and $k_Y[Y^{m+}] \gg k_L[L^{n+}]$ are met. At this point, k_{obsd} will approach the value of k_{-L}, where k_{-L} is the limiting rate of dissociation of L^{n+} from Ru(CN)$_5$L$^{(3-n)-}$. Similarily, as [Y^{m+}] is decreased, the observed rate constant approaches the rate of dissociation, k_{-Y}, of Y^{m+} from Ru(CN)$_5$Y$^{(3-m)-}$. The expression in eq 5 is consistent with the observed dependence of the rate on [Y^{m+}] for the substitution reactions in this study. With k_{-L} for the complexes with nitrogen heterocycles being greater (Table I) than the corresponding rate constant for the dimethyl sulfoxide complex, k_{obsd} increases to a limiting value (Figure 1) with increasing [Me$_2$SO]. In the substitution reactions of the dimethyl sulfoxide complex, an increase in [Y^{m+}] results in a decrease in k_{obsd} to a limiting value.

Rate constants and activation parameters have been reported for formation and dissociation reactions of the analogous Fe(CN)$_5$L$^{(3-n)-}$ complexes.[1,5,14] The enthalpies of activation associated with k_{-L} are similar for the two systems while the entropy values are slightly lower (5–10 cal K^{-1} mol^{-1}) for the ruthenium complexes. The decreased entropies of activation are suggestive of a shift from a purely dissociative (D) mechanism toward an interchange (I$_d$) process for the ruthenium system, but such a shift is not clearly supported by the kinetic behavior. The rate and equilibrium constants for the pentacyano(ligand) complexes of Ru(II) and Fe(II) are summarized in Table II. The ruthenium complexes are more inert than the iron species with respect to substitution of L^{n+}, including the coordinated water molecule. The decreased lability is expected because of the relatively stronger Ru–L bonds. The larger radial extension of the 4d orbitals on ruthenium would allow for greater π back-bonding to the cyanide ligands and to the N-heterocycle in the sixth position. The increased back-donation would enhance the M(III) character of Ru(II) relative to that of Fe(II) and account for the slower exchange in Ru(CN)$_5$OH$_2$$^{3-}$. For the ligands used in this study the equilibrium constants calculated from k_L/k_{-L} for the Fe(II) complexes are similar to those for the corresponding Ru(II) complexes. The trends in k_L and k_{-L} are also similar for the two metal systems, with dimethyl sulfoxide the most inert and imidazole the most labile with respect to substitution. Ligand-exchange rate constants have been reported for some other octahedral ruthenium(II) complexes of the type Ru(NH$_3$)$_5$L^{2+},[16,17] and Ru(edta)L^{2-}.[18] The rates of ligand substitution in these complexes are of similar magnitude and are found to be dependent on the nature of L, consistent with a dissociatively activated process.

The results of the present kinetic study and previous work on substitution of the Ru(CN)$_5$OH$_2$$^{3-}$ ion[12] have demonstrated that these pentacyano(ligand)ruthenate(II) complexes are relatively inert species in solution. Shepherd and co-workers[9,19] have recently employed these complexes and binuclear derivatives in spectroscopic studies for a comparison of the behavior of the low-spin d^6 moieties Fe(CN)$_5$$^{3-}$, Ru(CN)$_5$$^{3-}$, and Ru(NH$_3$)$_5$$^{2+}$. Further kinetic studies on Ru(CN)$_5$L$^{(3-n)-}$ complexes with other ligand types, including bridging metal species, are in progress in our laboratory.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada is acknowledged. We thank Queen's University for a graduate scholarship to J. M.A.H. and for a grant to D.H.M. from its Advisory Research Committee.

Registry No. Ru(CN)$_5$(*N*-mepyz)$^{2-}$, 84711-78-4; Ru(CN)$_5$(pyrpyr)$^{2-}$, 101953-46-2; Ru(CN)$_5$(bpy)$^{3-}$, 86260-22-2; Ru(CN)$_5$(pyz)$^{3-}$, 96455-66-2; Ru(CN)$_5$(py)$^{3-}$, 86260-15-3; Ru(CN)$_5$(im)$^{3-}$, 101953-47-3; Ru(CN)$_5$(isonic)$^{4-}$, 86260-17-5; Ru(CN)$_5$(Me$_2$SO)$^{3-}$, 101953-48-4; Me$_2$SO, 67-68-5; py, 110-86-1; im, 288-32-4; pyz, 290-37-9; *N*-mepyz$^+$, 17066-96-5.

