Similar fragmentation for Cu^{III}(H$_{-2}$Aib$_3$) gives the tertiary radical NH$_2\dot{C}$(CH$_3$)$_2$. Thus, the presence of the α-carbon hydrogen in the first peptide residue increases the favorability of carbon–carbon cleavage by paths B and C over path A. The dipeptide amide yield for σ- and π-LMCT irradiation is the same for both Cu^{III}(H$_{-2}$AAib$_2$) and Cu^{III}(H$_{-2}$Aib$_3$). This supports the argument that the dipeptide amide is formed from a prompt cleavage of the Cu^{II}L· state (eq 15b and 17b (path C)). Since the two tripeptides are identical at the carboxylate end, similar dipeptide amide yields are seen.

Conclusions

The ultraviolet–visible absorption spectra for copper(III)–peptide complexes show two ligand-to-metal charge-transfer bands. The assignment proposed for the bands is σ N(peptide)-to-copper(III) charge transfer for the 250–280 nm band and π N(peptide)-to-copper(III) charge transfer for the 360–400 nm band. The assignment is consistent with the photochemical behavior of copper(III)–peptide complexes as well as with the electronic spectral features of other d^8 transition-metal complexes of ligands with σ and π symmetries.

The photoredox decomposition of copper(III)–peptide complexes containing the α-aminoisobutyric acid residue is very efficient. The wavelength dependence of the disappearance quantum yield exhibits plateau regions for both the σ- and π-LMCT bands with $\phi(\sigma)$ varying from 0.008 to 0.45 and $\phi(\pi)$ varying from 0.09 to 0.23. The quantum yield spectrum depends on the length of the peptide ligand as well as the number of α-carbon methyl groups. The ϕ values decrease as hydrogen atoms are substituted for the methyl groups. It is suggested that an increased rate constant for nonradiative relaxation promoted by C–H vibrations is responsible for the decrease in ϕ.

The primary photoproducts proposed for the photodecomposition are σ and π copper(II)–amidyl radicals. For the tripeptide complexes both dissociation from copper(II) and fragmentation of the amidyl radicals are very rapid processes and occur before redox reactions with the copper(III) complex. The products of the photodecomposition of copper(III) tripeptides are copper(II) in 100% yield and the original tripeptide ligand in 50% yield (based on the initial amount of copper(III)) independent of the irradiation wavelength or solution pH. The remaining 50% of the tripeptide ligand is recovered as peptide fragments, acetone, carbon dioxide, and ammonia. The relative proportions and identity of peptide fragments depend on the LMCT band irradiated and on solution pH. In acid the copper(II)–amidyl radical dissociates into copper(II) and the amidyl radical. Initial fragmentation is by C–C bond cleavage followed by reduction of a second copper(III)–tripeptide complex and hydrolysis to give the amino acid, amino acid amide, dipeptide, and dipeptide amide. In base the divalent-metal-catalyzed formation of a 3-substituted hydantoin is the predominant reaction with smaller amounts of the peptide fragments seen in acid.

In summary, although the initially populated singlet LMCT excited state is probably very short-lived, another Cu^{II}L· state (triplet probably), **8**–**11**, has a lifetime long enough for reactions that are dependent on medium conditions to occur such as dissociation of the Cu^{II}L· species before fragmentation. When fragmentation of Cu^{II}L· occurs, the reactivity is governed by the σ or π symmetry of the radical species.

Acknowledgment. This investigation was supported by Public Health Service Grant No. GM 19775 from the National Institute of General Medical Sciences, by a Phillips Petroleum Fellowship (A.W.H.), and by American Chemical Society Analtyical Division Summer Fellowship sponsored by the Society of Analytical Chemists of Pittsburgh (A.W.H.). The assistance of Professor David R. McMillin during this work is gratefully acknowledged.

Registry No. **1**, 69990-31-4; **2**, 87783-57-1; Cu^{III}(H$_{-2}$AAib$_2$), 87801-41-0; Aib$_3$, 50348-89-5; AAib$_2$, 83917-78-6; Aib, 62-57-7; Aiba, 16252-90-7; Aib$_2$, 39692-70-1; Aib$_2$a, 87453-26-7; Aa, 7324-05-2; AAib, 84799-80-4; AAiba, 87453-25-6; (CH$_3$)$_2$C=O, 67-64-1; ammonia, 7664-41-7.

Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. 36. Electronic Spectra and Photochemistry of Some *trans*-(Tetraamine)ruthenium(III) Complexes

CHUNG-KWONG POON,* TAI-CHU LAU, and CHI-MING CHE

Received June 7, 1982

The electronic absorption spectra of an extensive series of tetraamine complexes of the type *trans*-[RuLX$_2$]$^+$ (X = Cl, Br, or I) have been analyzed. In general, two ligand-to-metal charge-transfer (CTTM) transitions of (p$_\pi$)$_X$ → d$_\pi$* origin are observed. The wavelength of the lowest energy band increases gradually with increasing chelation and steric congestion of the amine ligand L around the ruthenium(III) ion. The splitting of the (p$_\pi$)$_X$ → d$_\pi$* transition is largest for the two sterically congested teta and tetb complexes, where teta and tetb represent *C-meso-* and *C-rac-*5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively, but decreases with the nature of X, Cl > Br > I. The spectra of *trans*-[Ru(cyclam)X$_2$]X (X = Cl or Br) have been resolved at low temperature (~30 K), and (p$_\sigma$)$_X$ → d$_\pi$* transitions have been assigned to some of these resolved bands. Photochemistry of *trans*-[RuLIX]$^+$ (L = (en)$_2$, X = Cl, Br, or I; L = 2,3,2-tet or cyclam, X = I; en, 2,3,2-tet, and cyclam represent ethane-1,2-diamine, 3,7-diazanonane-1,9-diamine, and 1,4,8,11-tetraazacyclotetradecane, respectively) has been investigated. Irradiation at the lowest CTTM band (λ_{irr} > 500 nm) leads to stereoretentive aquation of X$^-$ with quantum yields independent of X but decreasing with increasing chelation of L. Domination of the Ru^{II}–I· entity in the CTTM excited state has been discussed. Irradiation of the second CTTM band leads to photoaquation with concomitant stereochemical change. The results are interpreted in terms of a quartet ligand field state as the photoreactive precursor, and a dissociative model previously proposed to explain the photostereochemistry of d^6 metal complexes has been useful also for this d^5 system.

