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Complexes of Ruthenium(III) and Ruthenium(II) with 1,4,8,11-Tetraazacyclotetradecane (Cyclam): Cis and Trans Isomers

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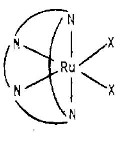
The reaction of $K_2[RuCl_5OH_2]$ with cyclam results in the formation of *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$. Separation of the two isomers was achieved by ion-exchange and gel-filtration chromatography. The two isomers were characterized by elemental analysis, UV spectra (for cis, λ_{max} 363 nm (280 M^{-1} cm^{-1}) and a shoulder at 300 nm (530 M^{-1} cm^{-1}); for trans, λ_{max} 358 nm (2.6×10^3 M^{-1} cm^{-1}) and 313 nm (1.2×10^3 M^{-1} cm^{-1})), IR spectra in the region 800–1000 cm^{-1}, and cyclic voltammetry (for cis, $\epsilon_{1/2} = -0.23$ V; for trans, $\epsilon_{1/2} = -0.19$ V vs. NHE). Reduction of the *cis*- and *trans*-dichlororuthenium(III) cyclam complexes with zinc amalgam results in the formation of the corresponding ruthenium(II) cyclam species. Reaction of the ruthenium(II) cyclam species with excess isonicotinamide (isn) produced the corresponding *cis*- and *trans*-$[Ru(cyclam)(isn)_2]^{2+}$ (for cis, λ_{max} 363 nm (4.5×10^3 M^{-1} cm^{-1}) and 465 nm (3.8×10^3 M^{-1} cm^{-1}); for trans, λ_{max} 485 nm (4.9×10^3 M^{-1} cm^{-1})). Isomeric purity of the ruthenium cyclam complexes can be determined from the UV spectra if small amounts of *trans*-$[Ru(cyclam)Cl_2]Cl$ are found in the *cis*-$[Ru(cyclam)Cl_2]Cl$. When small amounts of *cis*-$Ru(cyclam)Cl_2]Cl$ are found in the *trans*-$[Ru(cyclam)Cl_2]Cl$, isomeric purity can be determined by reduction to the corresponding ruthenium(II) species in the presence of 2,2′-bipyridine. The ligand 2,2′-bipyridine (bpy) can chelate to the cis ruthenium(II) cyclam complex, resulting in *cis*-$[Ru(cyclam)(bpy)]^{2+}$ (λ_{max} 488 nm (3.2×10^3 M^{-1} cm^{-1})), while the reaction of 2,2′-bipyridine to the trans ruthenium(II) cyclam isomer can result only in monodentate coordination of 2,2′-bipyridine to the trans isomer (λ_{max} 365 nm).

Macrocyclic complexes of ruthenium(III) and ruthenium(II), especially the saturated nitrogen donor macrocycles, are of interest because they provide one of the few instances where a direct comparison between the reactivity of the metal ion center can be made between simple monodentate ammine complexes[1-3] and the more elaborate macrocyclic complexes. Although this comparison can also be made for other kinetically inert complexes like Co(III) and Cr(III), studies on the ruthenium complexes provide opportunities for a more complete study of both the ruthenium(II) and ruthenium(III) oxidation states. This comparison will provide information on the effect of the macrocyclic structure on a soft (Ru(II)), as well as a hard (Ru(III)), metal ion center.

Extensive studies on the substitution, aquation, and base hydrolysis reactions of macrocyclic complexes with the 3d transition metal series have been reported.[4-8] In these studies macrocyclic ligands were found to provide a strong field ligand, to stabilize high oxidation states, and to react with high oxidation states of metal ions by oxidative dehydrogenation.[4-8] An extensive study of the effects of macrocyclic ligands on the spectrochemical properties of high-spin Ni(II) macrocyclic complexes, including ring-size effects, effects of unsaturation, and effects of methyl substitution have been reported.[6] Similar studies using 4d and 5d transition-metal complexes have been very limited.[9,10]

We are currently interested in using ruthenium macrocyclic complexes in place of similar cis and trans ruthenium tetraammines for our studies on electron-transfer reactions of Ru(II) and Ru(III).[11,12] The current methods for synthesizing and purifying ruthenium macrocycles are sparse, and in some cases mixtures of products are obtained.[10] We have therefore investigated the detailed synthesis, separation, and characterization of the *cis*- and *trans*-dichlororuthenium(III) complexes with 1,4,8,11-tetraazacyclotetradecane (cyclam), I and II. A method to differentiate between *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ is provided. Reduction of the *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ complexes to the corresponding ruthenium(II) species and some of the reactions of these ruthenium(II) cyclam complexes with pyridine heterocycles are also explored.



