Ruthenium(II) Macrocyclic Complexes with Inert Chloride and Labile Azines. Synthesis and Properties of the Macrocyclic Complexes *trans*-Chloro(azine)(1,4,8,11-tetraazacyclotetradecane)ruthenium(II), *trans*-[RuCl(cyclam)L]$^{+}$ [1]

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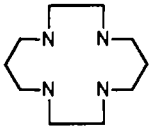
Received June 25, 1991

Reported are the syntheses and some properties of the ruthenium(II) macrocyclic complexes, *trans*-[Ru^{II}Cl(cyclam)L] (cyclam = 1,4,8,11-tetraazacyclotetradecane; L = 4-picoline (4-pic), pyridine (py), isonicotinamide (isn) or 4-acetyl-pyridine (4-acpy)). The syntheses of these complexes were performed by reducing *trans*-[$RuCl_2$(cyclam)]$^{+}$ to the Ru(II) form, which undergoes the labilization of only one chloride, and addition of excess L. The UV–vis spectra of the azine complexes display one visible range metal-to-ligand charge-transfer (MLCT) absorption, and one UV range intraligand band. Between these two absorptions there is a ligand-field band. The MLCT energies and Ru^{III}/Ru^{II} reduction potentials of the azine complexes are similar to those of the corresponding pentaammines, suggesting that back-bonding is similar in each pair of complexes. Surprisingly, in contrast to other ruthenium(II) ammine complexes, the chloride is substitution inert while the azine is labile.

Introduction

In this laboratory, we have been investigating the photosubstitution reactions of *trans*-[$Ru^{II}(NH_3)_4LL'$],[3] *cis*-[$Ru^{II}(NH_3)_4$(isn)L],[4] and *cis*-[$Ru^{II}(NH_3)_4LL'$][4b] (L, L′ = azine; isn = isonicotinamide). In these systems, photoaquation of L, L′, isn, and NH_3 is observed, implying labilization of the *x*, *y*, and *z* axes. In this context, the present study was undertaken with the goal of localizing the photosubstitution behavior to the *z* axis by coordinating the *x* and *y* axes with the tetradentate macrocyclic amine 1,4,8,11-tetraazacyclotetradecane (cyclam) (I). Cyclam complexes of Ru(II) have received much less attention than analogous complexes of other ammines.[5,6] Described in this paper are the synthesis, spectroscopy, cyclic voltammetry, and other properties of some *trans*-[RuCl(cyclam)L]$^{+}$ complexes with unsaturated ligands.



I

Experimental Section

Chemicals and Reagents. Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) (Strem) was the starting material for the ruthenium complex syntheses. Reagent grade pyridine (py) (Aldrich), 4-picoline (4-pic) (Aldrich), and 4-acetylpyridine (4-acpy) (Aldrich) were distilled under reduced pressure before use. Isonicotinamide (Aldrich) was recrystallized from hot water after treatment with activated charcoal. Acetone, methanol, and ethanol were purified according to literature procedures.[7] Ether was purified by modification of a described procedure.[7] A 250-mL portion of distilled ether was shaken with 20 mL of acidic iron(II) sulfate solution (60 g of $FeSO_4 \cdot 7H_2O$ and 6 mL of concentrated H_2SO_4 in 110 mL of water). The ether layer was subsequently shaken with 0.5% aqueous $KMnO_4$ solution, treated with 5% NaOH solution, and washed four times with water. The ether was then distilled, and the distillate, to which concentrated H_2SO_4 was added (150 mL for 1 L ether), was distilled again. Cyclam was purchased (Strem) or prepared as described[8,9] and was recrystallized from chlorobenzene before use. A solution of silver trifluoroacetate (AgTFA) was prepared by dissolving stoichiometric amounts of Ag_2O in trifluoroacetic acid such that the final pH of the solution was 1.0. Sodium tetrafluoroborate (Aldrich) was recrystallized from hot water before use. Doubly distilled water was used throughout. All other materials were reagent grade and were used without further purification.