Introduction

The chemistry of ruthenium(III) amine complexes has been an area of active research in recent years.[1–4] However, relatively little photochemical work has been reported. It is generally believed that the low-lying and partially vacant d$_\pi$*

---

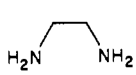
(1) Ford, P. C. *Coord. Chem. Rev.* **1970**, *5*, 75.

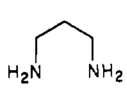
(2) Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17.

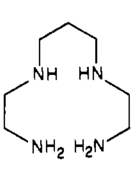
(3) Broomhead, J. A.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 826.

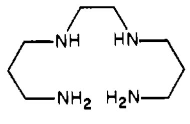
0020-1669/83/1322-3893$01.50/0

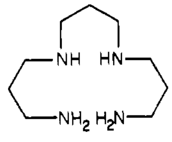
orbital on ruthenium(III) will significantly affect the photochemical behavior of these complexes. Excitation at the ligand-to-metal charge-transfer (CTTM) bands may be expected to lead to, among other pathways, photoredox reactions. However, in contrast to this expectation, most ruthenium(III) amine complexes do not undergo photoredox reactions but give rise to photosubstitutions and photoisomerizations.[5-8] Recently, the photochemical behavior of *cis*-$[Ru(NH_3)_4X_2]^+$ (X = Cl, Br, or I) has been interpreted in terms of some photoreactive quartet states.[9] Very recently, different photochemical reactions for the CTTM and ligand field (LF) excited states of *trans*-$[Ru(en)_2X_2]^+$ (X = Cl, Br, or I) have been separately observed.[8] As a continuous effort to understand more about the mechanisms of photochemical reactions from these two different excited states, we report here our investigation into the chelation effects of L and leaving group effects of X on the photochemistry of *trans*-$[RuLIX]^+$ complexes (L = $(en)_2$, X = Cl, Br, or I; L = 2,3,2-tet or cyclam, X = I; en, 2,3,2-tet, and cyclam (or $[14]aneN_4$) represent ethane-1,2-diamine, 3,7-diazanonane-1,9-diamine, and 1,4,8,11-tetraazacyclotetradecane, respectively). In order to understand the nature of the excited states, we also attempt to discuss the electronic absorption spectra of a series of related complexes of the type *trans*-$[RuLX_2]^+$ [X = Cl, Br, or I; L = $(NH_3)_4$, $(en)_2$, $(1,3\text{-}pn)_2$ (1,3-pn = propane-1,3-diamine), 2,3,2-tet, 3,2,3-tet (4,7-diazadecane-1,10-diamine), 3,3,3-tet (4,8-diazaundecane-1,11-diamine), cyclam, $[15]aneN_4$ (1,4,8,12-tetraazacyclopentadecane), $[16]aneN_4$ (1,5,9,13-tetraazacyclohexadecane), and teta and tetb (*C-meso*- and *C*-rac-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively)].

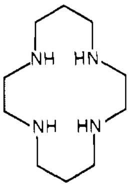

en

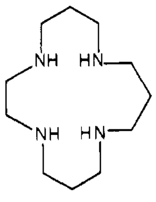

1,3-pn

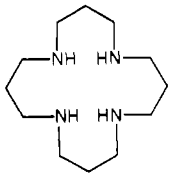

2,3,2-tet

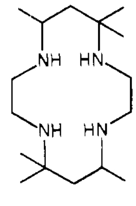

3,2,3-tet


3,3,3-tet


cyclam ([14]aneN$_4$)


[15]aneN$_4$


[16]aneN$_4$


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

Experimental Section

The complexes reported here were prepared according to published methods.[4,10] Photolyses were performed by using either a 350-W high-pressure mercury short-arc lamp (Illumination Industries Inc.) coupled with a high-intensity monochromator (Bausch and Lomb) or a 2000-W xenon-arc clinical photoirradiator system (Applied Photophysics Ltd.). Incident light intensities were taken from the average values measured just before and after each photolysis experiment by using either ferrioxalate actionometry[11,12] (below 450 nm) or Reineckate actinometry[13] (above 450 nm). Electronic absorption spectra were measured with a Beckman Acta CIII spectrophotometer. To minimize any effects arising from secondary photolysis, quantum yields were determined within the first 10% of the photolysis reactions. They were found to be independent of acid concentration (0.01–0.1 mol dm^{-3}), complex concentration [(1.0–8.0) × 10^{-4} mol dm^{-3}], and the presence or absence of oxygen in the reaction solutions.

