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# PHOTOCHEMISTRY OF HEXACOORDINATE COMPLEXES OF THE HEAVIER TRANSITION METALS

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ABBREVIATIONS

| | | | |
|---|---|---|---|
| bipy | 2,2'-bipyridine | bz | benzonitrile |
| cyclam | 1,4,8,11-tetraazacyclotetradecane | CTTS | charge transfer to solvent |
| | | dien | diethylenetriamine |
| en | ethylenediamine | gly | glycine |
| ISC | intersystem crossing | LF | ligand field |
| LMCT | ligand-to-metal charge transfer | MLCT | metal-to-ligand charge transfer |
| PDTA | 1,3-propylenediaminetetraacetate | phen | 1,10-phenanthroline |
| | | py | pyridine |

## A. INTRODUCTION

In the interval since the publication of the major review by Adamson and coworkers in 1968[1] and the Balzani and Carassiti monograph in 1970[2], a number of both new and established photochemists have turned their attention to coordination compounds of the heavier transition metals, thus making this area one of the fastest growing of photochemistry. This review will examine the photoreactions and some general properties of ground and excited states of the heavier elements in comparison to the more studied lighter elements and the scope of the hexacoordinate systems which have been studied. Discussion here will be limited primarily to quantitative photochemical studies of Werner-type complexes in homogeneous solution. A very major proportion of these studies involved $d^6$ complexes of the Group VIII metals.

Despite the many differences between analogous elements of the second and third transitions rows, the properties of these elements and their compounds differ far less from each other than from the first row analogs. For example, ionic and covalent radii of the 5*d* elements are nearly equal to those of the 4*d* elements in analogous oxidation states and compounds[3], as opposed to significant increases in atomic radii between the first and second transition series. Another distinction is the absence of high spin electronic configurations for the ground state complexes of the second and third transition series. This can be attributed both to smaller electron pairing energies in the 4*d* and 5*d* orbitals and to greater splitting of the 4*d* and 5*d* orbitals in a given ligand field. For example, ligand field splitting energy reported for the octahedral $d^6$ complex ions $Co(NH_3)_6^{3+}$ (22.9 kK), $Rh(NH_3)_6^{3+}$ (34.0 kK) and $Ir(NH_3)_6^{3+}$ (41.2 kK) increase about 50% in going from the 3*d* to the 4*d* complex and another 20% in going from the 4*d* to the 5*d* analog[4]. At the same time the Racah B interelectronic repulsion parameters show for the same complexes a significant decrease in going from $Co^{III}$ (615 $cm^{-1}$) to $Rh^{III}$ (430 $cm^{-1}$) and $Ir^{III}$ (470 $cm^{-1}$)[4]. Also, spin-orbit coupling constants are much higher for the heavier elements, especially in the third transition series, thus magnetic moments measured at room temperature often fall well below the "spin only" predicted moments[5]. Obviously these features are of utmost importance in determining the energies and other properties of the relevant excited states.

## B. SOME OBSERVATIONS CONCERNING SPECTRA AND EXCITED STATES

Qualitatively, the absorption spectra of the 4*d* and 5*d* metal complexes display these types of bands: ligand field (d–d) transitions (LF), metal-to-ligand charge transfers (MLCT), ligand-to-metal charge transfers (LMCT) and internal ligand transitions. The presence of these depends on the metal, its oxidation state, and the ligand field; however, clear identification of an electronic transition is often difficult owing to the frequent lack of clear distinction of the excited states' character. Classification of electronic states according to metal localized *d*-orbitals derives from electrostatic crystal field theory and may not be valid if extensive metal ligand covalency is evident[6]. Such covalent interactions can even involve significant delocalization of "*d* orbital" electrons into $\pi$-unsaturated ligands[7].

