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Structural and Mechanistic Studies of Coordination Compounds. 27. Synthesis and Characterization of Some Trans Ruthenium(III) Complexes with Four Different Saturated Macrocyclic Quadridentate Secondary Amines

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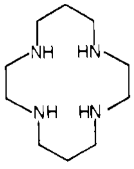
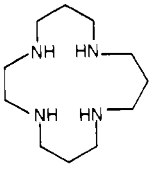
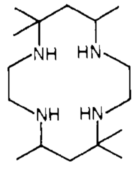
Some ruthenium(III) complexes of the type *trans*-$[Ru(L)X_2]^+$ with four different saturated macrocyclic quadridentate secondary amines [L = 1,4,8,11-tetraazacyclotetradecane (cyclam), X_2 = (Cl)Br, I_2, $(NCS)_2$, and $(CH_3COO)_2$; L = 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4), *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta and tetb respectively), X_2 = Cl_2 and Br_2] have been prepared and characterized. They are all monomeric, low-spin species with a trans configuration. The electronic and infrared absorption spectra of these complexes are discussed.

Introduction

As part of our program to study the photochemical, electrochemical, and thermal substitution reactions of macrocyclic amine complexes, we would like to extend our investigation to ruthenium(III) macrocyclic amine systems. To date very little is known about ruthenium macrocyclic amines. In fact the only saturated macrocyclic amine complexes that have been properly characterized in crystalline form are the dichloro- and dibromoruthenium(III) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam).[1-3] Recently, we have developed a general method[2] for the syntheses of *trans*-$[Ru(L)X_2]^+$, where L represents either two bidentate or one quadridentate saturated amine and X represents halide ligands. This paper describes the preparation and characterization of some trans ruthenium(III) complexes with the following macrocyclic amines: 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4), and *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta and tetb, respectively).


cyclam


[15]aneN_4


teta (*C-meso*) or
tetb (*C-rac*)

Experimental Section

Reagents. $K_2[RuCl_5(OH_2)]$ (Johnson and Matthey) and 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4) (Strem) were used as supplied. 1,4,8,11-Tetraazacyclotetradecane (cyclam)[4] and *C-meso*- and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta and tetb, respectively)[5] were prepared according to published methods.

Caution. Perchlorate salts of ruthenium amines can be highly explosive, especially during filtration and drying of the solids. Preparations should be carried out in small scale with care.

***trans*-Dichloro(1,4,8,12-tetraazacyclopentadecane)ruthenium(III) perchlorate, *trans*-$[Ru([15]aneN_4)Cl_2]ClO_4$,** was prepared by suspending $K_2[RuCl_5(OH_2)]$ (1 g) in methanol (preferably absolute methanol, 230 mL), and the suspension was heated to boiling under reflux and with vigorous stirring for about 15 min. A methanolic solution of [15]aneN_4 (0.05 g in 230 mL) was then added dropwise to the refluxinng solution, and the addition process took about 6 h for completion. After being further heated under reflux overnight (about 18 h), the solution was acidified with HCl and was then filtered while hot to remove the undissolved $K_2[RuCl_5(OH_2)]$. The yellowish brown filtrate was evaporated to dryness. The brown solid of crude *trans*-$[Ru([15]aneN_4)Cl_2]Cl$ was converted to the *perchlorate* salt by adding $NaClO_4$ to a saturated solution of the complex in dilute HCl. The brown product collected was recrystallized from dilute HCl. The microcrystalline light brown solid was collected and washed with a little water, acetone–ether mixture, and ether and was finally dried in vacuo at 78 °C; yield 70%.

***trans*-Dibromo(1,4,8,12-tetraazacyclopentadecane)ruthenium(III) perchlorate, *trans*-$[Ru([15]aneN_4)Br_2]ClO_4$,** was prepared by dissolving the crude *trans*-$[Ru([15]aneN_4)Cl_2]Cl$ (1 g) described in the previous preparation in a hot solution of bromine-free hydrobromic acid (4 M, 200 mL). Several pieces of granulated zinc (1–2 g) were added, and the mixture was heated on a steam bath for about 1 h. The mixture was filtered while hot, and the filtrate was concentrated to about 25 mL. After the filtrate was cooled, bright yellow *trans*-$[Ru([15]aneN_4)Br_2]Br$ precipitated out. The *perchlorate* salt was prepared by dissolving *trans*-$[Ru([15]aneN_4)Br_2]Br$ in 0.01 M HBr, followed by the addition of a concentrated solution of $NaClO_4$. The desired product was filtered off, washed with alcohol and ether, and dried in vacuo at 78 °C; yield 70%.