Results

When an acidic solution of *trans*-$[RuLIX]^+$ (L = $(en)_2$, X = Cl or Br; L = 2,3,2-tet or cyclam, X = I) (in either toluene-*p*-sulfonic acid (HpTS) or methanesulfonic acid (CH_3SO_3H) (0.01–0.1 mol dm^{-3})) was irradiated at the first charge-transfer band (~550 nm), the intensity of the band gradually decreased with isosbestic points maintained for about 2 h of the reaction [L = $(en)_2$, X = Cl (535 nm), Br (554 nm); L = 2,3,2-tet, X = I (490 and 540 nm); L = cyclam, X = I (578 nm)]. The spectral changes were identical with those of the corresponding stereoretentive aquation[14] of the complexes. Addition of an excess of the corresponding NaX to the partially photolyzed solution gave back quantitatively the starting *trans*-$[RuLIX]^+$ complex. The pH of the solution remained unchanged even at pH = 3.5 during photolysis indicating that amine hydrolysis could not be significant. Ruthenium(II) could not be detected. All these observations suggest that the charge-transfer excitation at ~550 nm leads to the production of *trans*-$[RuLI(H_2O)]^{2+}$. Quantum yields were determined spectrophotometrically from the known molar extinction coefficients. (L = $(en)_2$: $\epsilon_{ICl} = 2040$, $\epsilon_{IH_2O} = 780$ cm^{-1} mol dm^{-3} at 520 nm; $\epsilon_{IBr} = 2500$, $\epsilon_{IH_2O} = 700$ cm^{-1} mol dm^{-3} at 523 nm. L = 2,3,2-tet: $\epsilon_{I_2} = 3550$, $\epsilon_{IH_2O} = 1770$ cm^{-1} mol dm^{-3} at 579 nm. L = cyclam: $\epsilon_{I_2} = 2610$, $\epsilon_{IH_2O} = 1120$ cm^{-1} mol dm^{-3} at 603 nm).

Irradiation of these complexes, *trans*-$[RuLIX]^+$ [L = $(en)_2$, X = Cl or Br; L = 2,3,2-tet, X = I], at $\lambda_{irr} < 400$ nm, however, leads to a different kind of spectrophotometric change, also with isosbestic points maintained during the early stage of the reactions [L = $(en)_2$, X = Cl (543 nm), Br (555 nm); L = 2,3,2-tet, X = I (536 and 636 nm)]. Addition of an excess of the corresponding NaX to the partially photolyzed solution did not give back the starting complex. In the case of *trans*-$[Ru(en)_2ICl]^+$ where the corresponding cis isomer has been properly characterized,[15] it was deduced that treatment with NaCl of the photolyzed solution gave a mixture of *cis*- and *trans*-$[Ru(en)_2ICl]^+$. Since we have not been able to obtain a reliable spectrum of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$, we could not determine accurately the total aquation quantum yield and the isomeric composition of the $[Ru(en)_2I(H_2O)]^{2+}$ products. However, it could be estimated quite reliably that the product was mainly cis (>85%). The quantum yield for the production of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$ was determined by treating the photolyzed solution with excess NaCl, thus regenerating the $[Ru(en)_2ICl]^+$ complexes via the stereoretentive thermal anation reactions, and then measuring the amount of *cis*-$[Ru(en)_2ICl]^+$ produced (ϵ values for *trans*- and *cis*-$[Ru(en)_2ICl]^+$ are 2100 and 950 cm^{-1} mol^{-1} dm^3, respectively, at 520 nm). On the other hand, for the *trans*-$[Ru(en)_2IBr]^+$

---

(4) Poon, C. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1980**, 756.
(5) Wells, W. L.; Endicott, J. F. *J. Phys. Chem.* **1971**, *75*, 3075.
(6) Ohyoshi, A.; Takebayashi, N.; Hiroshima, Y.; Yoshikuni, K.; Tsuji, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1414.
(7) Rerek, M. E.; Sheridan, P. S. *Inorg. Chem.* **1980**, *19*, 2646.
(8) Poon, C. K.; Lau, T. C.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1982**, 531.
(9) Sakaki, S.; Tsuji, K.; Ohyoshi, A. *J. Phys. Chem.* **1979**, *83*, 1344.
(10) Poon, C. K.; Che, C. M. *Inorg. Chem.* **1981**, *20*, 1640.
(11) Parker, C. A.; Hatchard, G. C. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(12) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1967.
(13) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.
(14) Lau, T. C., unpublished results.
(15) Broomhead, J. A.; Kane-Maguire, L. A. P. *J. Chem. Soc.* **1967**, 546.

Table I. Quantum Yields for the Photolysis of Some *trans*-[RuLAX]$^+$ Cations in Acidic Aqueous Solutions (0.01 mol dm^{-3} HpTS)

L	A	X	λ_{irr}/nm	primary product^a	ϕ
$(en)_2$	I	I	310^b	*cis*-$[Ru(en)_2I(H_2O)]^{2+}$	2.5×10^{-3}
			310^c	*cis*-$[Ru(en)_2I_2]^+$	2.4×10^{-3}
			390^d	*cis*-$[Ru(en)_2I(H_2O)]^{2+}$	2.3×10^{-3}
			545^d	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	7.2×10^{-4}
			563^d	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	7.4×10^{-4}
	I	Br	380	*cis*-$[Ru(en)_2I(H_2O)]^{2+}$	$\sim 2 \times 10^{-3}$
			520	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	3.5×10^{-4}
			550	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	3.3×10^{-4}
	I	Cl	363	*cis*-$[Ru(en)_2I(H_2O)]^{2+}$	1.5×10^{-3}
			520	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	3.2×10^{-4}
			550	*trans*-$[Ru(en)_2I(H_2O)]^{2+}$	2.8×10^{-4}
2,3,2-tet	I	I	385	*cis*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$	$\sim 5 \times 10^{-4}$
			550	*trans*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$	1.8×10^{-4}
			580	*trans*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$	2.2×10^{-4}
cyclam	I	I	580	*trans*-$[Ru(cyclam)I(H_2O)]^{2+}$	3.1×10^{-5}

^{a} Cis primary product means >85% isomeric distribution except in the case of *cis*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$ the isomeric distribution of which is less certain; trans primary product means 100% retention of configuration. ^{b} In CH_3SO_3H (0.1 mol dm^{-3}). ^{c} In CH_3SO_3H (0.1 mol dm^{-3}) + KI (4 mol dm^{-3}). ^{d} Reference 8.