Complex Syntheses. $K_3[RuCl_6]$ was prepared according to the literature procedure.[10] *trans*-[$RuCl_2$(cyclam)]Cl was synthesized by a modification of described procedures.[11,12] Equimolar amounts of cyclam and $K_3[RuCl_6]$ were refluxed in ethanol under argon for 3 days. The solid formed was recrystallized from hot 0.1 M HCl, then purified by ion exchange chromatography on a Dowex AG-50-W-X4 resin column. Elution was performed with HCl solutions. The complex began to elute with 1.0 M HCl and finished with 1.8 M HCl. Each 10-mL aliquot was monitored spectrophotometrically. All *trans*-dichlorocyclam complex fractions were combined and evaporated to dryness, giving the solid as orange needles. The solid was dissolved in a small amount of warm 1.0 M HCl and filtered while warm. The volume of the filtrate was reduced to ~10 mL by rotoevaporation and cooled in the refrigerator for 3 h. The mixture was filtered and the solid washed with ethanol, ether, and acetone and then vacuum dried. After it was washed with acetone the solid became yellow in color. The UV–vis spectrum of the product shows bands at 358 nm (ϵ = 2580) and 315 nm (ϵ = 1230); literature values are 358 nm (ϵ = 2560) and 315 nm (ϵ = 1230).[11] Yields averaged 60%.

trans-[RuCl(cyclam)L]$^{+}$ complexes, where L = py, 4-pic, isn, or 4-acpy, were synthesized using two procedures.

Method 1. To 50 mg (~0.123 mmol) of *trans*-[$RuCl_2$(cyclam)]Cl dissolved in deaerated water (5 mL) was added Zn(Hg) (1.5 g), and argon was continuously bubbled through the solution. After 30 min, a 10-fold excess of the ligand was added to the solution. After 24 h of

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reaction in the dark, with continuous argon bubbling, the mixture was filtered into a freshly prepared, deaerated, saturated (1 g/1 mL), and filtered aqueous solution of $NaBF_4$. The resulting solution was concentrated under reduced pressure, and the solid formed was collected by filtration, washed with ether, and vacuum dried. The solid was recrystallized from deaerated water, washed with ether, and dried under vacuum to provide an average yield of 45%.

Method 2. To 50 mg (~0.123 mmol) of *trans*-$[RuCl_2(cyclam)]Cl$ dissolved in deaerated water (5 mL) was added Zn(Hg) (1.5 g), and the solution was stirred for 4 h in the dark under continuous argon bubbling. The mixture was then filtered, and oxygen was bubbled through the solution for 15 min. A 45-mg (~0.2-mmol) portion of AgTFA was then added with stirring. The AgCl formed was removed by filtration and Zn(Hg) (~1.5 g) was added to the filtrate solution, under continuous argon bubbling in the dark. After 15 min, a 10-fold excess of ligand was added. After 20 h of reaction in the dark, under continuous argon bubbling, the mixture was filtered into a freshly prepared, deaerated, saturated, and filtered aqueous solution of NH_4PF_6. The resulting solution was concentrated by evaporation under reduced pressure. The resulting solid was collected by filtration, washed with ether, and vacuum dried. The solid was dissolved in a minimum amount of acetone under argon, except for *trans*-[RuCl(cyclam)(isn)]$^+$, where ethyl acetate was used instead of acetone. The solution was filtered, and ether was added dropwise until precipitation began. The mixture was cooled in the refrigerator to complete precipitation. The complex was collected by filtration, washed with ether, and dried under vacuum to provide an average yield of 50%.

Elemental Analysis. Carbon, hydrogen, and nitrogen were determined by microanalysis at the Instituto de Química da Universidade de São Paulo. Anal. of *trans*-[RuCl(cyclam)L](BF_4). Calcd for L = py: C, 35.83; N, 13.93; H, 5.81. Found: C, 35.60; N, 13.74; H, 5.88. Calcd for L = 4-pic: C, 37.19; N, 13.54; H, 6.04. Found: C, 37.79; N, 13.24; H, 5.61. Calcd for L = isn: C, 35.52; N, 15.40; H, 5.54. Found: C, 35.52; N, 15.48; H, 5.44. Calcd for *trans*-[RuCl(cyclam)(4-acpy)]$(BF_4)\cdot 3H_2O$: C, 34.14; N, 11.69; H, 6.18. Found: C, 34.14; N, 11.45; H, 5.27.

Spectra. Electronic spectra were recorded at room temperature with a Varian 634-S or a Cary 2200 recording spectrophotometer using quartz cells. Solutions used to measure extinction coefficients were prepared gravimetrically with quantitative dilution.