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Synthesis and Photobehavior of Chromium(III) and Rhodium(III) Complexes of the Macrocyclic Ligand *C-meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-Tetraazacyclotetradecane

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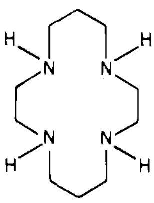
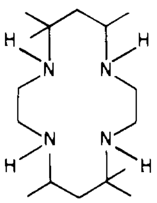
We have recently synthesized the Cr(III) complexes *cis*- and *trans*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$[1] and *trans*-Cr(cyclam)(CN)$_2$$^+$,[2] and the Rh(III) species *cis*- and *trans*-Rh(cyclam)(CN)$_2$$^+$,[3] where cyclam is the macrocyclic tetradentate amine ligand, 1,4,8,11-tetraazacyclotetradecane (I). The trans isomers display very unusual photobehavior in room-temperature solution. In addition to the near absence of any discernible photochemistry, they exhibit exceptionally strong, long-lived phosphorescence signals.[1,4,5] Furthermore, in the Cr(III) case, deuteration of the amine N–H protons results in marked increases in the intensity and lifetime of their emission.[1,4]



I
cyclam



II
tet a

In view of the novel photobehavior of these systems, we have extended our studies to include other macrocyclic ligands. We report here the synthesis and photobehavior of the complexes *trans*-Cr(tet a)(NH$_3$)$_2$$^{3+}$, *trans*-Cr(tet a)(CN)$_2$$^+$, and *trans*-Rh(tet a)(CN)$_2$$^+$, where tet a is *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (II). The tet a ligand contains the same basic 14-membered ring structure of cyclam, with the additional presence of six methyl groups on the ring periphery. Steric hindrance associated with these methyl groups is apparently responsible for the absence of stable cis complexes of the type *cis*-M(tet a)X$_2$$^{n+}$.[7-10] We were therefore interested in learning whether steric factors might substantially affect the photochemical and photophysical properties of tet a complexes with Cr(III) and Rh(III).

Experimental Section

Reagents. The ligand tet a·2H$_2$O was obtained from Strem Chemicals. The complex *trans*-[Cr(tet a)Cl$_2$]Cl was synthesized by the published method,[7] and the perchlorate salt was isolated by the addition of NaClO$_4$ to an aqueous solution of the chloride salt. The CrCl$_3$·6H$_2$O and RhCl$_3$·3H$_2$O were purchased from Fisher Scientific and Alfa Products, respectively.

Measurements. Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, and infrared data were collected on a Perkin-Elmer 283 instrument using KBr pellets. A Markson Electromark ana-

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lyzer (Model 4403) was used to measure conductance values. The equipment and procedures for obtaining emission lifetimes have been described elsewhere.[11] High-resolution steady-state emission spectra were obtained on a Jarrell-Ash 500 laser Raman spectrometer using a red-sensitive Hamamatsu 666 PMT as detector. Low-resolution emission spectra were recorded on a modified Aminco-Bowman spectrophotofluorometer (Model 48203-D) described elsewhere.[11] Ligand field (LF) photolyses were carried out with a 1-kW Hg–Xe lamp and associated optical train,[11] or a Rayonet RPR-100 photochemical reactor. All elemental analyses were performed by Midwest Microlabs.

Syntheses. ***trans*-[Cr(tet a)(CN)$_2$]ClO$_4$·$^3/_2$H$_2$O.** A 0.885-g sample (1.75×10^{-3} mol) of *trans*-[Cr(tet a)Cl$_2$]ClO$_4$·H$_2$O was dissolved in 13 mL of Me$_2$SO. A 0.816-g sample (1.6×10^{-2} mol) of finely ground NaCN was added, and the reaction mixture was stirred at room temperature for 45 min. The reaction mixture was then heated to 65 °C for 60 min. After the mixture was cooled to room temperature, the yellow solid present was collected and washed with absolute ethanol (30 mL) and ether. Yield: 0.714 g or 1.39×10^{-3} mol (79%). A 0.300-g sample (5.82×10^{-4} mol) of this yellow solid was dissolved in 175 mL of water (50 °C) and filtered to remove undissolved compound, and to the filtrate was added excess solid NaClO$_4$. The yellow precipitate was collected and washed with absolute ethanol and ether. Yield: 0.080 g or 1.55×10^{-4} mol (27%). Anal. Calcd for CrC$_{18}$H$_{39}$N$_6$ClO$_{5.5}$: C, 41.97; H, 7.65; N, 16.32; Cl, 6.88. Found: C, 42.02; H, 7.14; N, 15.86; Cl, 6.97.