Table II. Ultraviolet Absorption Spectra of Some *trans*-$[RuLCl_2]^+$ Cations in Aqueous Solutions

L	λ_{max}/nm^a
$(NH_3)_4$^{b}	331 (5.27), 290 br (sh) (0.900)
$(en)_2$^{c}	343 (3.85), 292 br (sh) (0.800), 272 br (sh) (0.900)
$(en)_2$^{d}	342 (4.08), 295 (sh) (0.745), 268 (sh) (0.810)
$(1,3\text{-pn})_2$^{c}	346 (3.46), 291 (1.38)
2,3,2-tet^c	349 (3.43), 297 (1.16)
3,2,3-tet^c	351 (2.56), 302 (1.23)
3,3,3-tet^c	353 (2.61), 305 (1.45)
cyclam^c	357 (2.26), 312 (1.25)
cyclam^e	358 (2.56), 315 (1.23)
[15]aneN_4^{e}	359 (2.41), 317 (1.35)
[16]aneN_4^{e}	360 (2.23), 318 (1.32)
teta^b	378 (2.31), 312 (1.70)
tetb^b	380 (2.34), 310 (1.82)

^{a} Molar absorptivities (cm^{-1} mol dm^{-3} $\times 10^3$) are given in parentheses; br = broad, sh = shoulder. ^{b} This work. ^{c} Reference 4; in 0.1–1 mol dm^{-3} HCl. ^{d} Broomhead, J. A.; Kane-Maguire, L.; Wilson, D. *Inorg. Chem.* **1975**, *14*, 2575. ^{e} Reference 17.

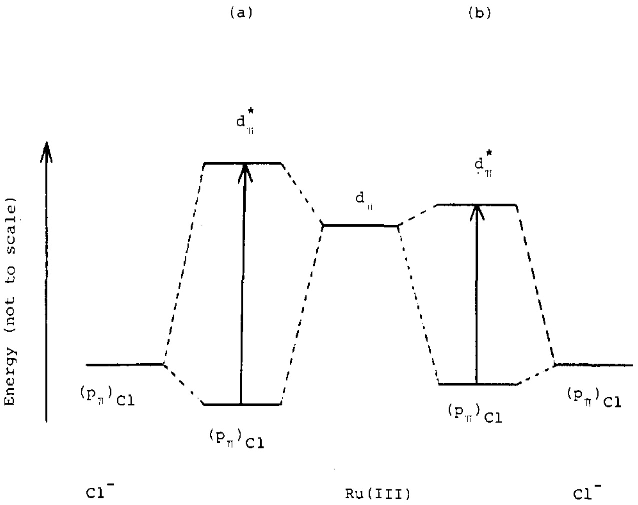


Figure 1. Effect of $d_\pi(Ru)$–$p_\pi(Cl)$ overlap on the relative λ_{max} value: (a) large overlap; (b) small overlap.

system, the corresponding cis isomer has not been characterized either in the solid state or in solution. On the assumption that the variation in the absorption spectra of *cis*- and *trans*-$[Ru(en)_2IX]^+$ (X = Cl, Br, or I) was systematic in the visible region and with knowledge of all the other five spectra, the visible spectrum of *cis*-$[Ru(en)_2IBr]^+$ was estimated and hence the quantum yields for the production of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$. Again the photoaquation gave mainly the cis product (>85%). Such a method only gave an approximate value for the quantum yield, which is accurate to about 40%. However, such an estimate is good enough to serve the present purpose of comparative studies. The situation of *trans*-$[Ru(2,3,2\text{-tet})I_2]^+$ is less fortunate since the absorption spectra of both *cis*-$[Ru(2,3,2\text{-tet})I_2]^+$ and *cis*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$ are unknown and they could not be easily estimated by the method described above. With the assumption that the spectral relationship in the 2,3,2-tet system is similar to that in the $(en)_2$ system, a quantum yield of about 5×10^{-4} could be estimated for the photoproduction of *cis*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$, which, again, constituted the major reaction product (>85%). These values, however, must only be regarded as approximate. The photochemical behavior of *trans*-$[Ru(cyclam)I_2]^+$ upon irradiation at $\lambda_{irr} < 400$ nm is rather complicated including aquation and possibly redox and ligand reactions. We have not yet been able, however, to identify all these reaction products and deduce the photochemical behavior of this complex. Finally, the photochemical behavior of *trans*-$[Ru(en)_2I_2]^+$ upon irradiation at 390 nm has been shown to give mainly the *cis*-$[Ru(en)_2I(H_2O)]^{2+}$ product (>85%).[8] This reaction is now also investigated at a shorter wavelength, 310 nm. Similar behavior for the generation of *cis*-$[Ru(en)_2I(H_2O)]^{2+}$ has been noted and the quantum yields were determined as described previously.[8] All these results are collected in Table I.