Spin-orbit coupling constants ($\zeta$) are much larger for heavier atoms, as they are a function of the fourth power of an atom's effective nuclear charge[8]. Examples from the Group VIII metals show that $\zeta$ values are about 2–3 times greater for the second transition row and about 8 times greater for the third transition row than for first row transition elements[9]. Substantial coupling makes accurate factoring of the total wave function into spin and orbital components impossible. Thus, the spin selection rule for electronic transitions cannot be strict, and the spin-forbidden transition becomes partially allowed owing to a mixing of terms in the ground and excited states having the same spin–orbit representations. Such forbidden bands involving states of different spin multiplicities are observed in the absorption spectra of some $5d^6$

osmium(II) and iridium(III) complexes[10]. Tris(2,2′-bipyridine)osmium(II) displays "singlet"–"triplet" charge transfer bands around 600–700 nm with extinction coefficients about $4 \times 10^3$ $M^{-1}$ $cm^{-1}$. Comparable bands cannot be distinguished in the spectrum of the ruthenium(II) analog except perhaps a poorly resolved and less intense shoulder on the multiplicity allowed charge transfer absorption. In discussion of photochemical processes, it is common practice to refer to excited states in terms of spin multiplicities. In general our discussion here will also conform to this practice. However, one should be reminded of warnings from several authors[9b,10,11] that, while such labelling is convenient and indeed is probably valid for the $3d$ metals, it very likely is not valid for many states of the $4d$ and $5d$ metal complexes.

When discussing the photochemistry of specific systems relevant luminescence data will also be considered. Unfortunately most photochemistry studies have been in fluid solution and near ambient temperature, while luminescence experiments have largely been carried out in rigid media at low temperatures approximating that of liquid nitrogen (77°K)[10–14]. With the rare exceptions of some chelates of ruthenium(II)[15,16] and iridium(III)[17] and pentaammine(4-*trans*-stilbazole)ruthenium(II)[18] (whose emission incidentally has been observed to be from an upper excited state), coordination compounds of the heavy metals have not been observed to luminesce at ambient temperature in fluid solution. However, one of the exceptions $Ru(bipy)_3{}^{2+}$ luminesces strongly in fluid solutions and quenching of its emission by various metal complexes is accompanied in some cases by sensitized reactions of those complexes[19,20]. For the $4d^6$ and $5d^6$ complexes, observed emissions are nearly always assigned triplet-to-singlet phosphorescence[12], although the significance of such multiplicity labelling has been subject to question[9b]. Depending on the identity of the central metal and its ligand field, phosphorescent emissions from $d$–$d$ states, from ligand $\pi$–$\pi^*$ states and from metal-to-ligand charge transfer states have all been identified. For example, Crosby and coworkers[12] have obtained $d$–$d$, MLCT and $\pi$–$\pi^*$ emissions from different iridium(III) complexes containing a 1,10-phenanthroline in the coordination sphere ($K[Ir(phen)Cl_4]$, [*cis*-$Ir(phen)_2Cl_2]Cl$, and [*cis*-Ir(5,6-dimethyl-1,10-phenanthroline)$_2Cl_2]Cl$, respectively) by variations of the balance of the ligand field. Such modifications in the emission properties by chemical modifications of the ligand field have been referred to by these workers as "tuning" and variations in emission energies by ligand substituents as "fine tuning"[21]. It is clear that such "tuning" has great potential for examining the chemical and electronic properties of transition metal excited states.

Luminescence absolute quantum yields and lifetimes have been measured for several $4d^6$ and $5d^6$ complexes[10,13,21,22]. Comparison of these parameters for a series of related compounds can provide insight as to the nature of the radiative and non-radiative electronic transitions between various states. For example, Demas and Crosby have examined the wavelength dependence of the absolute quantum yield of emission for some rhodium(III), ruthenium(II) and osmium(II) complexes (e.g., *trans*-$Rh(py)_4Br_2]Br$, at 77°K, $[Ru(bipy)_3]Cl_2$ at 300°K and 77°K, and $[Os(phen)_3]I_2$ at 77°K)[10,13]. In each case, emission was identified as a spin forbidden transition from the lowest excited state, and the quantum yield was invariant with excitation wavelength. These observations indicate that (under the luminescence experiment conditions) the quantum yields were near unity for internal conversion/intersystem crossing from the higher singlet states populated by initial excitation to the emitting lowest triplet state. The authors thereby postulated that such would always be the case for transition metal complexes with an unfilled *d*-shell, *if* photochemistry did not occur from upper excited states. In contrast, on the basis of photochemical results for some rhodium ammine complexes, Endicott[23] has suggested that higher energy LMCT charge transfer states do not undergo highly efficient interconversion to lower energy ligand field states but competitively undergo radiationless deactivation directly to the ground state (see below). This result is not necessarily incompatible with the observations of Demas and Crosby who did not examine emission behavior when excitation is to a LMCT state. However, the large differences in temperature between most luminescence studies (77°K) and the photochemistry studies (298°K) may also lead to different radiationless decay mechanisms in the two systems[22].