***trans*-Dichloro(*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)ruthenium(III) salts, *trans*-$[Ru(teta)Cl_2]Y$ (Y = *p*-$CH_3C_6H_4SO_3^-$, I^-, and ClO_4^-),** were prepared by suspending $K_2[RuCl_5(OH_2)]$ (1 g) in absolute ethanol (150 mL), and the suspension was heated under reflux and with vigorous stirring for about 15 min. This refluxinng process before the start of the reaction should be followed to ensure an inert atmosphere for the synthesis of the complex. An ethanolic solution of teta (0.8 g in 200 mL) was added dropwise to the refluxinng suspension, and the process took about 5 h for completion. After being further heated under reflux overnight, the solution was filtered while hot and the filtrate was immediately acidified with *p*-toluenesulfonic acid (2 g). The solution was then evaporated to dryness. The yellowish brown solid of *trans*-$[Ru(teta)Cl_2](p\text{-}CH_3C_6H_4SO_3)$ was recrystallized from hot dilute *p*-toluenesulfonic acid (0.1 M). The crystals collected were washed with absolute ethanol and ether and were dried in vacuo at 78 °C; yield 65%. The *perchlorate* or *iodide* salts were prepared by dissolving the *p*-toluenesulfonate salt in dilute HCl followed by the addition of $NaClO_4$ or NaI, respectively. The conversion yield in both cases was nearly quantitative.

***trans*-Dibromo(*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)ruthenium(III) perchlorate, *trans*-$[Ru(teta)Br_2]ClO_4$,** was similarly prepared with a similar yield to its cyclam analogue starting with *trans*-$[Ru(teta)Cl_2](p\text{-}CH_3C_6H_4SO_3)$.

***trans*-Dichloro(*C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)ruthenium(III) perchlorate, *trans*-$[Ru(tetb)Cl_2]ClO_4$,** was similarly prepared as its teta analogue by a dropwise addition of an ethanolic solution of tetb (0.8 g in 220 mL) to an ethanolic suspension of $K_2[RuCl_5(OH_2)]$ (1 g) which had been kept under reflux and with vigorous stirring for 15 min to ensure an inert atmosphere. After the addition of tetb (5–6 h), the solution was refluxed overnight, giving a light brown solution. The hot solution was treated with an excess of trichloroacetic acid (10 g), filtered while hot, and was then evaporated to dryness. The resulting solid of crude *trans*-[Ru-

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Table I. Analytical Data for Some Macrocyclic Amine Complexes of the Type *trans*-[RuL(X)Y]Z Synthesized in This Work

				analysis[a]						
L	X	Y	Z	% C	% H	% N	% Cl	% Br	% I	% S
cyclam	Br	Cl	ClO_4	23.7 (23.3)	4.45 (4.65)	11.2 (10.9)	14.3 (13.8)	16.0 (15.9)		
	I	1	I	17.9 (17.6)	3.80 (3.55)	8.30 (8.22)			55.3 (55.8)	
	NCS	NCS	ClO_4[b]	26.3 (26.9)	4.40 (4.85)	15.7 (15.7)				12.4 (12.0)
	CH_3COO	CH_3COO	ClO_4[c]	26.7 (27.1)	4.85 (5.00)	8.85 (9.04)	11.9 (11.5)			
[15]aneN_4	Cl	Cl	ClO_4	27.2 (27.2)	5.35 (5.35)	11.4 (11.5)	21.7 (21.9)			
	Br	Br	ClO_4	23.1 (23.0)	4.60 (4.52)	9.85 (9.75)		27.5 (27.8)		
teta	Cl	Cl	ClO_4	34.8 (34.6)	6.50 (6.48)	10.2 (10.1)	19.1 (19.1)			
	Cl	Cl	*p*-$CH_3C_6H_4SO_3$	44.0 (44.0)	6.80 (6.86)	8.90 (8.93)	11.5 (11.3)			
	Cl	Cl	I	32.8 (32.9)	6.30 (6.17)	9.60 (9.60)	12.4 (12.6)		22.2 (21.8)	
	Br	Br	ClO_4	30.0 (29.8)	5.65 (5.58)	8.60 (8.69)		25.2 (24.8)		
tetb	Cl	Cl	ClO_4	34.8 (34.6)	6.30 (6.48)	10.0 (10.1)	19.0 (19.1)			
	Br	Br	ClO_4	30.0 (29.8)	5.70 (5.58)	8.70 (8.69)		24.9 (24.8)		

[a] Calculated values are given in parentheses. [b] Hydrate with one H_2O of crystallization. [c] This complex contains one $HClO_4$ of crystallization.