***trans*-[Cr(tet a)(NO$_3$)$_2$]NO$_3$·HNO$_3$.** A solution composed of 1.00 g (2.26×10^{-3} mol) of *trans*-[Cr(tet a)Cl$_2$]Cl and 1.16 g (6.83×10^{-3} mol) of AgNO$_3$ in 25 mL of water was heated while being stirred to 95 °C. The solution was filtered when necessary to remove AgCl. After 30 min, concentrated nitric acid (22 mL) was added, and the solution was heated to near dryness (2 mL). The red crystalline precipitate, which resulted on cooling to room temperature, was collected and washed with 2/1 ether/acetone, 3/1 ether/acetone, and finally ether. Yield: 0.886 g or 1.51×10^{-3} mol (67%). Anal. Calcd for CrC$_{16}$H$_{37}$N$_8$O$_{12}$: C, 32.81; H, 6.38, N, 19.14. Found: C, 32.87; H, 6.74; N, 18.74.

***trans*-[Cr(tet a)(NH$_3$)$_2$](PF$_6$)$_3$·H$_2$O.** To a 0.400-g sample (6.83×10^{-4} mol) of *trans*-[Cr(tet a)(NO$_3$)$_2$]NO$_3$·HNO$_3$ was added enough liquid NH$_3$ to totally immerse the parent solid, and the solution was stirred for 15 min. The yellow *trans*-[Cr(tet a)(NH$_3$)$_2$](NO$_3$)$_3$ remaining after NH$_3$ evaporation was dissolved in 60 mL of 0.5 M HCl, the mixture filtered to remove impurities, and the product precipitated with excess solid NH$_4$PF$_6$. The salt was washed with 3/2 ether/acetone (80 mL) and then ether (70 mL). Yield: 0.328 g or 3.98×10^{-4} mol (58%). A 0.090-g sample (1.09×10^{-4} mol) was then dissolved in 20 mL of 0.02 M HCl (50 °C). The warm solution was filtered and excess solid NH$_4$PF$_6$ was added. The resulting yellow precipitate was collected and washed with 3/1 ether/acetone (80 mL) and ether. Yield: 0.050 g or 6.07×10^{-5} mol (56%). Anal. Calcd for CrC$_{16}$H$_{44}$N$_6$F$_{18}$P$_3$O: C, 23.33; H, 5.40; N, 10.21. Found: C, 23.92; H, 5.67; N, 9.64.

***trans*-[Rh(tet a)Cl$_2$]ClO$_4$.** A 0.250-g sample (1.2×10^{-3} mol) of RhCl$_3$·3H$_2$O and 0.418 g (1.3×10^{-3} mol) of tet a were placed in a 50-mL round-bottom flask containing 11 mL of water. The stirred solution was heated under reflux for 1 h, during which time the color changed from yellow to brown. The solution was filtered hot, and an aqueous NaClO$_4$ solution was added dropwise with stirring. The yellow precipitate was collected and washed with 9:1 ether/acetone and suction dried. Yield: 0.402 g or 6.8×10^{-4} mol (57%).

***trans*-[Rh(tet a)(CN)$_2$]ClO$_4$·H$_2$O.** A 0.402-g sample (6.3×10^{-4} mol) of *trans*-[Rh(tet a)Cl$_2$]ClO$_4$ and ground NaCN (3.00 g, 6.0×10^{-2} mol) were placed in a 50-mL round-bottom flask containing 20 mL of water. The stirred solution was heated under reflux for 1 h, during which time the solution changed from yellow to colorless. White crystals were obtained on cooling of the solution in ice for 1 h, were collected and washed with acetone and ether, and were suction dried. Yield: 0.217 g or 3.8×10^{-4} mol (54%). A 0.110-g sample of this product was recrystallized from 65 mL of hot water, and 0.050 g was recovered. Anal. Calcd for RhC$_{18}$H$_{38}$N$_4$ClO$_5$: C, 38.8; H, 6.88; N, 15.09; Cl, 6.37. Found: C, 38.50; H, 6.78; N, 14.83; Cl, 6.44.