Discussion

(1) Electronic Absorption Spectra of *trans*-$[RuLX_2]^+$ Species. The electronic absorption spectra of *trans*-dihalogeno(tetraamine)ruthenium(III) complexes (Table II) are dominated by ligand-to-metal charge-transfer (CTTM) transitions. Among the four different types of transitions, viz. $(p_\pi)_X \rightarrow d_\pi^*$, $(p_\sigma)_X \rightarrow d_\sigma^*$, $(p_\pi)_X \rightarrow d_\sigma^*$, and $(p_\sigma)_X \rightarrow d_\pi^*$, the former two types of transitions are expected to be much more intense than the latter two. For the most symmetrical *trans*-$[Ru(NH_3)_4Cl_2]^+$ of D_{4h} symmetry, only one electric-dipole-allowed $(p_\pi)_{Cl} \rightarrow d_\pi^*$ transition, i.e. $e_u \rightarrow e_g^*$, is expected and it is assigned to the first intense band at 331 nm.[16] Recently, Walker and Taube[17] commented that for *trans*-$[Ru(mac)Cl_2]^+$, where mac represents [*n*]aneN_4 (*n* = 14–16), the interaction between the chloride ligands and the hydrogen atoms attached to nitrogens of the much structured mac ligands would split the degeneracy of the chloride $(p_\pi)_{Cl}$ levels producing two Laporte-allowed transitions, viz. $a_u \rightarrow b_g^*$ and $b_u \rightarrow b_g^*$, and these are assigned to the bands near 358 and 315 nm, respectively. From Table II, it is quite obvious that the spectra of teta, tetb, and other open-chain tetraamine complexes also possess two $(p_\pi)_{Cl} \rightarrow d_\pi^*$ transitions, with the first λ_{max} gradually increasing with L in the following order: $(NH_3)_4$ < $(en)_2$ < $(1,3\text{-pn})_2$ < (2,3,2-tet) < (3,2,3-tet) < (3,3,3-tet) < cyclam < [15]aneN_4 < [16]aneN_4 < teta < tetb. This variation of λ_{max} with the nature of L can be explained in terms of steric constraints with large chelate ligands. The large steric repulsion distorts the position of chloride from the *z* axis and lengthens the Ru–Cl bond. This decreases the d_π–p_π overlap and destabilizes the d_π^* orbital to a lesser extent (Figure 1). Thus, a larger L results in a longer λ_{max}. Indeed the two most sterically hindered teta and tetb complexes have the longest λ_{max}. Further, it might have been thought that the

---

(16) Verdonck, E.; Vanquickenborne, L. G. *Inorg. Chem.* **1974**, *13*, 762.

(17) Walker, D. D.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2828.

Table III. Ultraviolet Absorption Spectra of *trans*-[Ru(cyclam)Br_2]$^+$ in Various Solvents

solvent	λ_{max}/nm	solvent	λ_{max}/nm
H_2O	428, 407 (sh), 355	CH_3CN	433, 412 (sh), 358
Me_2SO	431, 410 (sh), 357	C_2H_5OH	436, 415 (sh), 358
DMF	432, 409 (sh), 358	solid KBr pellet	435, 412, 352

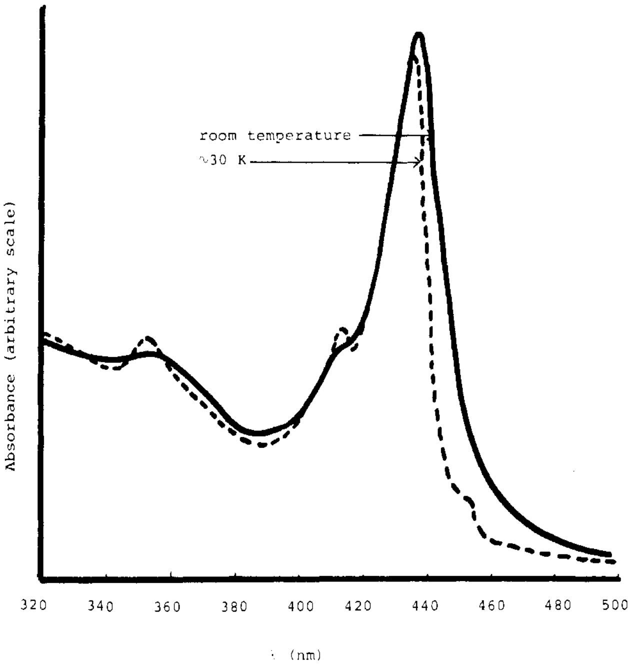


Figure 2. KBr-pellet spectra of *trans*-[Ru(cyclam)Br_2]Br: (a) room temperature, solid line; (b) ~30 K, dashed line.

much longer λ_{max} for the teta and tetb species could have arisen from solvation effects. The sterically hindered macrocyclic ligands would make the $(p_\pi)_{Cl}$ orbitals of the chloride ligand less solvated, hence leading to an overall increase in their energy levels. On the other hand, the metal $d_\pi{}^*$ levels are not much affected by solvation. Although solvation indeed affects the λ_{max} value (Table III), the effect is small as shown by the small difference in the λ_{max} value of *trans*-[Ru(cyclam)Br_2]$^+$ in water (significant solvation) and in KBr pellet (little solvation). Thus, the influence of solvation on the spectral feature seems minor. The splitting of the $(p_\pi)_X \rightarrow d_\pi{}^*$ transitions would be attributable to the interaction between the axial $(p_\pi)_X$ orbitals of the axial halide ligands and the equatorial amine ligand L in *trans*-[$RuLX_2$]$^+$. This interaction is expected to depend directly on the ability of X to hydrogen bond with the amine proton but inversely on the Ru–X bond length. Thus, it is to be expected that the separation between the two $(p_\pi)_X \rightarrow d_\pi{}^*$ transitions would decrease in the order of X = Cl > Br > I for a given amine ligand L. The absorption spectra of *trans*-[Ru(cyclam)X_2]$^+$ have been measured in dimethyl sulfoxide (Me_2SO).[10] It is obvious that the splitting of the $(p_\pi)_X \rightarrow d_\pi{}^*$ transitions indeed decreases in the above order of X (Cl, 4400 cm^{-1}; Br, 1200 cm^{-1}; I, band not resolvable).