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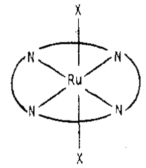

II

Experimental Section

Reagents. The 1,4,8,11-tetraazacyclotetradecane (cyclam) (Strem) and 2,2′-bipyridine (Aldrich) were used as supplied. Isonicotinamide (Aldrich) was recrystallized from water. Redistilled water (distilled water redistilled from alkaline permanganate solution) was used in the preparation of all the solutions.

Ruthenium Compounds. Potassium Tris(oxalato)ruthenium(III),[13] $K_3[Ru(C_2O_3)_3]$. Five grams of $RuCl_3 \cdot xH_2O$ (43% Ru) (Matthey Bishop) and 11.76 g of $K_2(C_2O_4) \cdot H_2O$ were dissolved in 100 mL of water. This solution was refluxed with stirring for 7 h. After the solution was cooled to room temperature, 100 mL of ethanol was added and the solution was cooled in the freezer overnight. The black solid was collected by filtration and washed with methanol; yield 6 g.

Potassium Pentachloroaquoruthenium(III), $K_2[RuCl_5(OH_2)]$.[13] Five grams of $K_3[Ru(C_2O_4)_3]$ was added to 100 mL of concentrated HCl. This solution was refluxed for 1 h and filtered while hot. After the filtrate was cooled, 100 mL of ethanol was added, and the solution was cooled at −5 °C. The black solid was collected by filtration and washed with ethanol and ether; yield 2.2 g.

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(1) S. S. Isied and H. Taube, *Inorg. Chem.*, **13**, 1545–51 (1974).
(2) S. S. Isied and H. Taube, *Inorg. Chem.*, **15**, 3070–5 (1976).
(3) J. A. Marchant, T. Matsubara, and P. C. Ford, *Inorg. Chem.*, **16**, 2160–5 (1977).
(4) Y. Hung, L. Y. Martin, S. Jackels, A. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029–39 (1977).
(5) J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, **14**, 1881–8 (1975).
(6) L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 2968–81 (1977), and references therein.
(7) L. F. Lindoy, *Chem. Soc. Rev.*, **4** (3), 421–41 (1975), and references therein.
(8) (a) F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974); (b) F. P. Hinz and D. W. Margerum, *J. Am. Chem. Soc.*, **96**, 4993–4 (1974); (c) C. T. Lin, D. B. Rorabacher, G. R. Cayley, and D. W. Margerum, *Inorg. Chem.*, **14**, 919–25 (1975).
(9) E. J. Bounsall and S. R. Koprich, *Can. J. Chem.*, **48**, 1481–91 (1970).
(10) P. K. Chan, D. A. Isabirye, and C. K. Poon, *Inorg. Chem.*, **14**, 2579–80, (1975).
(11) S. S. Isied and C. Kuehn, *J. Am. Chem. Soc.*, **100**, 6754–6 (1978).
(12) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198–200 (1973).
(13) C. Creutz, Ph.D. Thesis, Stanford University, 1970.

