274 *Inorg. Chem.* **1997,** *36,* 274−277

# Articles

## Photosubstitution Reactions of *trans*-Chloro(azine)(1,4,8,11-tetraazacyclotetradecane)ruthenium(II) Complexes[1]

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Visible range photolyses of *trans*-[RuCl(cyclam)L]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; L = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn), or 4-acetylpyridine (4-acpy)) were studied in acidic aqueous solution, and lead to exclusive azine photoaquation. The py and 4-pic complexes have a relatively high, and irradiation wavelength independent, quantum yield ($0.020 < \Phi < 0.025$), while the isn and 4-acpy complexes have lower quantum yields ($\Phi_{\mathrm{isn}} \approx 0.006$; $\Phi_{4-\mathrm{acpy}} < 0.001$). The relative Φs show patterns consistent with the excited-state tuning model proposed to explain the photochemistry of other related ruthenium(II) ammines. The results indicate that the excited-state precursor of the photochemistry should be a LF* and has a strong contribution from the $d_{z^2}$ orbital, which should lie lower in energy than the $d_{x^2-y^2}$. Accordingly, considering an approximate $C_{4v}$ symmetry for the complexes, this LF* should be a $^3$E. The results also suggest that the intramolecular hydrogen bonds to the chloride that occur in the ground state may be still operative in the excited state in order to prevent the photoaquation of chloride.

### Introduction

The macrocyclic complexes *trans*-[RuCl(cyclam)L]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; L = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn), or 4-acetylpyridine (4-acpy)) show some similarities and some striking differences from other analogous ruthenium(II) ammines, especially the pentaammines.[2,3] The UV−vis spectra of aqueous solutions of these macrocyclic complexes display one visible range metal-to-ligand charge-transfer (MLCT) absorption band, and UV range intraligand (IL) bands, as their pentaammine analogs.[2] However, between these MLCT and IL bands there is, in the isn and 4-acpy complexes with cyclam, a ligand-field (LF) band of lower intensity, which is not observed in the corresponding pentaammines.[2] The spectra of the py and 4-pic complexes do not display this intermediate band which is possibly masked by the much more intense MLCT band.[2] The MLCT energies and Ru$^{\mathrm{III}}$/Ru$^{\mathrm{II}}$ reduction potentials of these macrocyclic complexes are similar to those of the corresponding [Ru(NH$_3$)$_5$L]$^{2+}$ complexes with the same azine ligands.[2] In contrast to other Ru(II) ammine complexes, the chloride is substitution inert, while the azine is somewhat labile in these macrocyclic complexes.[2]

Photosubstitution reactions of low-spin d$^6$ complexes of the second and third row transition-metal elements follow the "tuning" model of Ford.[4,5] According to this model, initially proposed to explain the photoreaction patterns of [Ru(NH$_3$)$_5$L]$^{2+}$ complexes, the photosubstitution reactions originate from LF excited states (LF*). Complexes with MLCT* and LF* as lowest energy excited states (LEES) are photosubstitution reactive if the LEES is LF* in character and unreactive if the LEES is MLCT*. Changes in the L ligand and/or solvent can alter the energy order of the excited states, and, thus, alter the reactivity.[4,5] The similar systems *cis*-[Ru(NH$_3$)$_4$(isn)L]$^{2+}$,[6] *cis*-[Ru(NH$_3$)$_4$L$_2$]$^{2+}$,[6] and *trans*-[Ru(NH$_3$)$_4$LL′]$^{2+}$ [7] follow the tuning model and display photoaquation of L, L′, isn, and NH$_3$, implying labilization of ligands along the *x*, *y*, and *z* axes. The substitution of four ammines in *trans*-[Ru(NH$_3$)$_4$LL′]$^{2+}$ by cyclam would restrict the photosubstitution to the *z* axis.

Examination of the spectral data of low-spin d$^6$ ammine and cyclam complexes without back-bonding, namely Co(III)[8] and Rh(III),[9,10] indicates that the LF strength of cyclam is similar