(tetb)Cl_2]CCl_3COO) was purified by adding sufficient ether to a clear ethanolic solution of the compound. The *perchlorate* salt was obtained by dissolving the trichloroacetate salt in 1 M HCl followed by the addition of $NaClO_4$. The desired product was collected washed with ethanol and ether, and dried in vacuo at 78 °C; yield 50%.

***trans*-Dibromo(*C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)ruthenium(III) perchlorate, *trans*-[Ru(tetb)Br_2]ClO_4,** was prepared by essentially the same method with a similar yield to its cyclam analogue starting with *trans*-[Ru(tetb)Br_2]-(CCl_3COO) described in the previous preparation.

***trans*-Bromochloro(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) perchlorate, *trans*-[Ru(cyclam)(Cl)Br]ClO_4,** was prepared by heating a mixture of *trans*-[Ru(cyclam)Br_2]Br[2] (0.5 g) and LiCl (1 g) in absolute methanol (100 mL) on a steam bath for about 35 min. Excess $NaClO_4$ was then added to precipitate out a yellow solid of crude *trans*-[Ru(cyclam)(Cl)Br]ClO_4. The product so prepared was contaminated with a small quantity of unreacted *trans*-[Ru(cyclam)Br_2]ClO_4 which could be removed by suspending the crude yellow solid in water (30 mL) and then warming up the suspension on a steam bath for about 5 min. The relatively insoluble bromochloro product was then filtered off, washed with cold methanol and ether, and dried in vacuo at 78 °C; yield 70%.

***trans*-Diiodo(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) iodide, *trans*-[Ru(cyclam)I_2]I,** was prepared by refluxing an aqueous mixture (250 mL) of *trans*-[Ru(cyclam)Br_2]Br[2] (0.5 g) and NaI (10 g) for 4 h. After the solution was cooled, a microcrystalline dark purple product of the desired complex precipitated out. The solid was filtered off and washed with a small quantity of water and with ethanol until the ethanolic washings remained colorless. The solid was then washed with ether and air dried; yield 70%.

***trans*-Bis(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) perchlorate hydrate, *trans*-[Ru(cyclam)$(NCS)_2$]$ClO_4 \cdot H_2O$,** was prepared by dissolving *trans*-[Ru(cyclam)Br_2]Br[2] (0.5 g) in a minimum quantity of hot water (at ~70 °C). Excess NaNCS was added, and the resulting solution was heated on a steam bath for about 25 min. The color of the solution gradually turned to deep violet red. The solution was filtered while hot, and excess $NaClO_4$ was added. After the solution was cooled, a violet microcrystalline solid slowly came down, which was collected and recrystallized from hot dilute *p*-toluenesulfonic acid (0.01 M). The solid was filtered off, washed with a little ice-cold water, acetone–ether mixed solvent, and finally with ether, and was dried in vacuo at 78 °C; yield 70%.

***trans*-Bis(acetato)(1,4,8,11-tetraazacyclotetradecane)ruthenium(III)perchlorate hydroperchlorate, *trans*-[Ru(cyclam)$(CH_3COO)_2$]-$ClO_4 \cdot HClO_4$,** was prepared by dissolving *trans*-[Ru(cyclam)Br_2]Br[2] (0.5 g) in a minimum amount of hot water (at ~70 °C). Excess CH_3COONa was added, and the resulting solution was heated on a steam bath for about 1 h. The solution was filtered while hot and was then acidified with $HClO_4$ (70%, 5–7 mL). On standing, needle-shaped greenish brown crystals slowly appeared. These were filtered off, washed with a little ice-cold water, acetone, and ether, and were dried in vacuo at 78 °C; yield 70%.