Cyclic Voltammetry. The CV's of the complexes were taken with a CV-1B cyclic voltammograph from Bio-Analytical Systems and a Houston Instrument Omnigraph 100 X-Y recorder. Scan rates of 100, 200, 300, and 400 mV s^{-1} were employed. The electrochemical cells were of the three-electrode type with a saturated calomel electrode (SCE) as a reference electrode and a platinum wire as an auxiliary electrode. The working electrode was a glassy-carbon electrode. Electrochemical data in aqueous solutions were obtained in supporting electrolyte solutions of 0.1 M ionic strength at 25 °C prepared from HCl and with millimolar concentrations of the complex. All solutions were deaerated with argon. The formal reduction potentials (E_f) were calculated as the arithmetic mean of the anodic and cathodic peak potentials. E_f values were also converted to the SHE reference by adding 0.242 V to measurements made with SCE as reference electrode.

Infrared Spectra. The IR spectra were recorded in the 4000–400-cm^{-1} range using a Specord 75 instrument from Carl Zeiss Jena or a Model 257 Perkin-Elmer or a Model 1600 FTIR series Perkin-Elmer spectrophotometer. Spectra were taken in Nujol mulls and KBr disks.

Results and Discussion

Syntheses. The *trans*-[RuCl(cyclam)L]$^+$ (L = 4-pic, py, isn, or 4-acpy) syntheses use *trans*-$[RuCl_2(cyclam)]^+$ as the starting complex. For the trans tetraammine analogues the general procedure to prepare *trans*-$[Ru(NH_3)_4L_2]^{2+}$ involves reduction of *trans*-$[RuCl_2(NH_3)_4]^+$ to *trans*-$[RuCl_2(NH_3)_4]$, which rapidly aquates both chlorides, to form *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$. In the presence of an unsaturated ligand L, the latter species forms *trans*-$[Ru(NH_3)_4L_2]^{2+}$. Notably, the behavior of the cyclam complex is markedly different. In the reduced form, *trans*-$[RuCl_2$(cyclam)] has an unexpected affinity for chloride, when compared with ruthenium(II) ammine complexes.[6] Earlier studies indicate that chloride aquation from *trans*-$[RuCl_2(cyclam)]$ is slower than in $[RuCl(NH_3)_5]^+$ [13] and that aquation of the second chloride is even slower. Similar features are observed in the analogous isoelectronic complexes of Co^{3+}.[14] This difference in chloride affinities allowed us to devise a synthetic procedure to obtain *trans*-[RuCl(cyclam)L]$^+$. In method 1, a 20-h reaction time is needed to aquate the first chloride. In method 2, Ag^+ was employed to remove chloride from solution and the reaction time is reduced. A less than the stoichiometric amount of Ag^+ required to remove two chlorides, one ionic and one coordinated, from *trans*-$[RuCl_2(cyclam)]Cl$ solution was used since larger amounts would yield mixtures of species due to labilization of the second coordinated chloride. Notably, even though Ru(II) generally has a preference for unsaturated ligands, excess ligand was needed to form *trans*-[RuCl(cyclam)L]$^+$, because L appeared to be somewhat labile, probably for steric reasons.

Table I. Electronic Spectral Data for *trans*-[RuCl(cyclam)(py-x)]$^+$ and Related Complexes in Aqueous Solution[a]

	MLCT		IL		LF	
complexes	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
trans-[RuCl(cyclam)(4-pic)]$^+$	390	4000	244	3300	340[b]	350
trans-[RuCl(cyclam)(py)]$^+$	405	4100	245	3500	326[b]	450
trans-[RuCl(cyclam)(isn)]$^+$	480	6800	255	5000	345	600
trans-[RuCl(cyclam)(4-acpy)]$^+$	520	5300	270	2100	350	600
			220	4500		
$[Ru(NH_3)_5(py)]^{2+}$ [c]	407	7750	244	4570		
$[Ru(NH_3)_5(4\text{-pic})]^{2+}$ [c]	397	7750	244	4570		
$[Ru(NH_3)_5(isn)]^{2+}$ [d]	479	11480	260	4570		
$[Ru(NH_3)_5(4\text{-acpy})]^{2+}$ [e]	523	9330	271	3390		
			223	5750		

[a] λ_{max} in nm; ϵ in M^{-1} cm^{-1}. [b] By Gaussian analysis. [c] Reference 18. [d] Reference 19. [e] Reference 20.