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to that of four ammines. Irradiation of the similar complexes *trans*-[Rh(cyclam)X$_2$]$^+$ (X = Cl$^-$, or CN$^-$) with light corresponding to their LF* leads to interesting behavior.[11] Phosphorescence was reported to occur for the cyanide complex, with the absence of photosubstitution,[11a] whereas the complex with chloride undergoes photoaquation of the anion without emission.[11b] This was explained in terms of the LF* electronic configuration. Considering an approximate $D_{4h}$ symmetry, the lowest energy LF* would be a $^3A_{2g}$ excited state for the cyanide complex, whereas for the chloride it would be a $^3E_g$. Accordingly, for cyanide, the $d_{z^2}$ orbital is higher in energy than the $d_{x^2-y^2}$ and thus the LEES would involve population of the $d_{x^2-y^2}$ orbital, and then, in this case, it was expected that inhibition of the photosubstitution of the cyclic ligand would lead to the enhancement of the phosphorescence.[11a] On the other hand, for the chloro complex, the LEES has $d_{z^2}$ character, leading to photosubstitution of the anion.[11a] More recently, the photochemistry and photoluminescence of these and other cis and trans Rh(III) complexes with related macrocycles were investigated in more detail;[12] the energy order of the LF excited states in the *trans*-dicyano and *trans*-dichloro complexes agrees with that previously reported, and the photophysical properties of the luminescent complexes were studied in more depth.[12] Thus, in the somewhat similar *trans*-[RuCl(cyclam)L]$^+$ complexes, the photochemical behavior may also give indication of the electronic configuration of the LF* precursor of the photochemistry. In addition, understanding of the properties of macrocyclic trans complexes, such as those reported here, can help to design building blocks to synthesize linear oligomers and polymers for specific purposes in supramolecular chemistry and photochemistry.[13]

In this paper, the photosubstitution reactions of the abovementioned *trans*-[RuCl(cyclam)L]$^+$ complexes in aqueous solutions are described.

## Experimental Section

**Chemicals and Reagents.** "RuCl$_3$·$n$H$_2$O" (Aldrich or Strem) and cyclam (Aldrich) were used for the Ru−cyclam complex synthesis. Cyclam (Aldrich) was recrystallized from chlorobenzene when needed. Pyridine (py) (Aldrich), 4-picoline (4-pic) (Aldrich), and 4-acetylpyridine (4-acpy) (Aldrich) were distilled under reduced pressure before use. Isonicotinamide (isn) (Aldrich) was recrystallized from hot water, after treatment with activated charcoal, before use. NaBF$_4$ was recrystallized from hot water. Methanol, ethanol, and acetone were purified before use.[14] Ether was purified as described.[2] Doubly distilled water was used throughout this work. All other materials were reagent grade and were used without further purification.

**Ruthenium Complexes Syntheses.** *trans*-[RuCl$_2$(cyclam)]Cl and *trans*-[RuCl(cyclam)L]BF$_4$ complexes (L= py, 4-pic, 4-acpy, or isn) were synthesized according to literature procedures.[2]

**Spectra.** Electronic spectra were recorded at room temperature with a HP8452A Hewlett-Packard or a 634S Varian recording spectrophotometer using quartz cells.

**Photolysis Procedures.** These are quite similar to previously described procedures.[4,7] Irradiations at 365, 404, 436, 480, and 520 nm were carried out by using an Osram 150 W/l Xenon lamp in an Oriel Model 8500 universal arc lamp source with an Oriel interference filter for monochromatization (band-pass ~ 10 nm), an infrared filter, and a thermostated cell holder. Photolyses were carried out in aqueous solutions of ~$10^{-4}$ M Ru(II) complex concentration at pH 3.5−4.0 (with CF$_3$COOH). Ferrioxalate actinometry was used for light intensity measurements at 365 and 404 nm and Reinecke ion actinometry was used at 436, 480, and 520 nm. Solutions for photolyses and dark reactions were prepared and deaerated with purified argon in a Zwickel flask[6] and transferred to the 2.0 cm path length quartz cells using an all glass apparatus. During photolysis, the solution was stirred by a small magnetic bar in the cell. All photolyses were carried out at 25.0 ± 0.1 °C. For spectrophotometric quantum yield determinations, the reactions under photolysis were monitored periodically by recording their UV−vis spectra. Analogous reaction mixtures allowed to react in the dark, under the same conditions of the photolyzed solution, displayed either no observable or just negligible spectral changes, which were taken into account for quantum yields calculations. Inner filter effects were compensated and secondary photolysis was minimized by limiting the extent of the reaction up to 10% and by extrapolating stepwise quantum yields to 0% reaction.[15] A PM600 Analion digital pHmeter was employed in the determinations of the pH changes. Analion Cl-651-IS562 chloride-selective and Ag/AgCl electrodes were employed to verify and evaluate [Cl$^-$] changes. The chloride electrode was calibrated before each experiment against sodium chloride solutions of known concentrations.