Caution! Perchlorate salts of TM complexes are potentially explosive.

Results and Discussion

Syntheses. The preparation of *trans*-[Cr(tet a)(CN)$_2$]ClO$_4$ and *trans*-[Cr(tet a)(NH$_3$)$_2$](PF$_6$)$_3$ followed procedures similar to those employed for the cyclam analogues. However for the synthesis of *trans*-[Cr(tet a)(NO$_3$)$_2$]NO$_3$·HNO$_3$ the ready availability of the *trans*-dichloro parent avoided the necessity of employing the *trans*-dicyano complex as an intermediate. For *trans*-[Rh(tet a)(CN)$_2$]ClO$_4$, the marked steric preference for the trans isomer[7–10] simplified the synthetic approach adopted, since an initial separation of *cis*- and *trans*-[Rh(tet a)Cl$_2$]ClO$_4$ was not needed.

Table I. UV–Visible Spectral Data for Cr(III) and Rh(III) Complexes in Aqueous Solution

complex	$\lambda_{\max}$[a]	ref
	Cr(III) Species	
trans-Cr(NH$_3$)$_4$(CN)$_2^+$	440 (42.6), 344 (41.5)	16
trans-Cr(en)$_2$(CN)$_2^+$	432 (49.0), 337 (42.7)	18
trans-Cr(cyclam)(CN)$_2^+$	414 (62.5), 328 (62.5)	2
trans-Cr(tet a)(CN)$_2^+$	425 (67.8), 336 (70.0)	this work
trans-Cr(tet a)(H$_2$O)$_2^{3+}$	514 (14.5), 419 (34.4), 354 (49.4)	14
trans-Cr(cyclam)(H$_2$O)$_2^{3+}$	510 (24), 405 (39), 350 (53)	12
trans-Cr(en)$_2$(NH$_3$)$_2^{3+}$	454 (47), 347 (37)	19
trans-Cr(cyclam)(NH$_3$)$_2^{3+}$	445 sh (32), 420 (36), 334 (50)	1
trans-Cr(tet a)(NH$_3$)$_2^{3+}$	435 (42.6), 344 (54.6)	this work
	Rh(III) Species	
trans-Rh(cyclam)Cl$_2^+$	406 (48), 242 sh (3300)	20
trans-Rh(tet a)Cl$_2^+$	416 (70), 250 sh (2525)	this work
trans-Rh(cyclam)(CN)$_2^+$	267 (270)	3
trans-Rh(tet a)(CN)$_2^+$	262 (332)	this work

[a] Absorption wavelengths in nanometers. Values in parentheses are the molar absorptivities.

Characterization. ***trans*-[Cr(tet a)(NO$_3$)$_2$]NO$_3$·HNO$_3$.** The infrared spectrum displays bands at 1522 and 1270 cm^{-1} characteristic of coordinated *unidentate* NO$_3^-$.[1,12,13] An intense ionic NO$_3^-$ band observed at 1384 cm^{-1} remains after washing of the complex with ether/acetone and is attributed to an HNO$_3$ adduct. When the complex is allowed to stand for a short time in aqueous solution, the visible spectrum matches closely that of a genuine sample of *trans*-Cr(tet a)(H$_2$O)$_2^{3+}$ (Table I).[14] In view of the well-documented stereorigidity of Cr(III) acid hydrolyses[15] and the known geometric preference of tet a systems, it is concluded that the parent nitrato compound has the trans configuration.

***trans*-[Cr(tet a)(CN)$_2$]ClO$_4$·1.5H$_2$O.** The molar conductance of a 5.28×10^{-4} M aqueous solution (91 Ω^{-1} cm^2 mol^{-1}) compares favorably with the value of 90 Ω^{-1} cm^2 mol^{-1} reported for *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$[2] and is reasonable for a 1:1 electrolyte. The question of geometric configuration was investigated via an acid hydrolysis study:

$$\mathrm{Cr(tet\ a)(CN)_2^{+} \xrightarrow[H^+]{\Delta} Cr(tet\ a)(H_2O)_2^{3+} + 2HCN}$$

The complex's marked resistance to acid hydrolysis was similar to that for the cyclam complex.[2] The UV–vis spectrum obtained after a 1 M HNO$_3$ solution was heated for several hours matches closely that of *trans*-Cr(tet a)(H$_2$O)$_2^{3+}$ (Table I),[14] implying that the parent dicyano complex has the trans configuration.