Physical Measurements. Visible and UV spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 577 spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method with use of mercury tetrakis(thiocyanato)cobaltate(II) as the calibrant.[6]

Results and Discussion

The methods reported here for the syntheses of macrocyclic amine complexes of ruthenium(III) are reproducible. The cyclam complexes are stable in solution, and inert atmosphere is not required for their syntheses. On the other hand, teta and tetb complexes are rather unstable in neutral or basic solutions. The complexes can easily undergo aerial dehydrogenation of the coordinated macrocycles.[7-10] Therefore, their syntheses should best be carried out under an inert atmosphere. However, it was found that the refluxing of the starting material, $K_2[RuCl_5(OH_2)]$, in absolute ethanol for about 15 min before the addition of either teta or tetb to start the synthetic reaction would, in practice, produce a sufficient inert atmosphere. The acidification with *p*-toluenesulfonic acid during the isolation of *trans*-[Ru(teta)Cl_2]$^+$ (or trichloroacetic acid for the tetb analogue) is necessary to stop any undesirable side reactions originating from aerial dehydrogenation in neutral or basic media. For *trans*-[Ru(tetb)Cl_2]$^+$, attempts to prepare the *p*-toluenesulfonate salt were unsuccessful, but trichloroacetic acid proved to be useful. It was, however, quite difficult to purify the trichloroacetate salt of *trans*-[Ru(tetb)Cl_2]$^+$ and

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Table II. Magnetic Moments (μ_{eff}) and Molar Conductivities (Λ) of Some *trans*-Tetraamineruthenium(III) Complexes

complex	μ_{eff},[a] μ_{B}	Λ,[b] Ω^{-1} cm^2 mol^{-1}
$[\mathrm{Ru(cyclam)Cl_2}]\mathrm{Cl}$[c]	2.10	110
$[\mathrm{Ru(cyclam)Br_2}]\mathrm{Br}$[c]	2.17	104
$[\mathrm{Ru(cyclam)I_2}]\mathrm{I}$	2.12	*d*
$[\mathrm{Ru(cyclam)(Cl)Br}]\mathrm{ClO_4}$	2.05	101
$[\mathrm{Ru(cyclam)(NCS)_2}]\mathrm{ClO_4 \cdot H_2O}$	2.10	105
$[\mathrm{Ru([15]aneN_4)Cl_2}]\mathrm{ClO_4}$	2.13	103
$[\mathrm{Ru([15]aneN_4)Br_2}]\mathrm{ClO_4}$	2.10	102
$[\mathrm{Ru(teta)Cl_2}]\mathrm{ClO_4}$	2.06	102
$[\mathrm{Ru(teta)Br_2}]\mathrm{ClO_4}$	2.10	101
$[\mathrm{Ru(tetb)Cl_2}]\mathrm{ClO_4}$	2.11	110
$[\mathrm{Ru(tetb)Br_2}]\mathrm{ClO_4}$	2.04	104

[a] Determined by Gouy method at room temperature. [b] In deionized water at 18 °C. [c] Reference 2. [d] This complex is insoluble in water.

only the perchlorate salt was prepared and characterized. The [15]aneN$_4$ complexes are stable in neutral media but aerial dehydrogenation was also observed in a large scale preparation of *trans*-$[\mathrm{Ru([15]aneN_4)Cl_2}]^+$. Therefore, an inert atmosphere and acidification of the resulting methanolic *trans*-$[\mathrm{Ru([15]aneN_4)Cl_2}]^+$ before its isolation are preferred. The evidence of the absence of any ligand dehydrogenation in the final products reported here was derived mainly from infrared spectroscopy as absorption peaks around 1500–1700 cm^{-1} which are characteristic of $>\mathrm{C{=}N}$ vibration were absent.