**Table 1.** Electronic Spectra and Quantum Yields for the Photoaquation Reactions of *trans*-[RuCl(cyclam)(L)]$^+$ Complexes in Aqueous Solution[a]

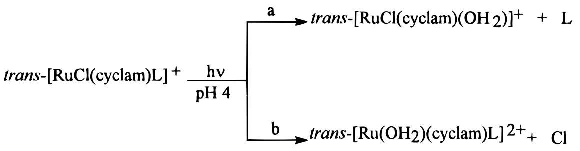
| L | $\lambda_{max}$/nm ($\epsilon$)[b] | $\lambda_{irr}$/nm | $\Phi_L/10^{-3}$ [c] |
|---|---|---|---|
| 4-pic | 340 (350) (LF)[d] | 365 | 25 ± 1 |
| | 390 (4000)[d] | 404 | 21 ± 3 |
| | | 436 | 20 ± 2 |
| py | 326 (450) (LF)[d] | 365 | 20 ± 3 |
| | 405 (4100)[d] | 404 | 16 ± 1 |
| | | 436 | 21 ± 3 |
| | | 480 | 18 ± 2 |
| isn | 345 (600) (LF)[d] | 365 | 6 ± 0.6 |
| | 480 (6800)[d] | 480 | 5 ± 0.5 |
| 4-acpy | 350 (600) (LF)[d] | 365 | < 1 |
| | 520 (5300)[d] | 520 | < 1 |

[a] [Ru complex] ≅ $10^{-4}$ M; pH ≅ 3.5−4.0 (adjusted with CF$_3$COOH); temperature = 25.0 ± 0.5 C; cell pathlengths: 1.0 or 2.0 cm. [b] MLCT bands, except where noted. [c] Average of at least three independent determinations. [d] Reference 2.

## Results and Discussion

Table 1 summarizes photosubstitution quantum yields and some relevant electronic spectral properties of the *trans*-[RuCl(cyclam)L]$^+$ complexes studied in this work.

Irradiation of deaerated acidic (pH ≈ 4.0) aqueous solutions of *trans*-[RuCl(cyclam)(4-pic)]$^+$ and of *trans*-[RuCl(cyclam)(py)]$^+$ at the irradiation wavelengths listed in Table 1, which are in the range of the MLCT band energy of each complex, leads to a decrease of the absorbance of the MLCT band of the complex. This observation is consistent with aquation of the L ligand (eq 1a), responsible for the MLCT band.



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In addition to the decrease of the MLCT absorption, pH changes are observed which are consistent with the basicity of

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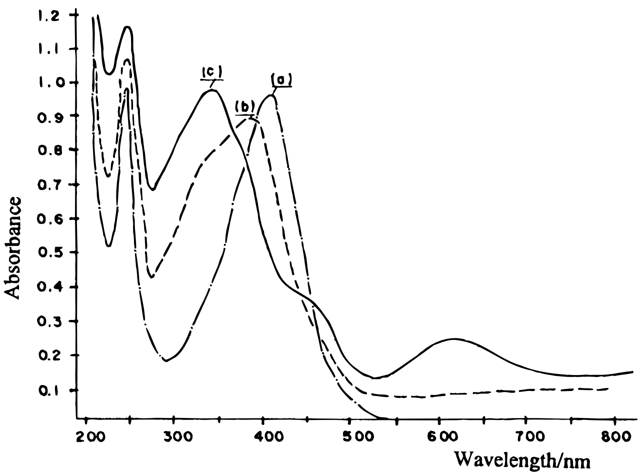

**Figure 1.** Electronic spectra of a $1.2 \times 10^{-4}$ M aqueous solutions of *trans*-$[RuCl(cyclam)(py)]^+$ at pH 4.0, adjusted with $CF_3COOH$, temperature 25 ± 0.5 C, and 1.0 cm cell pathlength: (a) deaerated solution before photolysis; (b) blank nondeaerated solution (recorded after time spent for photolysis); (c) nondeaerated solution after photolysis.

the released azines, which can be protonated at the pH of the irradiated solution. As a matter of fact, the azines are the only ligands released and the only source for $H^+$ uptake (vide infra), allowing their determination by pH changes. These pH changes were determined, taking into account the p$K_a$s of the azines, and used to check quantum yields, which match those calculated by spectrophotometry. Under these conditions, the limit of the photoaquation quantum yields of the amines is $2 \times 10^{-3}$, as calculated.

Aquation of chloride can not be followed spectrophotometrically in these cases. Although the MLCT spectrum of the possible product, *trans*-$[Ru^{II}(OH_2)(cyclam)L]^+$, is not known, it is not expected to be very different from that of the parent compound, and thus, absorbance changes would not be a reliable measure of the photolysis reaction, as far as chloride aquation is concerned. However, examination of the irradiated and blank solutions with the chloride selective electrode gave no indication of chloride ion in solution, indicating that chloride is not being labilized, as far as the limit of detection of the electrode. The calculated upper limit for the chloride photoaquation quantum yield is $2 \times 10^{-3}$.