0020-1669/80/1319-0911$01.00/0

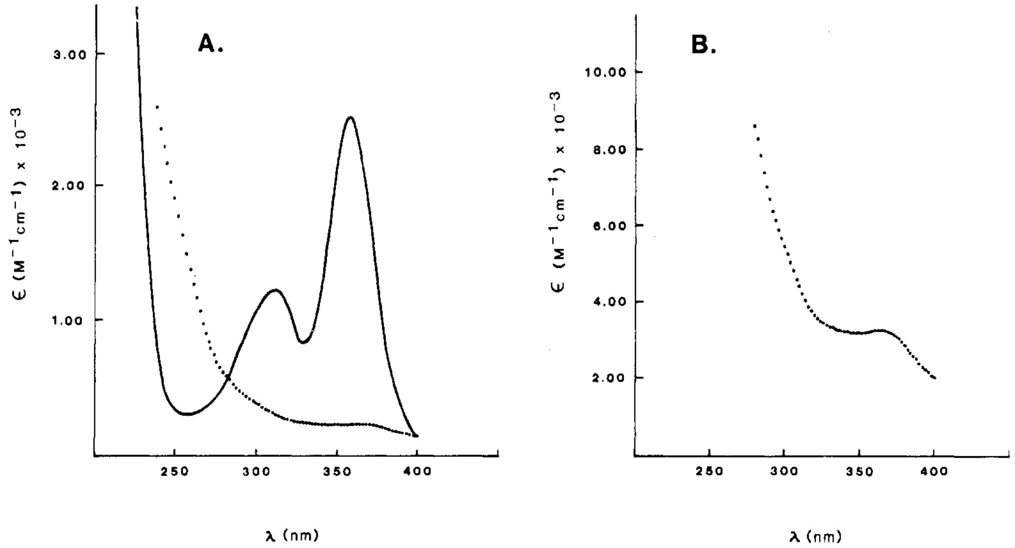

Figure 1. (A) UV spectra of *cis-* (···) and *trans-* (—) [Ru(cyclam)Cl_2]Cl. (B) UV spectrum of *cis*-[Ru(cyclam)Cl_2]Cl (all in 0.1 M HCl).

Preparation of *cis-* and *trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) Chloride, *cis-* and *trans*-[Ru(cyclam)Cl_2]Cl. A solution of 1 g (2.7 mmol) of $K_2[RuCl_5(OH_2)]$ and 0.53 g (2.6 mmol) of cyclam in 79 mL of methanol was refluxed for 3 days, according to the procedure reported by Poon[10] for the preparation of *trans*-[Ru(cyclam)Cl_2]Cl. The solution was rotoevaporated to dryness, and then the solid was redissolved in 0.1 M HCl. This solution was loaded onto a freshly cleaned cation-exchange resin (Bio-Rad AG 50W-X8, 200–400 mesh, acid form) (column $^1/_2$ × 10 in.). Several volumes of 0.1 M HCl were passed through the resin in order to elute some purple anionic or neutral species. Then 1 M HCl was poured onto the column, and the yellow or brown eluant solution was collected as separate fractions (~5 mL each). Because of the yellow color of the ruthenium(III) cyclam species, UV spectra were taken of the separate fractions in order to differentiate them. UV–visible spectra of the eluted fractions clearly showed two species with different UV spectra. The eluted fractions having the same UV spectrum were combined and rotoevaporated. The first species eluted, with a band at 363 nm, was identified as *cis*-[Ru(cyclam)Cl_2]Cl and the second species as *trans*-[Ru(cyclam)Cl_2]Cl, as will be described in this paper. (A brown band of presumably higher charge, which did not elute with 1–2 M HCl, was not further identified.) Since the two eluted compounds still showed the presence of impurity peaks in the visible region of the spectrum, these two compounds were separately dissolved in 0.01 M HCl and separately purified by using gel filtration (Bio-Rad, Bio Gel P-2) ($^1/_2$ × 16 in. column). An unidentified orange species eluted slightly ahead of each of the ruthenium(III) cyclam species. The yellow ruthenium(III) cyclam species was in each case rotoevaporated and reprecipitated by the addition of 1 mL of concentrated HCl and ethanol. The solids were washed with ethanol and ether, resulting in pale yellow solids, final yield 0.23 g of the cis isomer (22%) and 0.35 g of the trans isomer (33%). Anal. Calcd for $[Ru(C_{10}H_{24}N_4)Cl_2]Cl$: C, 29.5; H, 5.9; N, 13.7; Ru, 24.8. Found for the cis isomer: C, 29.2; H, 5.90; N, 13.68; Ru, 24.0. Found for the trans isomer: C, 29.1; H, 5.69; N, 13.65; Ru, 24.0.