The IR spectra of the *trans*-[RuCl(cyclam)L]$(BF_4)\cdot H_2O$ complexes were close to the superposition of the ligand L, cyclam, and BF_4^- spectra. The absence of any band in the 2800–1700-cm^{-1} range indicates the absence in this case of oxidation of cyclam to the imine analogs.[15]

The stereoretentive behavior of ruthenium(II) ammines[16] and Ru(macrocycle)[6] substitution reactions was assumed to hold for the present cyclam complexes, and a trans geometry was assigned for the complexes *trans*-[RuCl(cyclam)L]$^+$ obtained in this work.[17] In all cases it was assumed that the ligand L does not labilize the remaining Cl^- ligand. Indeed, the aquation of chloride from *trans*-[RuCl(cyclam)(HpyCN)]$^{2+}$ (HpyCN = 4-cyanopyridinium, nitrile bound) has been shown to have a half-life of 71 h at 25 °C.[6]

Spectra in Aqueous Solutions. The electronic spectra of *trans*-[RuCl(cyclam)L]$^+$ complexes and those of related compounds are summarized in Table I. Figure 1 shows the UV-vis absorption spectra of *trans*-[RuCl(cyclam)(isn)]$^+$ and *trans*-[RuCl(cyclam)(py)]$^+$ in aqueous solutions.

The strong absorption bands of *trans*-[RuCl(cyclam)L]$^+$ (L = 4-pic, py, isn, or 4-acpy) in the UV region are similar in intensity and position to bands observed in the spectra of the free ligands and can be assigned as intraligand (IL) $\pi-\pi^*$ in character.

The electronic spectra of these complexes are dominated in the visible region by one intense absorption band (see ϵ in Table I), which is assigned as metal-to-ligand charge-transfer (MLCT) transition in analogy to spectral assignments of similar absorptions in the analogous $[Ru(NH_3)_5L]^{2+}$,[18-20] due to its high extinction coefficient and solvent dependent energy (see below). The MLCT

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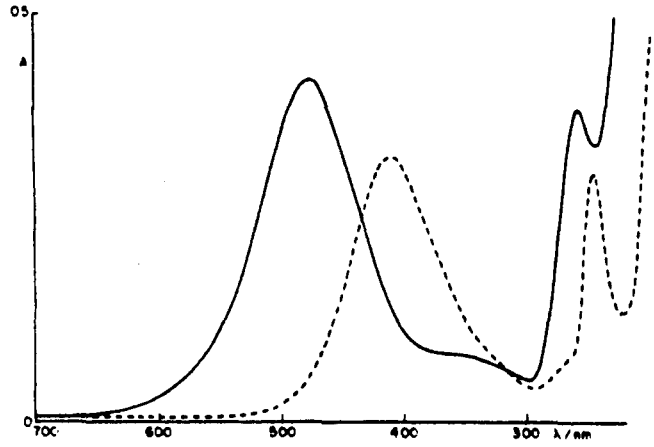

Figure 1. Electronic spectra of *trans*-[RuCl(cyclam)L]$^+$ aqueous solutions: (—) L = isn; (--) L = py.

band energy of each *trans*-[RuCl(cyclam)L]$^+$ complex is similar to that of the respective pentaammine analog $[Ru(NH_3)_5L]^{2+}$ (Table I). Notably, the absorbances of the MLCT bands of these *trans*-[RuCl(cyclam)L]$^+$ solutions decrease with time, probably because the L ligands responsible for the MLCT absorption appeared to be labile. Therefore, the reported extinction coefficients should be considered as lower limit values of the actual ones.

For each complex there is a third band with an energy intermediate to those of the IL and MLCT bands. This band was assigned as a ligand field (LF) band (vide infra). However, in the py and 4-pic complexes spectra it is enveloped by the MLCT band, and the energies of the LF bands in these two complexes were obtained by simple Gaussian analysis of the MLCT band.

The assignment of the LF band was based on the following reasoning: (a) These complexes are related to $[Ru(NH_3)_5L]^{2+}$ analogs that show only one MLCT band in their electronic spectra.[21] For $[Ru(NH_3)_5L]^{2+}$, the simple molecular orbital model[22] used to explain the MLCT absorption of $[Ru(NH_3)_5L]^{2+}$ predicts only one transition in the visible region. A similar analysis for the present complexes also predicts only one MLCT in the visible region. (b) While there is a solvent dependence for the energy of MLCT, this band is much less solvent sensitive, as expected for LF transitions.[23] (c) The spectra of the complexes in different solvents show a slow decrease in absorbance of the MLCT band up to its complete bleaching, as the result of ligand aquation (vide infra). In contrast, there is only a small change in the LF band, and after release of L there is still a relatively low intensity band at ~330 nm, characteristic of the expected LF band of *trans*-[RuCl(cyclam)S]$^+$. (S = solvent.)