The infrared spectrum of the dicyano complex displays a weak cyanide ligand stretch at 2080 cm^{-1}. The wavelength of the first spin-allowed LF band $^4B_{1g} \rightarrow {}^4B_{2g}, {}^4E_g$ (D_{4h}) for *trans*-Cr(tet a)(CN)$_2^+$ (425 nm) is lower than that of *trans*-Cr(NH$_3$)$_4$(CN)$_2^+$ (440 nm) and *trans*-Cr(en)$_2$(CN)$_2^+$ (432 nm) but higher than that of *trans*-Cr(cyclam)(CN)$_2^+$ (414 nm) (Table I). These data support the following order for these amine ligands in the spectrochemical series: cyclam > tet a > en > NH$_3$. The same relative positions for cyclam and tet a are also found for their corre-

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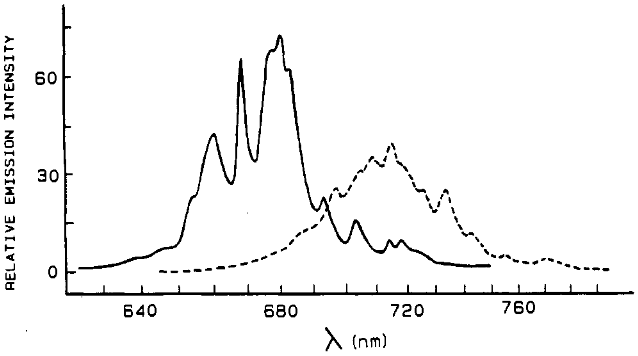

Figure 1. *High*-resolution steady-state emission spectra at 22 °C for 488-nm Ar ion laser excitation (Jarrell-Ash 500 laser Raman spectrometer) of acidified 10^{-3} M aqueous solutions of *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$ (—) and *trans*-$Cr(tet\ a)(CN)_2^+$ (---). The corresponding *low*-resolution spectra (Aminco-Bowman spectrometer) are very similar to those previously reported for the cyclam analogues.[1,4]

sponding diaquo complexes (Table I).

***trans*-[Cr(tet a)$(NH_3)_2](PF_6)_3 \cdot H_2O$.** The molar conductance of a 9.22×10^{-4} M aqueous solution (346 Ω^{-1} cm^2 mol^{-1}) is consistent with the 3:1 electrolyte status of the complex. The visible spectrum of the tet a complex shows evidence of slight splitting in the first spin-allowed LF band, $^4B_{1g} \rightarrow {}^4B_{2g}, {}^4E_g$ (D_{4h}), as is also observed for the corresponding *trans*-cyclam diammine complex.[1] The first LF maximum for *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$ (435 nm) occurs at a shorter wavelength than that of *trans*-$Cr(en)_2(NH_3)_2^{3+}$ (454 nm) but at a longer wavelength than that of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ (420 nm). The same conclusions can be drawn as were made earlier concerning relative ligand field strengths (cyclam > tet a > en $\sim$ NH_3).

The compound *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$ appears to be thermally stable in acidic aqueous solution. However, the complex is very sensitive to base hydrolysis (as is also observed for *trans*-$Cr(cyclam)(NH_3)_2^{3+}$).[1]

***trans*-[Rh(tet a)$(CN)_2]ClO_4 \cdot H_2O$.** The molar conductance of a 1.0×10^{-3} M aqueous solution (105 Ω^{-1} cm^2 mol^{-1}) compares favorably with the value of 90 Ω^{-1} cm^2 mol^{-1} reported for *trans*-$[Rh(cyclam)(CN)_2]ClO_4$,[3] and is in the range expected for a 1:1 electrolyte. The infrared spectrum displays a strong, unsplit cyanide stretch at 2120 cm^{-1}, consistent with an assignment of trans-geometry.

In Table I, the UV spectra of the new tet a dichloro and dicyano species are compared with the literature values for the corresponding cyclam complexes. The band appearing at longest wavelength is assigned as the spin-allowed $^1A_{1g} \rightarrow {}^1A_{2g}, {}^1E_g$ (D_{4h}) LF transition.