For the preparation of dianiono–cyclam complexes, *trans*-$[\mathrm{Ru(cyclam)Br_2}]\mathrm{Br}$ proved to be a better starting material than the dichloro complex probably because the former is slightly more reactive. The use of the dibromo complex as the starting material was rather critical for the preparation of *trans*-$[\mathrm{Ru(cyclam)(Cl)Br}]\mathrm{ClO_4}$. The reaction time was controlled in such a way that it was long enough for the reaction between *trans*-$[\mathrm{Ru(cyclam)Br_2}]^+$ and excess LiCl to proceed to give sufficient *trans*-$[\mathrm{Ru(cyclam)(Cl)Br}]^+$ but not too long to yield the disubstituted dichloro complex. The desired product of *trans*-$[\mathrm{Ru(cyclam)(Cl)Br}]\mathrm{ClO_4}$ so prepared was contaminated with a small quantity of the unreacted *trans*-$[\mathrm{Ru(cyclam)Br_2}]\mathrm{ClO_4}$, which was much more soluble in water than the bromochloro complex and hence could be removed. Had the bromochloro product been contaminated with *trans*-$[\mathrm{Ru(cyclam)Cl_2}]\mathrm{ClO_4}$, which is of much the same low solubility, it would have been a problem to purify the desired complex. For the preparation of *trans*-$[\mathrm{Ru(cyclam)(NCS)_2}]^+$, it should be noted that prolong heating should be avoided and the reaction solution should never be heated up to boiling with use of a hot plate, otherwise some ill-defined products would have been formed. Reactions between *trans*-$[\mathrm{Ru(cyclam)X_2}]^+$ ($\mathrm{X^-} = \mathrm{Cl^-}$ or $\mathrm{Br^-}$) and excess $\mathrm{NaN_3}$ were attempted. Addition of perchlorate or hexafluoro phosphate to the reaction mixtures gave dark green crystalline solids of what was probably the diazido complex; however, these materials were unstable and readily decomposed to ill-defined dark solids. On the basis of their infrared spectra, these solids did not contain coordinated dinitrogen. Since they were so unstable, we have not obtained the elemental analytical data or other physical measurements on these diazido complexes. Accordingly, we did not include the preparation of these complexes in the Experimental Section.

The reactions of *trans*-$[\mathrm{RuLCl_2}]^+$ (L = teta or tetb) with a variety of $\mathrm{X^-}$ ($\mathrm{X} = \mathrm{I^-}, \mathrm{NCS^-}, \mathrm{NO_2^-}$, or $\mathrm{N_3^-}$) have been tried, and, in every case, only the ruthenium(II) complexes were obtained. However, the isolated products usually consisted of a mixture of some partially dehydrogenated complexes, and they were quite difficult to separate and purify. The reactions between $\mathrm{K_2[RuCl_5(OH_2)]}$ and teta or tetb have also been tried in other solvents such as methanol, dioxan, dimethyl sulfoxide, and water, and in every case, some ill-defined products resulted. Absolute ethanol appeared to be the most suitable solvent for the syntheses of *trans*-$[\mathrm{RuLCl_2}]^+$ (L = teta or tetb).

All the new complexes are highly colored and give well-formed crystals. The isomeric purity of each complex was confirmed by the observation that the electronic absorption spectrum of the complex was unaffected by repeated recrystallization. This was further confirmed by adsorbing the complexes on a Dowex 50W-X8 (20–50 mesh) cation exchanger in the acid form. Only a single band was developed which could be eluted out. The elemental analytical data (Table I), magnetic moments, and molar conductivities (Table II) of these complexes confirm that they are low-spin, monomeric species.

The assignment of a trans configuration to these complexes was made on the basis of infrared spectroscopy (Table III). A comparison of the far-infrared spectra of the dichloro complexes with their corresponding dibromo complexes enabled the ν(Ru–X) stretching frequencies to be determined. In all cases, only one ν(Ru–X) stretch was observed which unambiguously showed that these dichloro and dibromo complexes have a trans configuration. The ν(Ru–I) stretching frequency of $[\mathrm{Ru(cyclam)I_2}]\mathrm{I}$ was expected to occur well below our instrumental limit of 200 cm^{-1} and hence could not be determined, but its geometrical configuration and that of other

Table III. Infrared Spectra in the 3100–3300, 750–950, and 200–400-cm^{-1} Regions of Some *trans*-Tetraamineruthenium(III) Complexes