Although the two-band pattern is rather typical for most *trans*-[$RuLX_2$]$^+$ complexes, the situation is less clear-cut for *trans*-[Ru(en)$_2Cl_2$]$^+$. Apart from the intense band at 343 nm, a broad band that is probably resolvable into several individual transitions is found at about 292 nm. It is not certain as to whether this broad 292-nm band is due to the other $(p_\pi)_{Cl} \rightarrow d_\pi{}^*$ transition or due to the $(p_\sigma)_{Cl} \rightarrow d_\pi{}^*$ transition or indeed a combination of the two. According to Jørgensen's relationship[18] between the energy of a charge-transfer band and the optical electronegativities of the donor and the acceptor orbitals, it could be deduced that the $(p_\sigma)_X \rightarrow d_\pi{}^*$ transitions occur at about 290 nm for X = Cl, 340 nm for X = Br, and 380 nm for X = I. Thus, the absorption bands at 292 nm for *trans*-[Ru(en)$_2Cl_2$]$^+$ in 0.1 mol dm^{-3} HCl and at 348 and 388 nm for *trans*-[Ru(en)$_2X_2$]$^+$, X = Br and I, respectively, in methanolic solution[4] could be assigned to the $(p_\sigma)_X \rightarrow d_\pi{}^*$ transition. A closer look at the shape of the electronic absorption spectra of most *trans*-[$RuLCl_2$]$^+$ complexes suggested that the absorption bands might be resolvable into sums of several transitions. At room temperature, the KCl pellet of *trans*-[Ru(cyclam)Cl_2]Cl displays two bands at 363 and 317 nm and a rising tail below 295 nm. When the KCl pellet is cooled down to ~30 K, the first two bands are sharpened and a shoulder appears at 280 nm along the rising tail. The band at 280 nm is thus assigned to the $(p_\sigma)_{Cl} \rightarrow d_\pi{}^*$ transition. Similarly, the low-temperature spectrum of the KBr pellet of *trans*-[Ru(cyclam)Br_2]Br (Figure 2) gives four bands at 452 (sh), 435, 412, and 352 nm. The 352-nm band is assignable to the $(p_\sigma)_{Br} \rightarrow d_\pi{}^*$ transition, and the 435- and 412-nm bands are assignable to the two $(p_\pi)_{Br} \rightarrow d_\pi{}^*$ transitions. The band at 452 nm is very weak ($\epsilon \sim 100$ cm^{-1} M^{-1}) and has not been observed in the room-temperature spectra of any *trans*-[$RuLBr_2$]$^+$ species. This may probably be a Laporte-forbidden ligand field transition. Furthermore, a closer look at the low-temperature spectrum of *trans*-[Ru(cyclam)Cl_2]Cl revealed that the 363-nm band is not quite Gaussian. The tail at the low-energy side is rather broad. This indicates the possible overlapping of one or more weaker transitions under this strong 363-nm band. Unfortunately, the spectrum cannot be resolved further. These weaker transitions may represent the Laporte-forbidden ligand field transitions, but the exact assignment still awaits further spectroscopic investigation.

(2) Photochemistry of *trans*-[RuLIX]$^+$ Complexes. Previously we have shown[8] that the CTTM transition of *trans*-[Ru(en)$_2I_2$]$^+$, unlike the corresponding dichloro and dibromo systems, is well separated from the ligand field band that occurs at much higher energy and, therefore, two distinctly different types of chemical reactions could be observed from these two different excited-state precursors. Irradiation at 545 nm (or 563 nm) puts the complex into the CTTM excited state with the metal ion formally in the ruthenium(II) state ($t_{2g}{}^6$ configuration). The observed photoaquation with complete stereoretention is fully consistent with the known thermal aquation stereochemistry of this class of complexes, *trans*-[Ru(en)$_2X_2$]$^{n+}$ (*n* = 0 or 1, X = Cl, Br, or I).[14,19] On the other hand, irradiation at 390 nm would eventually put the complex into the ligand field excited state, which leads to photoaquation with concomitant stereochemical change.[8] The possibility of interstate crossing to the lowest CTTM excited state is unlikely; otherwise, the same photochemistry of stereoretentive aquation would have been observed. In this paper, we have investigated the photochemistry of *trans*-[$RuLI_2$]$^+$ with increasing chelation of L on the one hand, and of *trans*-[Ru(en)$_2$IX]$^+$ with different leaving groups X (X = Cl, Br, or I), in order to understand better the mechanism of the photochemical reactions. It is obvious from Table I that the behavior of all the complexes under present investigation is consistent with the two reaction precursor models for this class of complexes.

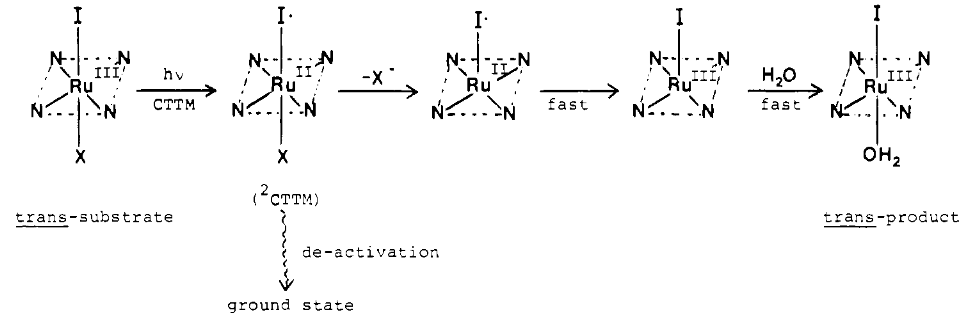
For the stereoretentive aquation of *trans*-[$RuLI_2$]$^+$ from the CTTM excited states ($\lambda_{irr} > 500$ nm), the gradual decrease in quantum yields is closely related to the corresponding decrease in the thermal aquation rates of *trans*-[$RuLX_2$]$^{n+}$ (*n* = 1 or 0)[14,19] with increasing chelation around the ruthenium ion. For the thermal reactions, a dissociative mechanism