Photobehavior. *trans*-[Cr(tet a)$(CN)_2]ClO_4 \cdot 1.5H_2O$. In accord with the behavior of the cyclam analogue,[4] *trans*-$Cr(tet\ a)(CN)_2^+$ displays no discernible photoreaction in acidified aqueous solution (20 °C) after 8 h of excitation at 436 nm using a 1000-W Hg-Xe lamp. The compound exhibits an intense, highly structured, steady-state emission signal in room temperature solution, which is assigned to $^2A_{1g}, {}^2B_{1g} \rightarrow {}^4B_{1g}$ (D_{4h}) phosphorescence (Figure 1). For example, the lifetime in acidified aqueous solution at 20 °C (395 μs, Table II) is 18% longer than that observed for *trans*-$Cr(cyclam)(CN)_2^+$ (335 μs).[4] This value constitutes one of the longest lifetimes yet reported for an undeuterated Cr(III) complex in room temperature aqueous solution.

The steady-state emission spectrum on 436-nm excitation of an acidified aqueous solution of *trans*-$Cr(tet\ a)(CN)_2^+$ at 20.0 °C was also 1.20 times as intense as that of an absorbance-matched solution of *trans*-$Cr(cyclam)(CN)_2^+$. Since this value matches the corresponding emission lifetime ratio, it appears that the $^4B_{2g}$, $^4E_g \rightsquigarrow {}^2A_{1g}, {}^2B_{1g}$ (D_{4h}) intersystem crossing yield (ϕ_{ISC}) and the $^2A_{1g}, {}^2B_{1g} \rightarrow {}^4B_{1g}$ radiative rate constant values for these two species are very similar. The difference in phosphorescence intensity then is primarily associated with a difference in the summed nonradiative rate constants (k) from the doublet emitting level (i.e. $k_{tet\ a} < k_{cyclam}$). Due to the large energy gap anticipated,[1,4,21,22] back-ISC is considered an ineffective doublet-state deactivation pathway for both macrocyclic dicyano complexes and also for *cis*- and *trans*-$Cr(en)_2(CN)_2^+$. The longer room-temperature phosphorescence lifetimes for the macrocyclic species may therefore be attributed to their photoinertness—an interpretation that argues for a direct photochemical role for the ^2E_g (O_h) level in the non-macrocyclic cases.

Table II. Phosphorescence Lifetimes (μs) for Cr(III) and Rh(III) Complexes[a]

compd	T, K	lifetimes H_2O	 Me_2SO	 DMF
		Cr(III) Species		
$Cr(NH_3)_6^{3+}$ [17]	297	2.2	4	
	77		70	
trans-$Cr(cyclam)(NH_3)_2^{3+}$ [1]	293	55	136	
	77		180, 202[b]	
trans-$Cr(tet\ a)(NH_3)_2^{3+}$	323	2.6	16.5	
	319		22.0	
	314		29.8	
	313	4.7	28.8	
	303	11.1	58.4	
	293	22.0	88.5	
	77		179, 212[b]	
trans-$Cr(en)_2(CN)_2^+$ [4]	295	1	1[c]	
	77		210	
trans-$Cr(cyclam)(CN)_2^+$ [4]	295	335	330	
	77		355, 500[b]	
trans-$Cr(tet\ a)(CN)_2^+$	293	395	460[b]	
	77		560[b]	
		Rh(III) Species		
trans-$Rh(tet\ a)(CN)_2^+$	293	4.9	12.8	16.0
	77		247	258
trans-$Rh(cyclam)(CN)_2^+$	296[d]	8.0	16.0	16.7
	293	8.6		
	77[d]		189	292

[a] Solutions were acidified with several drops of 0.5 M HNO_3 to prevent possible base quenching. [b] 1:1 Me_2SO/H_2O. We thank a referee for pointing out that this solvent mixture forms a satisfactory glass at 77 K, in contrast to the extensive shattering that occurs with pure Me_2SO. [c] The corresponding *trans*-$Cr(NH_3)_4(CN)_2^+$ species has a 20 °C solution lifetime of 65 μs.[27] The origin of the large lifetime differences between these en and NH_3 analogues is not clear. [d] Reference 5.

***trans*-[Cr(tet a)$(NH_3)_2](PF_6)_3 \cdot H_2O$.** As found for the cyclam analogue,[1] the tet a compound exhibits a markedly decreased photoreactivity relative to that of $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$. For example, 350-nm photolysis (Rayonet RPR-100) of 0.02 M $HClO_4$ solutions of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ and *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$ for several hours results in only relatively small changes in the UV-visible spectra. A more detailed investigation of this inefficient photochemical pathway ($\phi_{rn} \leq 0.01$) is in progress.