The relatively high extinction coefficients of these LF bands may be due to a high distortion from octahedral symmetry. Enhanced LF bands have been observed in other Ru(II) complexes, e.g., $[Ru(CN)_5L]$ (L = H_2O or NH_3) complexes,[24] which have LF bands with ϵ 1 × 10^3 M^{-1} cm^{-1}.

Spectra in Nonaqueous Solvents. Table II shows the spectral data for *trans*-[RuCl(cyclam)L]$^+$ (L = 4-pic, py, isn, or 4-acpy) in acetone (AC), acetonitrile (ACN), *N*,*N*-dimethylformamide (DMF), 1,2-dichloroethane (DCE), nitromethane (NM), and dimethyl sulfoxide (DMSO). The energy of the MLCT band of each *trans*-[RuCl(cyclam)L]$^+$ is solvent dependent as can be seen in Table II. In Figure 2 the energies of the MLCT band of *trans*-[RuCl(cyclam)(py)]$^+$ are plotted against Guttman's donor number (DN) of the solvent.

Table II. MLCT λ_{max} ($\bar{\nu}_{max}$) of *trans*-[RuCl(cyclam)L]$^+$ in Aprotic Solvents[a]

solvents	DN	4-pic	py	isn	4-acpy
DCE	0.0	425 (23.53)	436 (22.93)	485 (20.62)	540 (18.52)
NM	2.7	420 (23.81)	440 (22.73)	500 (20.00)	540 (18.52)
AC	14.1	420 (23.81)	444 (22.52)	495 (20.20)	549 (18.21)
ACN	17.0	429 (23.31)	446 (22.42)	495 (20.20)	552 (18.12)
DMF	26.6	429 (23.31)	450 (22.22)	502 (19.90)	561 (17.82)
DMSO	29.8	431 (23.20)	452 (22.12)	507 (19.72)	574 (17.42)

[a] λ_{max} in nm; $\bar{\nu}_{max}$ in 10^{-3} cm^{-1}.

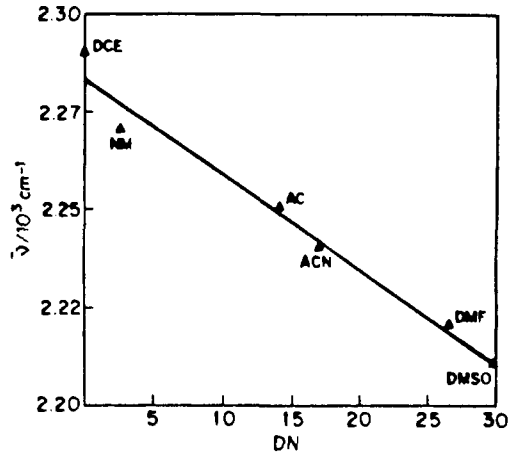

Figure 2. Energies of MLCT λ_{max} of *trans*-[RuCl(cyclam)(py)]$^+$ as a function of the DN of the solvent.

The model developed by Meyer et al,[25] based on the observations made on the solvent effects on several ruthenium amine complexes, will be used in the discussion of the solvatochromic behavior. The origin of the solvent effect was described by a microscopic interaction between the solvent donor and the nitrogen-bound hydrogen atoms of the ammines. This model[25] was based on observations that (a) plots of E_{MLCT} vs DN are linear for ruthenium(II) ammine complexes and the slopes for these cationic Ru(II) complexes are negative, (b) plots of $\Delta E_{1/2}$ vs DN for $[Ru^{II}(NH_3)_5(MCP)]^{3+}$ (MCP = *N*-methyl-4-cyanopyrydinium) are also linear and (c) plots of E_{MLCT} vs $\Delta E_{1/2}$ are linear.