Reactions of Ru(II) Cyclam Complexes with Pyridine Heterocycles. A weighed amount of Ru(III) cyclam complex was dissolved in degassed water. A piece of Zn/Hg was added, and an argon flow was maintained through the solution for about 1 h. Either 10–100 times excess solid isonicotinamide was added and the argon flow was maintained for 2–8 h to fully develop the orange-red color or a 1:1 ethanol–water solution, containing 10–100 times excess dissolved 2,2′-bipyridine, was added to the Ru(II) cyclam solution and an argon flow was maintained for 2–8 h in order to develop the color. For a speedup of the reaction, the solution was placed in a 70 °C water bath, while the argon flow was maintained.

Physical Measurements. UV–visible spectra were obtained by using a Cary 17D spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 283 instrument. Electrochemical measurements were done by using a computer-interfaced electrochemical instrument (Jersey Technical Electronics, Lockwood, N.J.).

Results

Synthesis of Ruthenium(III) and -(II) Cyclam Complexes. Refluxing $K_2[RuCl_5OH_2]$ with 1,4,8,11-tetraazacyclotetradecane (cyclam) in methanol[10] resulted in the isolation of two ruthenium(III) complexes of cyclam, when the reaction mixture was chromatographed on a Bio-Rad AG 50W-X8 (200–400 mesh, acid form) cation-exchange resin and eluted with 1 M HCl. By monitoring the UV spectra of eluted fractions, it was possible to clearly separate the two different fractions from one another. These fractions were still contaminated with minor amounts of colored (orange or purple) components. Further purification of these fractions was carried out by gel filtration of each separate fraction. Two different Ru(III) cyclam complexes were obtained as chloride salts. Identical elemental analyses were obtained for the two compounds, and they were taken to be cis and trans Ru(III) cyclam salts. One of the two compounds corresponded closely to the earlier assigned *trans*-[Ru(cyclam)Cl_2]Cl.[10]

UV–Visible Spectra. The UV spectra of the purified *cis*- and *trans*-dichlororuthenium(III) cyclam complexes are found in Figure 1. As expected, these cyclam complexes have no visible bands. The absorbance maxima in 0.1 M HCl for the *trans*-[Ru(cyclam)Cl_2]Cl are 358 nm (2.6 × 10^3 M^{-1} cm^{-1}) and 313 nm (1.2 × 10^3 M^{-1} cm^{-1}) and for the *cis*-[Ru(cyclam)Cl_2]Cl are 363 nm (2.8 × 10^2 M^{-1} cm^{-1}) and a shoulder at 300 nm (5.3 × 10^2 M^{-1} cm^{-1}). The UV spectrum of the *trans*-[Ru(cyclam)Cl_2]Cl in 0.1 M HCl is stable for long periods of time (days), but that of the *cis*-[Ru(cyclam)Cl_2]Cl is not stable with time. Reduction of *trans*-[Ru(cyclam)Cl_2]Cl complex with zinc amalgam in 0.1 M HCl results in a solution of the trans ruthenium(II) cyclam complex with λ_{max} at 282 nm (1.37 × 10^3 M^{-1} cm^{-1}), and similarly reduction of the *cis*-[Ru(cyclam)Cl_2]Cl complex results in a solution of the cis ruthenium(II) cyclam complex with λ_{max} at 350 nm (3.0 × 10^2 M^{-1} cm^{-1}) and 297 nm (2.08 × 10^3 M^{-1} cm^{-1}). Because of the low affinity of ruthenium(II) for chloride, these spectra of the ruthenium(II) cyclam complexes correspond to partially aquated species.

Reduction of the *cis*- and *trans*-dichlororuthenium(III) cyclam complexes with zinc amalgam under an atmosphere of argon in the presence of 0.1 M isonicotinamide solution (isn = 4-pyridinecarboxamide) at pH 5 for 4 h resulted in the formation of an orange-red solution of the *cis*- and *trans*-$[Ru(cyclam)(isn)_2]^{2+}$ complexes, respectively. The spectra (λ_{max} and ϵ) of these solutions are found in Table I. Spectra of the *cis*- and *trans*-$[Ru(cyclam)(isn)_2]^{2+}$ complexes bear