The tet a species displays an intense, highly structured steady-state emission spectrum (Figure 1), which is assigned to $^2A_{1g}, {}^2B_{1g} \rightarrow {}^4B_{1g}$ (D_{4h}) phosphorescence. The phosphorescence lifetime in acidified aqueous solution at 19.9 °C is 22 μs (Table II), which is substantially longer than that reported for $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$, but 2.5 times shorter than that of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ (55 μs). A comparison of the steady-state emission intensities of absorbance-matched solutions of *trans*-$Cr(tet\ a)(NH_3)_2^{3+}$ and *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ in 0.1 M $HClO_4$ at 20.0 °C on 436-nm excitation, indicate the tet a phosphorescence quantum yield, ϕ_P, is 1.9 times smaller (thus $\phi_P(\text{tet a}) = 4.3 \times 10^{-4}$).[1] Despite these room-temperature differences, the macrocyclic lifetimes at 77 K are almost identical (Table II). These observations suggest that (i) ϕ_{ISC} is smaller for the cyclam species and (ii) the summed nonradiative rate constants (k) from the doublet level are greater for the tet a complex at room temperature.

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For acidified Me_2SO solution the lifetime data in Table II yield an activation energy of 12 kcal mol^{-1} over the range 29.4–50.2 °C; while those for 0.10 M $HClO_4$ provide a value of 14 kcal mol^{-1} between 19.9 and 50.0 °C. The corresponding values reported for *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ in Me_2SO (H^+) and 0.10 M $HClO_4$ are 16 and 18 kcal mol^{-1}, respectively.

These data are accommodated by a doublet excited-state relaxation model proposed by Endicott and co-workers[21-23] involving thermally activated surface crossing to a ground-state intermediate species, with subsequent partitioning between a reaction decay channel and nonradiative relaxation, which regenerates the parent ground state. For systems with highly constrained ligands, the reaction channel may be largely eliminated, which may result in very low reaction quantum yields. This possibility rationalizes the photobehavior of *trans*-$Cr(cyclam)(NH_3)_2^{3+}$,[1] $Cr(sep)_3^{3+}$,[21-23] and $Cr((9)aneN_3)_2^{3+}$ [24] (where sep is a sepulchrate ligand and $(9)aneN_3$ is 1,4,7-triazacyclononane). For *trans*-Cr(tet a)-$(NH_3)_2^{3+}$ a lower activation energy for doublet $\rightsquigarrow$ intermediate surface crossing than that for the cyclam analogue is in accord with the lifetime temperature dependencies and could result in a more prominent role for this decay process at room temperature. Such a situation would account for the shorter emission lifetimes of *trans*-Cr(tet a)$(NH_3)_2^{3+}$ in room-temperature solution, while the cyclam and tet a complexes have essentially identical lifetimes at 77 K (Table II).

***trans*-[Rh(tet a)(CN)$_2$]ClO$_4$·H$_2$O.** Under D_{4h} symmetry the lowest lying excited state, $^3T_{1g}$ (O_h), is split into ^3E_g and $^3A_{2g}$ sublevels. Since the $^3A_{2g}$ component is expected to be lower lying,[5] photolabilization should be primarily associated with Rh–amine bond cleavage. As found for its cyclam analogue,[5] the compound is essentially photoinert under LF excitation—an observation that attests to the effectiveness of such macrocyclic rings in eliminating amine ligand release. The compound displays a strong, broad, structureless emission centered at 480 nm in room-temperature aqueous, or Me_2SO solution, similar to that of *trans*-Rh(cyclam)$(CN)_2^+$, which is assigned to $^3A_{2g} \rightarrow {}^1A_{1g}$ (D_{4h}) phosphorescence. The emission is quenched in strongly basic solution and regenerated on reacidification.