Oxidation of the complex to its Ru(III) analog would also lead to bleaching of the MLCT absorption. Nondeaerated solutions of these cyclam complexes display some changes in their spectra after some time in the dark. Irradiation of freshly prepared nondeaerated solutions of these complexes leads to marked changes in spectra, with appearance of several bands in the UV and visible ranges, as illustrated for the *trans*-$[RuCl(cyclam)(py)]^+$ complex (Figure 1), where bands in the neighborhood of 345 nm, with shoulders at 315 and 370 nm occur.

Bands due to Ru(III)−Cl ligand to metal charge transfer (LMCT) transitions occur in the 315−360 nm range for complexes such[8,16] as $[RuCl(NH_3)_5]^{2+}$, *cis*-$[RuCl_2(NH_3)_4]^+$, *trans*-$[RuCl_2(NH_3)_4]^+$, and *trans*-$[RuCl_2(cyclam)]^+$. Thus, the absence of such bands during the photolysis of the deaerated solutions rules out the occurrence of ruthenium photooxidation.

Thus, taking in consideration the absence of chloride aquation or ruthenium photooxidation, the decrease of absorbance of the MLCT band upon irradiation can be assigned solely to the photoaquation of L, according to eq 1a.

The spectral properties of the photoproduct *trans*-$[RuCl(cyclam)(OH_2)]^+$ are not known. However, it is expected to have LF bands at low energy, probably lying around 400 nm. Considering that the *trans*-$[RuCl(cyclam)L]^+$ complexes studied show spectral features similar to those of their pentaammine analogs,[2] and that the lowest energy LF band of $[Ru(NH_3)_5(OH_2)]^{2+}$ ($\lambda_{max} = 415$ nm; $\epsilon = 40$ mol$^{-1}$ L cm$^{-1}$)[17] is similar[18] to that of $[Ru(NH_3)_6]^{2+}$ ($\lambda_{max} = 390$ nm; $\epsilon = 40$ mol$^{-1}$ L cm$^{-1}$),[17,19] it is reasonable to assume a spectrum for *trans*-$[RuCl(cyclam)(OH_2)]^+$ similar to those of the aquapentaammine and hexaaammine complexes and then neglect its absorbance at this wavelength when compared with the much more intense MLCT band of the *trans*-$[RuCl(cyclam)L]^+$ complexes ($\epsilon > 4000$ mol$^{-1}$ L cm$^{-1}$). With these assumptions, absorbance changes at this wavelength were used to calculate quantum yields, which match those calculated from pH changes.

The isn and 4-acpy complexes were irradiated with light of 365 or 480 nm and 365 or 520 nm, respectively (Table 1), and the photosubstitution reactions were monitored at 480 or 520 nm, the MLCT band maxima of these complexes, respectively. Observations similar to those described above were also noticed for these complexes. The monitoring wavelengths (MLCT $\lambda_{max}$; Table 1) in these last complexes are located far from the expected bands for *trans*-$[RuCl(cyclam)(OH_2)]^+$, and the spectroscopic quantum yields are then more accurate.

Examination of Table 1 indicates that the 4-pic and py complexes have photosubstitution quantum yields higher than those of the isn and 4-acpy complexes. In addition, the 4-pic and py complexes have irradiation wavelength independent quantum yields in the MLCT energy ranges studied. The 4-acpy complex shows much lower quantum yields whether irradiated with 365 nm, close to the LF band energy, or with 520 nm, close to the MLCT band energy. The isn complex displays intermediate quantum yields at either 365 nm or 480 nm.

This photosubstitution pattern allows the classification of *trans*-$[RuCl(cyclam)(py)]^+$ and *trans*-$[RuCl(cyclam)(4\text{-pic})]^+$ as photosubstitution "reactive" complexes, and *trans*-$[RuCl(cyclam)(4\text{-acpy})]^+$ as "unreactive". This behavior follows closely the photochemical pattern of the analogous ruthenium(II) pentaammines, i.e., there appears to be a crossover from a reactive to an unreactive complex, as the MLCT bands move to the red with more electron-withdrawing substituents in the pyridine ring; the crossover for the pentaammines is at ≅ 460 nm, and $[Ru(NH_3)_5(isn)]^{2+}$ is classified as "unreactive".[4] However, the *trans*-$[RuCl(cyclam)(isn)]^+$ complex shows a sort of intermediate behavior, although the quantum yields are clearly lower than those of the 4-pic and py complexes. This "intermediate" behavior may simply be indicating that the crossover in the *trans*-$[RuCl(cyclam)L]^+$ is at lower energy than that of the analogous pentaammines and that the cyclam complexes may have a LEES at lower energies, when compared with the analogous pentaammines. Therefore, the photoreactions of the present ruthenium(II) cyclam complexes can be explained by the tuning model.[4,5]