---

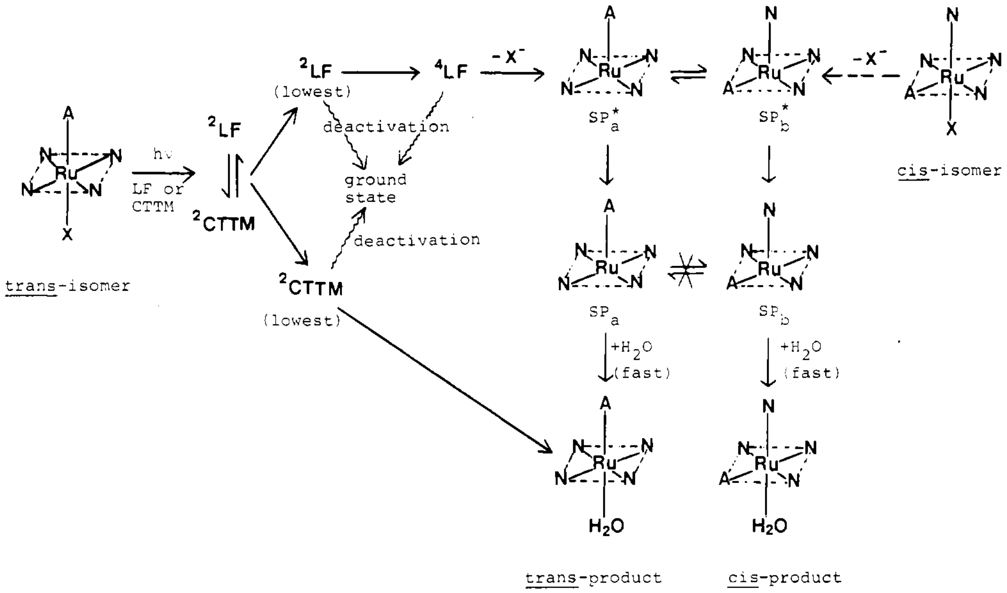
[18] Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Oxford University Press: Oxford, England, 1962.

[19] Poon, C. K.; Isabirye, D. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2115.

Scheme I



Scheme II



involving a square-pyramidal intermediate with the remaining halide in the apical position (apical isomer) was suggested.[19] This apical square-pyramidal intermediate is also favorable for reactions in the CTTM excited states since no electron is located in the σ^* level along the I–Ru–I axis (see later text for ligand field excited states). Therefore, the decreasing rates of dissociation of an iodide ion with increasing chelation from *trans*-$[RuLI_2]^+$ in the CTTM excited states mean that the quantum yields would also decrease. This assumes that the deactivation processes are less affected by this chelation effect. The observation that the excitation of the $(p_\pi)_I \rightarrow d_\pi{}^*$ transition, momentarily generating a ruthenium(II) ion and an iodine radical, only leads to the aquation of X^- is very significant in demonstrating that the leaving group initially departs as a halide ion, not a free radical, from the CTTM-excited *trans*-$[Ru(en)_2IX]^+$, with heterolytic bond fission. This explains the absence of photoreduction observed in this system. It has been suggested[20] by Adamson and co-workers for cobalt(III) acidoamines that CTTM excitation first generated a cobalt(II) ion and a halogen free radical within the molecule in the excited state. The halogen free radical then departed from the cobalt(II) ion. The final distribution between the observed reduction and aquation of the original cobalt(III) complex would depend on the competition between the rate of departure of the free radical and the rate of electron return from the cobalt(II) ion back to the departing free radical. A faster electron return meant less reduction of the original complex. For *trans*-$[Ru(en)_2IX]^+$ (X = Cl or Br) in the present investigation, the iodine radical remains coordinated to the ruthenium(II) center during the course of dissociation of the leaving halide X^-. Rapid electron return within the excited five-coordinate intermediate returns it back to the ground electronic state, which then rapidly picks up a solvent molecule to give the *trans*-$[Ru(en)_2I(H_2O)]^{2+}$ product (Scheme I). According to this scheme, no photoreduction is expected, at least, as a major reaction path from the CTTM excited state. The lack of photoreduction for the reaction of *trans*-$[Ru(en)_2I_2]^+$ seems to suggest that the CTTM excitation leads to two nonequivalent iodine sites, one coordinated iodine radical and one coordinated iodide ion. The latter iodide ion eventually departs from the reduced metal center. The above model can also explain the relatively small quantum yields of the CTTM photolysis reactions. Usually, high quantum yields observed in other systems involve efficient breakage of the bond between the ligand radical and the reduced metal ion in the CTTM excited states relative to the deactivation processes. In the present *trans*-$[Ru(en)_2IX]^+$ system, the bonding between the iodine radical and the ruthenium(II) ion appears to be relatively stable toward dissociation. The dissociation of a halide ion from the ruthenium(II) center, however, cannot be too efficient relative to the deactivation of the excited molecules back to the ground state. The domination of the Ru^{II}–I· entity in the CTTM excited states is also reflected by the observation that the quantum yields are independent of the nature of X^- after a statistical factor of 2 has been applied to the diiodo complex.

Irradiation of *trans*-$[Ru(en)_2I_2]^+$ at 390 nm initially puts the molecule into some CTTM as well as possibly some ligand field (LF) excited states. However, in view of the diverse photochemical behavior from that occurring at the 545-nm excitation, it was argued previously[8] that the photoaquation with concomitant stereochemical change could be best described to occur from a LF excited state. This would require

---

(20) Adamson, A. W. *Discuss. Faraday Soc.* **1960**, *29*, 163.