For the cyclam complexes described here the plot of E_{MLCT} vs DN (Figure 2) shows a straight line with a negative slope, as expected for MLCT transitions of cationic complexes. However, the slope is small, falling in the range –0.02 to –0.03. According to the model,[25] the magnitude of the slope is roughly proportional to the number of coordinated ammines. For cyclam complexes, there is only one hydrogen atom bound to each of the four macrocycle nitrogens, instead of three as is the case with NH_3. In addition, the probable higher pK_as of the nitrogen-bound hydrogens of the cyclam should influence the interaction with the donor solvent. The slope of –0.025 for the cyclam complexes falls between the slopes for complexes that have one NH_3 and two NH_3, but closer to those that have one NH_3. The solvatochromism observed indicates that some N–H's are available to interact with solvent but it is impossible to determine the exact number, especially as several conformational isomers are possible.

Cyclic Voltammetry. Table III shows the formal Ru^{III}/Ru^{II} reduction potentials, in aqueous solutions, of *trans*-[RuCl(cyclam)L]$^+$ (L = 4-pic, py, isn, or 4-acpy) and $[Ru(NH_3)_5py]^{2+}$. The cyclic voltammograms of these species display, in all cases, one anodic peak with the corresponding cathodic peak in the region scanned (–700 to +700 mV vs SHE). Cyclic voltammetry (CV) values of each complexes fitted most of the criteria employed for a reversible couple.[26] However, a more thorough electrochemical study is needed, since there is a small deviation

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Table III. Formal Reduction Potentials of *trans*-[RuCl(cyclam)L]$^+$ in Aqueous Solution

ligand	$E_{f_{obs}}$/V vs NHE	ligand	$E_{f_{obs}}$/V vs NHE
4-pic[a]	0.280	bzn[b]	0.505
py[a]	0.320	4-CNpyH$^+$ [b]	0.710
isn[a]	0.400	water[b]	−0.015
4-acpy[a]	0.420		

[a] This work. [b] Reference 15.

of peak ratios from unity. The formal reduction potentials of *trans*-[RuCl(cyclam)L]$^+$ range from 280 mV vs SHE for L = 4-pic to 420 mV vs SHE for L = 4-acpy, showing slightly higher values than the corresponding pentaammines,[18-20] which range from about 305 mV vs SHE for $[Ru(NH_3)_5(py)]^{2+}$ to 392 mV vs SHE for $[Ru(NH_3)_5(4\text{-acpy})]^{2+}$. The similarity of the E_f values for analogous $[Ru(NH_3)_5L]^{2+}$ and *trans*-[RuCl(cyclam)L]$^+$ would suggest that back-bonding may be similar in these two cases for a specific L.

Lability of the L Ligands. Besides the solvatochromic behavior, there is a slow decrease in the absorbance of the MLCT bands of *trans*-[RuCl(cyclam)L]$^+$ (L = 4-pic, py, isn, or 4-acpy), in NM, AC, ACN, DMF, DMSO, or H_2O. Addition of excess ligand L, or a different L′, to the solution leads to partial regeneration of the MLCT band of the starting complex or of *trans*-[RuCl(cyclam)L′]$^+$. Oxidation with some drops of 30% H_2O_2 leads to complete bleaching of the MLCT band, and addition of excess ligand L to this last solution does not regenerate the MLCT band. These results indicate that L is being labilized. This is a somewhat striking feature, since Ru(II) shows in general a preference for unsaturated nitrogen heterocyclic ligands. Given that $[Ru^{II}(NH_3)_5L]$, *trans*-$[Ru^{II}(NH_3)_4LL']$, *cis*-$[Ru^{II}(NH_3)_4L_2]$, and *cis*-$[Ru(NH_3)_4(isn)L]$ are thermally substitution inert, the lability of L in the cyclam complex must result from the presence of the macrocycle. It is noteworthy that, despite the similar back-bonding between Ru(II) and L apparent for *trans*-[RuCl(cyclam)L]$^+$ and corresponding pentaammine complexes (according to spectral and cyclic voltammetric data), L is labile in the cyclam complexes. In addition, this behavior is opposite to that observed in the analogous *trans*-$[RuCl(NH_3)_4L]^+$, where the chloride is labile and L is inert.[13] The kinetics of L labilization, and the reasons for such a behavior (a steric repulsion argument seems logical) are currently under investigation in our laboratory.

Acknowledgment. This work was supported by grants from CNPq and FAPESP. E.T. acknowledges a research fellowship from the CNPq. R.S.S. acknowledges a fellowship from CAPES. We thank Dr. G. Chiericato, Jr., for the use of his CV apparatus. We thank Dr. H. Taube, S. S. Isied, P. C. Ford, A. B. P. Lever, and J. F. Endicott for helpful discussions and suggestions.