 3670 M·cm^{-1}) to ∼550 (ϵ = 450 M·cm^{-1}), 357 (ϵ = 1060 M·cm^{-1}), and 256 nm (ϵ = 700 M·cm^{-1}) (**III**)).[52] This solution has its blue color slowly changing to pink (**IV**) (∼495 nm (sh) (ϵ = 670 M·cm^{-1}), 357 nm (ϵ = 2070 M·cm^{-1}), 312 nm (ϵ = 1350 M·cm^{-1}), 260 nm (ϵ = 4350 M·cm^{-1}), and 228 nm (ϵ = 4600 M·cm^{-1})). The CVs of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ (**II**) after chemical reduction (blue solution) (**III**), with scan rates from 10 to 100 mV·s^{-1}, in the −600 mV to +200 mV range, starting at 0 V and going toward negative potentials, show, at 25 °C, two cathodic peaks at −280 (1c) and −400 mV (2c), and two anodic peaks at −220 (1a) and −340 mV (2a). Both have ΔE_p = 60 mV and involve one electron each. At 10 °C, only the peaks at −280 (1c) and −220 mV (1a) are seen. This strongly suggests that the more negative pair of peaks (2a/2c) is a result of a chemical reaction, the linkage isomerization to the O-bonded amide species. The CVs of the pink (**IV**) solution, with scan rates from 10 to 100 mV·s^{-1}, in the −500 mV to +300 mV range, starting at 0 V and going toward negative potentials, show, at 25 °C, only one cathodic peak at −400 mV and one anodic peak at −340 mV. At smaller scan rates (25 and 10 mV·s^{-1}), and still at 25 °C, an anodic shoulder at −220 mV and a cathodic shoulder at −289 mV start to appear. When the scan is held at ≈−550 mV, the anodic shoulder at −220 mV becomes a peak with an intensity higher than that of the anodic peak at −340 mV, and the cathodic shoulder at −280 mV becomes more discernible. At 10 °C, only the pair of peaks at −340 and −400 mV appears. These results mean that the pink solution displays one pair of peaks at −340 and −400 mV, and that, in the blue solution, two species should be present, the pink (**IV**), with peaks at −340 and −400 mV, and the blue (**III**), with peaks at −220 and −280 mV. In summary, these results altogether are consistent then with the pair of peaks 1a/ac and 2a/2c being the N-bonded isomer and O-bonded isomer, respectively.

The specific rate constant for the N/O isomerization in the Ru(II) cyclam complex was estimated to be ∼2 × 10^{-2} s^{-1}, from the CV data. This value is smaller than in Ru(II) pentaammines and, for instance, is at least about 4 orders of magnitude smaller than that of [Ru^{II}(NH_3)$_5$(NHCOCONH$_2$)]$^+$, which is >10^2 s^{-1}.[5] This smaller value is consistent with the larger acidity of cyclam when compared with pentaammines, as judged by the chloride affinities to both systems (see synthesis discussion). It is also consistent with the macrocyclic effect and the intramolecular hydrogen bonding (see carboxamide spectral discussion) which forms a six-membered ring, restricting rotation of the Ru−N(amide) axis. However, since this Ru(cyclam) amide system is the only thus far studied, other amide complexes with Ru(cyclam) need to be investigated for confirmation.

Reaction of [Ru^{II}(NH_3)$_5$(OH_2)]$^{2+}$ and (NH_2C(O)-4-py-me)(CF_3SO_3) in alkaline medium results in a blue species, with λ_{max} = 695 nm, assigned as [Ru^{II}(NH_3)$_5$(NHC(O)-4-py-Me)]$^{2+}$ [8] Oxidation of [Ru^{II}(NH_3)$_5$(4-mcp)]$^{3+}$ results in [Ru^{III}(NH_3)$_5$(NHC(O)-4-py-Me)]$^{3+}$, which, upon reduction to the corresponding Ru(II) complex, develops a blue color (λ = 690 nm),[8] which fades as this complex undergoes fast aquation forming [Ru^{II}(NH_3)$_5$-(OH_2)]$^{2+}$ and 1-methyl-4-carboxamidepyridinium,[8,11,16] with a half-life of 30 s at 5 °C. The observed rate of aquation at room temperature, pH 1, for the blue species (**III**) was estimated to be ∼2.4 × 10^{-5} s^{-1}. Considering that the rate of linkage isomerization is ∼2.2 × 10^{-2} s^{-1}, this value would be the sum of both aquation rates, from N-bonded and O-bonded isomers. This value is much smaller than the smallest value of 6 s^{-1}, for amide aquation in [Ru^{II}(NH_3)$_5$(NHC(O)-4-py-Me)]$^{3+}$,[8] found for pentaammine analogues.[8,11] Again, the same reasoning used to explain the slower rate of isomerization can be used for the slower rate of aquation in the cyclam species. The smaller rate of aquation of the cyclam system is consistent with the macrocyclic effect, the larger acidity of cyclam when compared with pentaammines, and the intramolecular hydrogen bonding which forms a six-membered ring, restricting aquation.

Summary. The results can be interpreted as follows. Oxidation of *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH)]$^{2+}$ (**I**), at pH 1, to *trans*-[Ru^{III}Cl(cyclam)(4-NCpyH)]$^{3+}$ is followed by hydrolysis of the coordinated nitrile to give *trans*-[Ru^{III}Cl(cyclam)(NHC-(O)-4-pyH)]$^{2+}$ (**II**), where the amide is coordinated through the nitrogen. The identity of the species is pH dependent. In addition to protonation/deprotonation, linkage isomerization occurs at pH > 8 resulting in the oxygen-bonded species. Reduction of the metal center, in acidic medium, does not result in fast aquation as occurs for other amides with ruthenium(II) pentaammine, but is followed by a relatively slow linkage isomerization to form the oxygen-bonded species. Aquation and isomerization rates are smaller than in the pentaammines. Other related systems are currently under investigation in our laboratories, especially with respect to the proposed linkage isomerization, in basic medium, of the Ru(III) complex, the behavior of which is opposite to that of the pentaammines.

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(52) The molar absorptivities were estimated from concentration of starting material and absorbance measurements, considering full conversion.