Table I. UV-Visible Spectral Data for Cis and Trans Isomers of Ruthenium-Cyclam and Related Complexes

	cis	trans
	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})	λ_{max}, nm ($\epsilon \times 10^{-3}$, M^{-1} cm^{-1})
$[Ru(cyclam)Cl_2]Cl$	363 (0.28), 300 sh (0.53)	358 (2.6), 313 (1.2)
$[Ru(en)_2Cl_2]Cl$[a]	354 (1.75), 314 (1.42), 269 (0.9)	343 (3.85), 292 sh (0.80), 272 (0.90)
$[Ru(NH_3)_4Cl_2]Cl$[b]	350 (1.5), 308 (1.3)	331 (5.0), 295 sh (0.70)
$[Ru(cyclam)(isn)_2]^{2+}$	465 (3.8), 363 (4.5)	485 (4.9)
$[Ru(NH_3)_4(isn)_2]^{2+}$[c]	476, 413	490
$[Ru(cyclam)(bpy)]^{2+}$	488 (3.2)	365 (2.0)
$[Ru(NH_3)_4(bpy)]^{2+}$[d]	522 (3.3), 366 (5.5), 295 (32.0)	

[a] Reference 10. [b] Reference 3. [c] Reference 18. [d] Reference 17.

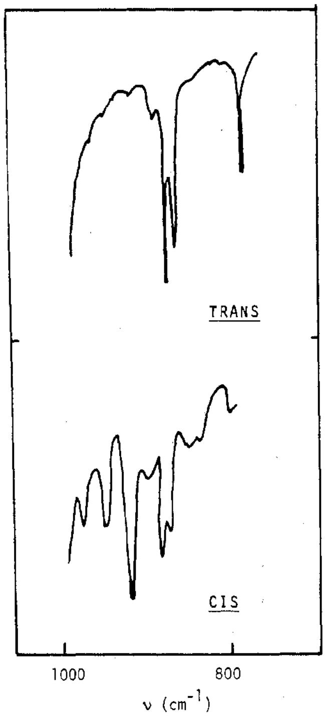

Figure 2. Infrared spectra in the region 800–1000 cm^{-1} for *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ (KBr pellets).

strong resemblance to those of the corresponding *cis*- and *trans*-$[Ru(NH_3)_4(isn)_2]^{2+}$ complexes.[2]

The reduced trans ruthenium(II) cyclam complex at pH 5 reacts with 2,2′-bipyridine (bpy) in aqueous ethanol solution (for 5 h), resulting in the formation of a yellow solution with λ_{max} 365 nm (ϵ 2 × 10^3 M^{-1} cm^{-1}). The reaction of cis ruthenium(II) cyclam with 2,2′-bipyridine (for 5 h) resulted in a red solution with λ_{max} 488 nm (ϵ 3.2 × 10^3 M^{-1} cm^{-1}) (Table I).[19]

Infrared Spectra of *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$. Figure 2 shows the infrared spectra for the region 800–1000 cm^{-1} of both *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ as KBR pellets. This region of the infrared spectra has been assigned to vibrational modes of both the secondary amines and the methyl groups of the ligand.[14] The spectra reported here (Figure 2) for the two ruthenium isomers are in agreement with the infrared spectra of the analogous *cis*- and *trans*-$[Co(cyclam)Cl_2]Cl$ complexes.[14]

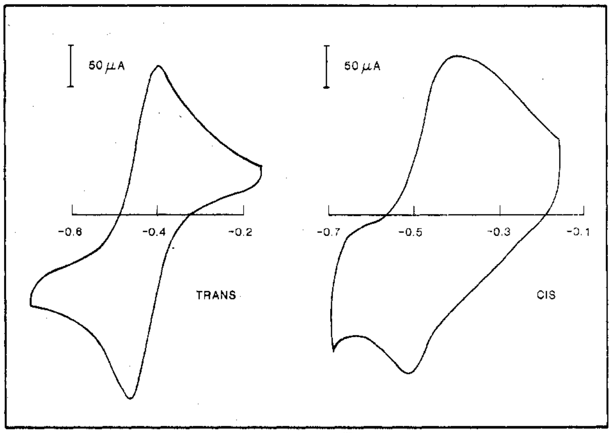

Figure 3. Cyclic voltammetry (rate 100 mV/s) for *trans*- and *cis*-$[Ru(cyclam)Cl_2]Cl$ in 0.1 M NaCl on a Pt-button electrode (potentials vs. SCE).