	absorption bands, cm^{-1} [a]				
complex	NH str	CH$_2$ and/or NH vib			Ru–X str
trans-$[\mathrm{Ru(cyclam)Cl_2}]\mathrm{ClO_4}$	3230 s	938 w, 925 w sh, 902 w, 888 s, 878 s	800 s		322 s
trans-$[\mathrm{Ru(cyclam)Br_2}]\mathrm{ClO_4}$	3210 s	932 w, 925 w, 900 w, 882 m, 870 m	798 m		220 m
trans-$[\mathrm{Ru(cyclam)I_2}]\mathrm{I}$	3140 s	940 w, 925 w, 905 w, 890 s, 878 s	800 s		*b*
trans-$[\mathrm{Ru(cyclam)(Cl)Br}]\mathrm{ClO_4}$	3220 s	938 w, 925 w, 902 w, 888 m, 876 m	800 m		322 s, 210 m
trans-$[\mathrm{Ru(cyclam)(NCS)_2}]\mathrm{ClO_4 \cdot H_2O}$	3170 s, 3230 s	930 w, 920 w, 900 w, 888 m, 880 m, 824 m[c]	810 m sh		328 m
trans-$[\mathrm{Ru(cyclam)(CH_3COO)_2}]\mathrm{ClO_4 \cdot HClO_4}$[d]	3228 s	945 w, 905 w, 890 m, 880 m	805 m		
trans-$[\mathrm{Ru([15]aneN_4)Cl_2}]\mathrm{ClO_4}$	3200 s	930 m, 908 m, 898 m, 882 m		770 w	330 s
trans-$[\mathrm{Ru([15]aneN_4)Br_2}]\mathrm{ClO_4}$	3220 s	935 m, 912 m, 900 m, 886 m		775 w	230 m
trans-$[\mathrm{Ru(teta)Cl_2}]\mathrm{ClO_4}$	3190 s	936 w, 922 w, 895 m, 866 m, 824 s		778 s	330 s
trans-$[\mathrm{Ru(teta)Br_2}]\mathrm{ClO_4}$	3190 s	920 w sh, 894 m, 862 m, 820 m		774 m	210 m
trans-$[\mathrm{Ru(tetb)Cl_2}]\mathrm{ClO_4}$	3200 s	930 w, 920 w, 890 w, 865 w, 820 m		770 m	328 m
trans-$[\mathrm{Ru(tetb)Br_2}]\mathrm{ClO_4}$	3190 s	930 w, 920 w, 910 w, 892 w, 862 w, 820 w		774 m	230 m

[a] Bands other than ν(Ru–X) in the 200–400-cm^{-1} region are not given in this table; abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] Occurs well below the instrument limit of 200 cm^{-1}. [c] This band is assigned as ν(C–S) of the coordinated NCS ligand. [d] The spectrum of this complex in the 750–950-cm^{-1} region has a very broad and medium intense background absorption due to the coordinated CH$_3$COO groups. Bands are not well resolved.

Table IV. Visible and UV Absorption Spectra of Some Macrocyclic Tetraamineruthenium(III) Complexes in Dimethyl Sulfoxide

complex	$\lambda_{\max}$, nm[a]
trans-[Ru(cyclam)Cl_2]Cl	360 (2950), 311 (1380)
trans-[Ru(cyclam)Br_2]Br	431 (4380), ~410 sh (2320), 355 br (860)
trans-[Ru(cyclam)(Cl)Br]ClO_4	~430 sh (980), 405 (2180), 360 (1270), 316 (980)
trans-[Ru(cyclam)I_2]I	601 (3170), ~380 sh (2420), 315 (9330)
trans-[Ru(cyclam)$(NCS)_2$]$ClO_4 \cdot H_2O$	558 (7350), ~485 sh (940), 378 br (2310), ~340 sh (1700)
trans-[Ru(cyclam)$(CH_3COO)_2$]$ClO_4 \cdot HClO_4$	~326 br (1800), 285 br (1970)
trans-[Ru([15]aneN_4)Cl_2]ClO_4	362 (2840), 320 br sh (1570)
trans-[Ru([15]aneN_4)Br_2]ClO_4	429 (4410), ~410 sh (2140), 362 br (970)
trans-[Ru(teta)Cl_2]ClO_4[b]	382 (2270), 315 (1490)
trans-[Ru(teta)Br_2]ClO_4	452 (3730), ~430 sh (1720), 365 br (620)
trans-[Ru(tetb)Cl_2]ClO_4[b,c]	386 (~2300), 311 (~2000)
trans-[Ru(tetb)Br_2]ClO_4[b]	455 (3290), ~430 sh (1470), 365 br (700)

[a] Molar absorption coefficients (ϵ, M^{-1} cm^{-1}) are given in parentheses; abbreviations: br, broad; sh, shoulder. [b] The solution was acidifed with *p*-toluenesulfonic acid (0.1 M). [c] This complex is not stable in solution. The spectrum was obtained by extrapolating the changing spectra to "zero" time.