At 20 °C and 280-nm excitation, the steady-state emission intensity of an acidified aqueous solution of *trans*-Rh(tet a)$(CN)_2^+$ was 0.46 times that of an absorbance matched solution of *trans*-Rh(cyclam)$(CN)_2^+$. The emission lifetimes are exceptionally long by normal Rh(III) standards.[5] The lifetime in acidified aqueous solution at 20 °C is 0.57 times that of *trans*-Rh(cyclam)$(CN)_2^+$, while their lifetimes are comparable at 77 K (Table II). These room-temperature differences are accompanied by substantial differences in the apparent activation energies for emission. Aqueous lifetime data from 12.3 to 53.0 °C yield an activation energy of 9.0 kcal mol^{-1} for the cyclam species, while the tet a value from 11.2 to 39.0 °C is only 6.0 kcal mol^{-1}. A thermally activated process such as $^3A_{2g} \rightsquigarrow {}^3E_g$ internal back-conversion may be an important $^3A_{2g}$ relaxation pathway near room temperature—the smaller tet a energy gap then accounting for the compound's shorter lifetime and smaller steady-state emission intensity at 20 °C.

It is tempting to link the enhanced room-temperature emission intensity and lifetime of *trans*-Rh(cyclam)$(CN)_2^+$ and *trans*-Rh(tet a)$(CN)_2^+$ with elimination of the $^3A_{2g}$ photoreaction, since reaction and emission are competitive processes out of this excited level. However, for Rh(III) systems where the ^3E_g sublevel lies lower, *non*reactive radiationless processes are often the dominant ^3E_g relaxation pathways.[25] We have noted for *trans*-Rh(cyclam)$(CN)_2^+$ that since the lower lying $^3A_{2g}$ level involves excitation in the in-plane amine positions, the macrocyclic ring may minimize the distortion normally expected in the equilibrated triplet level. The absence of significant distortion may significantly reduce the rate constants for $^3A_{2g}$ radiationless deactivation processes.[26] A clearer assessment of the actual role played by the tet a and cyclam macrocyclic rings may be possible from a study of the photobehavior of *trans*-Rh(en)$_2(CN)_2^+$, which also has a lower lying $^3A_{2g}$ level.

Conclusion

The present findings are similar to those previously observed for related Cr(III) and Rh(III) complexes with the macrocyclic ligand cyclam.[1,4,5] It appears that steric and electronic factors associated with the additional presence in the tet a ligand of six methyl groups on the ring periphery have only a small influence on the photophysical and photochemical properties of these complexes.

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Registry No. *trans*-[Cr(teta)$(CN)_2$]ClO_4, 101347-93-7; *trans*-[Cr(teta)$(NO_3)_2$]NO_3, 101374-85-0; *trans*-[Cr(teta)$(NH_3)_2$]$(PF_6)_3$, 101347-95-9; *trans*-[Rh(teta)Cl_2]ClO_4, 101469-38-9; *trans*-[Rh(teta)$(CN)_2$]ClO_4, 101375-05-7; *trans*-[Cr(teta)Cl_2]ClO_4, 86916-01-0.

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Crystal Structures of the Tetra-*n*-butylammonium Salts of the $AuCl_2^-$, $AuBr_2^-$, and AuI_2^- Ions

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The dihaloaurate(I) complex ions $[AuX_2]^-$ (X = Cl, Br, I) have been known for some time[2,3] although their systematic synthesis and isolation as tetraalkylammonium salts were only achieved quite recently, according to reactions 1–3.[4]

$$2[R_4N][AuCl_4] + PhNHNH_2{\cdot}HCl \rightarrow [R_4N][AuCl_2] + [R_4N][PhAuCl_3] + N_2 + 4HCl \tag{1}$$

$$[R_4N][AuBr_4] + CH_3COCH_3 \rightarrow [R_4N][AuBr_2] + BrCH_2COCH_3 + HBr \tag{2}$$

$$[R_4N][AuBr_2] + 2[R_4N]I \rightarrow [R_4N][AuI_2] + 2[R_4N]Br \tag{3}$$

These reactions involve the easily available ionic precursors $AuCl_4^-$ and $AuBr_4^-$ and selective reducing agents. Thus, phenylhydrazine was used in reaction 1 because it is less reducing than hydrazine, which would lead to metallic or colloidal gold. The mechanism of this interesting reaction, which also led to the arylgold(III) complex $[PhAuCl_3]^-$, has been investigated and found to involve a 1,2-shift of the phenyl ring from a nitrogen atom of Ph*N*HNH$_2$ to the gold center via a coordinated nitrene intermediate.[5] Reaction 2 is very clean since the organic product formed upon oxidation of acetone is volatile. This reaction is

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