Cyclic Voltammetry of *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$. The cyclic voltammograms of the *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ complexes in 0.1 M NaCl solution (100 mV/s) are shown in Figure 3. A clear difference in the behavior of these two complexes can be seen. Whereas the trans complex shows a single reversible wave, the cis complex shows two overlapping waves. The reduction potential of the *trans*-$[Ru(cyclam)Cl_2]Cl$ complex is −0.19 V vs. NHE at the scan rates used (100 mV/s), and no aquation of chloride is detected electrochemically. In the cis complex however two overlapping waves are taken to correspond to the couples *cis*-$[Ru(cyclam)Cl_2]^{+/0}$ and *cis*-$[Ru(cyclam)Cl(OH_2)]^{2+/+}$, with the more positive potential corresponding to the aquated species. The chloride aquation observed here corresponds well to the rate of chloride aquation observed for the *cis*-$[Ru(NH_3)_4Cl_2]Cl$, where the first chloride is aquated 32 times faster than for the trans isomer.[3] Estimation of the formal reduction potential of the *cis*-$[Ru(cyclam)Cl_2]Cl$ complex from Figure 3 leads to a value of −0.23 V vs. NHE. Both the reduction potentials for the *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ complexes are similar to the potentials observed for the *cis*- and *trans*-$[Ru(NH_3)_4Cl_2]Cl$ complexes, −0.11 and −0.16 V vs. NHE, respectively.[3]

Discussion

Cis and Trans Isomers of $[Ru(cyclam)Cl_2]Cl$: Isomeric Purity. By use of the earlier published synthetic procedure[10] for the preparation of *trans*-$[Ru(cyclam)Cl_2]Cl$, a brown solid was obtained as reported. The spectra of solutions (in 0.1 M HCl) of this solid showed ill-defined bands in the visible region, indicating impurities. Note that the $[Ru(NH_3)_4Cl_2]Cl$ and the $[Ru(en)_2Cl_2]Cl$ complexes are transparent in the visible region of the spectra.[3,16] Therefore, a more elaborate purification procedure was followed (i.e., ion-exchange chromatography, followed by gel filtration). The purified *cis*- and *trans*-$[Ru(cyclam)Cl_2]Cl$ compounds pale yellow solids are completely transparent in the visible region of the spectra, as expected. The faint yellow color of the ruthenium(III) cyclam solutions makes the visual chromatographic separation of these two isomers difficult; however, with UV spectra as a monitor, the cis and trans ruthenium(III) cyclam species, which have distinctly different UV spectra, were separated. Elemental analyses of both the cis and trans complexes after purification showed them to be identical. Some orange and purple species are also byproducts of the reaction of $K_2[RuCl_5(OH_2)]$ with cyclam. The orange species was mixed with both isomers even

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(14) C. K. Poon, *Inorg. Chim. Acta*, **5**, 322–4 (1971).

after ion-exchange separation. These colored species were however removed when the crude *cis*- and *trans*-[Ru(cyclam)Cl_2]Cl complexes (after ion-exchange chromatography) were subjected to gel filtration in acidic media (pH 2).

From the UV spectra and extinction coefficients reported here for the ruthenium(III) cyclam complexes, it can be concluded that if small amounts of trans isomer are contaminating the cis isomer, the UV spectrum of the mixture can be very diagnostic, since the position of the bands (λ_{max} 358 and 313 nm) of the trans isomer are characteristic and the extinction coefficients of the trans isomer are 10 times greater than that of the cis isomer at the above wavelengths (Figure 1). The reverse, i.e., contamination of small amounts of cis isomer in the trans, can go undected in the UV spectrum of the mixture (Figure 1). It is therefore probable that the earlier reported *trans*-[Ru(cyclam)Cl_2]Cl[10] had some cis contaminant undetected, unless the solubility of the cis isomer is different enough to allow purification by fractional recrystallization.