cyclam complexes can be inferred from their infrared spectra in other regions of interest. In the 750–950-cm^{-1} region, consistent variation between cis and trans isomers of cyclam complexes has been observed, and this variation has been found to be quite independent of the nature of central metal ions, other ligands, and counterions. Those complexes assigned a trans configuration showed two groups of relatively intense bands separated by >70 cm^{-1}. The group at a lower frequency, which arises essentially from the methylene vibration,[11,12] consisted of one sharp band near 800 cm^{-1}, while the group at a higher frequency, which is due predominantly to the secondary amine vibration,[11,12] mainly consisted of two bands near 890 cm^{-1}. It is clear from Table III that all the cyclam complexes prepared here have a trans configuration. For all these complexes, except [Ru(cyclam)$(NCS)_2$]$ClO_4 \cdot H_2O$, the assignment is further supported by the presence of only one sharp intense band near 3200 cm^{-1}, arising from the secondary amine vibration. For [Ru(cyclam)$(NCS)_2$]$ClO_4 \cdot H_2O$, the splitting of the amine vibration near 3200 cm^{-1} is probably a consequence of hydrogen bonding involved between the secondary amines and the water of crystallization in the crystal lattice. In any case its infrared pattern in the 750–950-cm^{-1} region and the presence of only one ν(Ru–NCS) stretch unambiguously confirm that it is a trans isomer. Furthermore, the infrared spectrum of *trans*-[Ru(cyclam)$(NCS)_2$]$ClO_4 \cdot H_2O$ clearly indicates that the ambidentate thiocyanate ligand is N bonded since the ν(C–S) vibration at 824 cm^{-1} is well above 780 cm^{-1}[13] and the ν(Ru–NCS) stretch at 328 cm^{-1} occurs at a slightly higher frequency than ν(Ru–Cl) at 322 cm^{-1} of the corresponding dichloro complex.[14]

The electronic absorption spectra of these complexes in dimethyl sulfoxide are collected in Table IV. These spectra are dominated by the intense charge-transfer transitions. The lowest energy bands are essentially ligand-to-metal in nature, as confirmed by the observation that the $\lambda_{\max}$ increases from chloro through bromo to iodo complexes. It is interesting to note that the UV spectrum of *trans*-[Ru(cyclam)(Cl)Br]$^+$ is essentially the summation of those of *trans*-[Ru(cyclam)Cl_2]$^+$ and *trans*-[Ru(cyclam)Br_2]$^+$ in so far as the number and position of absorption bands are concerned. This seems to indicate that the energy levels of the partially filled metal t_{2g} and the fully filled π_{Cl} in the dichloro or π_{Br} in the dibromo complexes remain essentially unchanged in the mixed-halogeno complex. In other words, there is at most very weak interaction between the π_{Cl} and π_{Br} levels in *trans*-[Ru(cyclam)(Cl)Br]$^+$. The interaction has been found to be rather significant in the case of mixed-halogeno bis(ethylenediamine) complexes.[2]

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Registry No. *trans*-[Ru(cyclam)Cl_2]ClO_4, 74202-82-7; *trans*-[Ru(cyclam)Br_2]ClO_4, 76705-13-0; *trans*-[Ru(cyclam)I_2]I, 76705-14-1; *trans*-[Ru(cyclam)(Cl)Br]ClO_4, 76705-16-3; *trans*-[Ru(cyclam)$(NCS)_2$]ClO_4, 76705-18-5; *trans*-[Ru(cyclam)$(CH_3COO)_2$]ClO_4, 76705-20-9; *trans*-[Ru([15]aneN_4)Cl_2]ClO_4, 76721-67-0; *trans*-[Ru([15]aneN_4)Br_2]ClO_4, 76721-69-2; *trans*-[Ru(teta)Cl_2]ClO_4, 76792-47-7; *trans*-[Ru(teta)Br_2]ClO_4, 76792-49-9; *trans*-[Ru(tetb)Cl_2]ClO_4, 76705-22-1; *trans*-[Ru(tetb)Br_2]ClO_4, 76705-24-3; *trans*-[Ru(teta)Cl_2](*p*-$CH_3C_6H_4SO_3$), 76740-66-4; *trans*-[Ru(teta)Cl_2]I, 76740-67-5; *trans*-[Ru([15]aneN_4)Cl_2]Cl, 76705-25-4; *trans*-[Ru([15]aneN_4)Br_2]Br, 76705-26-5; *trans*-[Ru(tetb)Br_2](CCl_3COO), 76705-27-6; *trans*-[Ru(cyclam)Br_2]Br, 74202-83-8; *trans*-[Ru(cyclam)Cl_2]Cl, 56172-98-6; $K_2[RuCl_5(OH_2)]$, 14404-33-2.

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