According to this model, the observed photosubstitution should come from a LF* state. Initial excitation to a $^1$MLCT* state is followed by relatively efficient intersystem crossing/internal conversion to the lower energy $^3$LF* in the reactive complexes, i.e., py and 4-pic complexes. For isn and 4-acpy complexes, the LEES should be of MLCT character, similar to analogous pentaammines.[2,4,5,20] The isn and 4-acpy cyclam

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complexes, although having as LEES a $^3$MLCT*, which is not expected to undergo labilization, show some photoreactivity, and the observed lower quantum yield values may reflect some higher energy LF* photoreactivity competitive with decay to the lowest energy $^3$MLCT*.

An interesting comparison can be made between the photoreactivity of the py and 4-pic complexes and the photochemical/photophysical behavior of *trans*-[Rh(cyclam)X$_2$]$^+$ (X = Cl$^-$, or CN$^-$). In these rhodium complexes, the LEES are LF in character. In the photosubstitution reactive chloro complex, the d$_{z^2}$ orbital is lower in energy than the d$_{x^2-y^2}$ orbital, while in the cyano complex their order is inverted.[11a,12] A similar, but not identical situation occurs for the *trans*-[RuCl(cyclam)L]$^+$ complexes here described.

The d$_\pi$ orbitals in the present cyclam complexes are split not only by the symmetry of the complex, but also by the different ligand field strength of the ligands. Considering Cl−Ru−L lying in the $z$ axis, this would be the weaker LF axis, and the d$_{z^2}$ orbital would be lower in energy relative to the d$_{x^2-y^2}$ orbital. This agrees with the photoreactivity observed. So, the reactivity should come from a lower energy $^3$LF* state which should have contribution from the d$_{z^2}$ orbital. Considering an approximate $C_{4v}$ symmetry for the *trans*-[RuCl(cyclam)L]$^+$ complexes, the LEES should be a $^3$E, involving depopulation of the d$_\pi$ orbitals d$_{xz}$ and d$_{yz}$ and population of the $\sigma$ antibonding d$_{z^2}$ orbital. Thus, labilization of py-X may come not only from d$_{z^2}$ orbital population, but also possibly from depopulation of d$_\pi$ orbitals involved in back-bonding, as happens for the good $\pi$-acceptor and poor $\sigma$-donor CO in *trans*-[Ru(NH$_3$)$_4$(P(OEt)$_3$)(CO)]$^{2+}$ (Et = ethyl), which photolabilizes CO, but not P(OEt)$_3$.[21]

On the other hand, chloride would be expected to be labile. However, the X-ray results for *trans*-[RuCl(cyclam)(4-acpy)](BF$_4$) indicate that the Ru(II)-bonded chloride is hydrogen bonded to two cyclam nitrogen hydrogens,[3] which helped to explain the thermal inertness of the chloride toward substitution reactions.[2,3] These hydrogen−chloride bonds are still present in dmso and acetone solutions, as shown by NMR results.[3] Considering that a cooperative effect between a $\pi$-donor chloride trans to a $\pi$-acceptor ligand (L) was claimed to explain the chloride inertness on other Ru(II) systems, the authors also claimed a similar cooperative effect would be occurring in *trans*-[RuCl(cyclam)(4-acpy)](BF$_4$), contributing, with the hydrogen bonds, to the chloride inertness.[3] In addition, taking into account that the LEES is $^3$E, the chloride ligand in these *trans*-[RuCl(cyclam)L]$^+$ complexes would also be expected to be photolabilized (in other Ru(II)−ammines, specifically *cis*-[Ru(NH$_3$)$_4$(isn)L]$^{2+}$),[6] while the ligand preferentially photolabilized is the one with lower back-bonding ability. Since Cl$^-$ is a $\pi$-donor ligand, then *trans*-[RuCl(cyclam)L]$^+$ would be expected to show Cl$^-$ photolabilization with higher $\phi$ than py−X. Furthermore, since the LEES is $^3$E, which involves depopulation of d$_{xz}$ and d$_{yz}$ orbitals, involved in $\pi$ bonding, and population of the d$_{z^2}$ orbital, which is $\sigma$ antibonding, then ligands in the $z$ axis (Cl−Ru−L) are expected to be labilized. Thus, the hydrogen bonds, present in the ground state, may also be present in the $^3$E responsible for the observed photochemistry, preventing the labilization of the chloride.

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