that the interstate crossing must be very efficient. The present observation that the quantum yields are independent of wavelengths of irradiation, 310–390 nm, clearly supports the above assumption of an efficient interstate crossing. Sakaki, Tsuji, and Ohyoshi[9] have recently analyzed the photochemistry of *cis*-$[Ru(NH_3)_4X_2]^+$ (X = Cl, Br, or I) and concluded that the efficiency of intersystem crossing from doublet CTTM states to some quartet states directly determined the quantum yields of the photochemical reactions. The present experimental observations of isomerization and small but wavelength-independent quantum yields associated with the 310–390-nm irradiation of *trans*-$[Ru(en)_2I_2]^+$ can be satisfactorily explained in terms of a photoreactive ^{4}LF state. Upon irradiation, the molecule is possibly excited into some ^{2}CTTM $[(p_\pi)_X \rightarrow d_\pi^*]$ and ^{2}LF states that can very efficiently move into the lowest ^{2}LF state by interstate crossing. Here, the excited molecule can either be deactivated back to the ground state or be passed into the lowest ^{4}LF state by intersystem crossing through the spin–orbit coupling interaction. The small quantum yields probably arise from an inefficient intersystem crossing relative to deactivation in the latter conversion process. This situation is quite different from the case of Sakaki et al.[9] in which the irradiation was at a higher energy (254 nm). The large quantum yield for *cis*-$[Ru(NH_3)_4(OH_2)X]^{2+}$ formation was considered to arise from an efficient intersystem crossing from the first excited ^{2}CTTM $[(p_\pi)_X \rightarrow d_\sigma^*]$ state to some quartet excited states. The alternative scheme of interstate crossing from this ^{2}CTTM excited state initially to the lowest ^{2}LF state and then crossing over to quartet states is expected to become less possible. In the present case, the photostereochemistry at the ^{4}LF state can be explained by a dissociative model previously proposed[21,22] for d^6 transition-metal complexes. This is illustrated in Scheme II. A molecule of general formula *cis*- or *trans*-$[RuN_4AX]^+$ in the lowest ^{4}LF excited state undergoes dissociation to form an electronically excited square-pyramidal intermediate, the cis complex giving a basal isomer (SP_b^*) and the trans complex giving an apical isomer (SP_a^*). Photoisomerization occurs as a result of the rapid interconversion between SP_a^* and SP_b^*. On the other hand, these two excited intermediates can be deactivated to the respective SP_a and SP_b intermediates in the electronic ground state. A knowledge[14,19,23] of the stereoretentive nature of known thermal substitution reactions of ruthenium(III) and -(II) amine complexes suggests that the interconversion between SP_a and SP_b is very unlikely. Final rapid pickup of a solvent molecule or a suitable nucleophile by SP_a or SP_b gives the corresponding trans or cis product, respectively. The observation that ligand field excitation of *trans*-$[RuLAX]^+$ (L = $(en)_2$, AX = Cl_2,[8] Br_2,[8] I_2,[8] ICl, IBr; L = 2,3,2-tet, AX = I_2) leads to aquation with extensive stereochemical change (>85%) seems to indicate that the dominant path of deactivation is through the basal isomers. Although the presence of a σ^* electron along the apical axis in the electronically excited square-pyramidal intermediate means that the equilibrium between SP_a^* and SP_b^* is shifted to the former species, if the deactivation of SP_b^* is much more rapid than the deactivation of SP_a^*, it is still possible that the major reaction route is through the basal isomers.[22] The observation of Rerek and Sheridan[7] that the ligand field photoaquation of *cis*-$[Ru(en)_2Cl_2]^+$ gives 84% *cis*-$[Ru(en)_2Cl(H_2O)]^{2+}$ and 16% *trans*-$[Ru(en)_2Cl(H_2O)]^{2+}$ is fully consistent with this model. It should be noted that the trans product in Scheme II can be also formed from the lowest ^{2}CTTM excited state because the small energy difference between the lowest ^{2}LF and the lowest ^{2}CTTM makes easy the interstate crossing from ^{2}LF to the lowest ^{2}CTTM. This reaction path may be also responsible for the partial retention of configuration in the final photoaquation products. The nature of the ^{4}LF state remains uncertain. However, the presence of a σ^* electron along the A–Ru–X axis is clearly demonstrated by the absence of amine aquation and the preferential labilization of the weak-field A–Ru–X axis and in particular the stronger ligand field ligand X (Cl or Bu) from *trans*-$[Ru(en)_2IX]^+$. For this *trans*-$[Ru(en)_2IX]^+$ system, the quantum yields are virtually independent of the nature of X (X = Cl, Br, or I) indicating that the leaving ligands do not play an important role in deciding the fate of the ^{4}LF states, dissociation vs. deactivation.

Acknowledgment. We acknowledge support from the Committee on Research and Conference Grants of the University of Hong Kong.

Registry No. *trans*-$[Ru(en)_2I_2]^+$, 87655-42-3; *trans*-$[Ru(en)_2IBr]^+$, 74215-81-9; *trans*-$[Ru(en)_2ICl]^+$, 74244-40-9; *trans*-$[Ru(2,3,2\text{-tet})I_2]^+$, 87655-43-4; *trans*-$[Ru(cyclam)I_2]^+$, 87655-44-5; *cis*-$[Ru(en)_2I(H_2O)]^{2+}$, 87655-45-6; *cis*-$[Ru(en)_2I_2]^+$, 45839-24-5; *trans*-$[Ru(en)_2I(H_2O)]^{2+}$, 87725-97-1; *cis*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$, 87655-46-7; *trans*-$[Ru(2,3,2\text{-tet})I(H_2O)]^{2+}$, 87725-98-2; *trans*-$[Ru(cyclam)I(H_2O)]^{2+}$, 87655-47-8; *trans*-$[Ru(cyclam)Br_2]^+$, 76705-12-9; *trans*-$[Ru(NH_3)_4Cl_2]^+$, 29871-95-2; *trans*-$[Ru(teta)Cl_2]^+$, 76740-65-3; *trans*-$[Ru(tetb)Cl_2]^+$, 76705-21-0.

---

(21) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.

(22) Petersen, J. D. *Inorg. Chem.* **1981**, *20*, 3123.

(23) Poon, C. K.; Che, C. M.; Kan, Y. P. *J. Chem. Soc., Dalton Trans.* **1980**, 128.