An alternative method to determine the presence of cis isomer with the trans isomer is to reduce the ruthenium(III) cyclam complex to the ruthenium(II) cyclam complex in the presence of aqueous ethanolic 2,2′-bipyridine. From the spectra (Table I) the λ_{max} at 488 nm for *cis*-[Ru(cyclam)(bpy)]$^{2+}$ can be used to quantitate the amount of cis isomer present. Note that this procedure assumes that the reduction of ruthenium(III) to ruthenium(II) is not accompanied by any isomerization, a fact already established from studies of [Ru$(NH_3)_4Cl_2$]Cl,[15] as well as other ammine complexes of Ru(III).[16]

Infrared and Electrochemical Properties of *cis*- and *trans*-[Ru(cyclam)Cl_2]Cl. The infrared spectra of the cis and trans ruthenium(III) cyclam complexes in the region between 800 and 1000 cm^{-1} (Figure 2) correspond to the analogous cis and trans cobalt(III) cyclam complexes; however, these data alone cannot be used as criteria of high purity.

The electrochemical properties of both *cis*- and *trans*-[Ru(cyclam)Cl_2]Cl complexes show significant differences, especially with respect to the aquation of chloride ion. Whereas the trans isomer shows a reversible wave in the cyclic voltammogram (0.1 M NaCl) (Figure 3), the cis isomer shows two overlapping waves. The difference in the electrochemical behavior of the trans and cis isomers can be attributed to the rate differences in chloride aquation, which for the cis isomer, occurs on the same time scale as the cyclic voltammetry experiment. This interpretation is consistent with the results on rates of chloride aquation in other *trans*-tetraammine complexes, e.g., the chloride aquation for *trans*-[Ru$(NH_3)_4Cl_2$]Cl proceeds 32 times slower than for the cis isomer.[3] It is also noteworthy that no significant difference in the reduction potentials of the ruthenium cyclam complexes and the corresponding ruthenium tetraammine complexes is found.

Reactions of the Ruthenium(II) Cyclam Complexes with Pyridine-Type Ligands. The reaction of the cis and trans ruthenium(II) cyclam complexes with isonicotinamide is another method for differentiating both isomers. In the presence of excess isonicotinamide, the cis ruthenium(II) cyclam complex reacts with isonicotinamide to form *cis*-[Ru(cyclam)$(isn)_2$]$^{2+}$, which has two large charge-transfer bands in the visible at λ_{max} 465 and 363 nm, whereas the trans ruthenium(II) cyclam complex reacts with isonicotinamide to form *trans*-[Ru(cyclam)$(isn)_2$]$^{2+}$ which has only one charge-transfer band in the visible at λ_{max} 485 nm. A comparison of the spectral characteristics of the isonicotinamide-substituted complexes of ruthenium(II) cyclam and ruthenium(II) tetraammine[2] (Table I) shows only slight differences, as expected. A more significant difference is observed between the spectra of the *cis*-[Ru(cyclam)(bpy)]$^{2+}$ (λ_{max} 488 nm) and the *cis*-[Ru$(NH_3)_4$(bpy)]$^{2+}$ (λ_{max} 522 nm),[17] which is not understood at this time.

The use of *cis*- and *trans*-[Ru(cyclam)Cl_2]Cl complexes to replace *cis*- and *trans*-[Ru$(NH_3)_4Cl_2$]Cl complexes in substitution and electron-transfer studies with Ru(II) and Ru(III) will be reported on in a later publication.

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Registry No. *cis*-[Ru(cyclam)Cl_2]Cl, 72300-89-1; *trans*-[Ru(cyclam)Cl_2]Cl, 56172-98-6; *cis*-[Ru(cyclam)$(isn)_2$]$^{2+}$, 72275-22-0; *trans*-[Ru(cyclam)$(isn)_2$]$^{2+}$, 72300-90-4; *cis*-[Ru(cyclam)(bpy)]$^{2+}$, 72275-23-1; *trans*-[Ru(cyclam)$(bpy)_2$]$^{2+}$, 72275-24-2; $K_3[Ru(C_2O_4)_3]$, 29475-51-2; $K_2[RuCl_5(OH_2)]$, 14404-33-2.

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(15) P. C. Ford and C. Sutton, *Inorg. Chem.*, **8**, 893 (1969).

(16) H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, **8**, 893 (1969).

(17) G. M. Brown and N. Sutin, *J. Am. Chem. Soc.*, **101**, 883–92 (1979).

(18) A. M. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).

(19) Over long times (ca. > 12 h) a new band at 365 nm appears in the spectrum of *cis*-[Ru(cyclam)(bpy)]$^{2+}$. This new band may be attributed to cis–trans isomerization since the trans complex has a band at 365 nm.