Crosby and co-workers[10,13,21,22] have also attempted to correlate differences in spin–orbit coupling with lifetime and quantum yield data. On the basis of semiempirical calculations, they have concluded that if other factors are constant, increases in spin–orbit coupling (between ground and excited state) leads to rate increases both for radiative and for non-radiative processes with a resultant decrease in excited state lifetimes. For example, differences in spin–orbit coupling (owing to the heavier ligand) between $Rh(NH_3)_5I^{2+}$ and $Rh(NH_3)_5Cl^{2+}$ have been used to rationalize[22] the shorter radiative lifetime of $Rh(NH_3)_5I^{2+}$. However, unfortunately there appears to be little or no correlation for these rhodium(III) ammine complexes between luminescence lifetimes and quantum yield[22] and photochemical reaction quantum yields. The lack of correlation no doubt is in large part due to the major difference in conditions used for the two kinds of experiment, luminescence in rigid glasses at low temperature (~ 110°K) and photochemistry in fluid solution at ambient temperatures (298°K), and it is clear that a prominent need in the area of transition metal complex photochemistry is a better correspondence of these conditions so that photophysical and photochemical data may be compared. Such has been done for several chromium(III) systems and there is much potential for this type of correlation with heavy metal complexes.

## C. COMPLEXES OF $4d^6$ AND $5d^6$ METAL IONS

Photochemical and/or luminescence data have been reported for complexes of these $4d^6$ or $5d^6$ metal ions: ruthenium(II), osmium(II), rhodium(III), iridium(III) and platinum(IV). These form strong field, spin paired complexes, but as expected, show fundamental differences in the character of excited states observable in absorption and emission spectra. Rhodium(III) is neither easily oxidized to the +4 oxidation state nor easily reduced to the +2 state. Charge transfer states, when observed, are normally high energy and ligand field states are lower. Thus in luminescence spectroscopy of various $Rh^{III}$ complexes of amines, halogens, thiols, pyridines, and chelating nitrogen heterocycles, the emitting (and lowest energy) state has proved to be a LF triplet[6a,13,22,24]. (In several cases, however, such as the tris-*o*-

phenanthroline and tris 2,2′-bipyridyl complexes of $Rh^{III}$, the lowest states have been identified as triplet ligand localized states)[25]. In contrast, iridium(III) complexes of unsaturated ligands such as pyridine and bipyridine often display prominent, relatively low energy MLCT bands in their absorption spectrum[10,12,21] and in some cases, MLCT "triplets" are the lowest states[10,12,21]. In this respect, the difference between homologous $Rh^{III}$ and $Ir^{III}$ complexes no doubt lies in the greater ease by which $Ir^{III}$ is oxidized to $Ir^{IV}$ [26]. Complexes of the more highly charged $Pt^{IV}$ have spectra dominated by LMCT and LF transitions[27]. The luminescence spectra reported to date for complexes $PtCl_6{}^{2-}$, $PtBr_6{}^{2-}$, $PtCl_4py_2$ and $PtCl_4$(phen) show a LF triplet as the luminescing lowest state[28] in each case. Complexes of $Ru^{II}$ and $Os^{II}$ with unsaturated ligands have prominent low energy MLCT bands in their absorption spectra and the lowest excited states of phenanthroline and bipyridine complexes have been identified by luminescence spectroscopy as MLCT triplets[13]. For ruthenium(II) complexes of saturated amines, ligand field bands are evident in the absorption spectra[29].

For low spin $4d^6$ or $5d^6$ complexes of octahedral-type coordination, the three "$t_{2g}$" orbitals are fully occupied. Therefore all ligand field excited states (e.g., those with the configuration $t_{2g}{}^5e_g{}^1$) and LMCT excited states must involve electronic population of an "$e_g$" type orbital having antibonding character with respect to metal–ligand sigma bonds. Consequently, whether accompanied by reduction of the central metal ion or not, labilization of coordinated ligands is an expected reaction characteristic of either of these types of excited states. In contrast, there is no obvious suggestion that a MLCT state, which results from promotion of a $t_{2g}$ electron into low lying, empty ligand $\pi$-orbitals, should be particularly substitution labile since analogous $d^5$ complexes, e.g. $Ru^{III}$ and $Ir^{IV}$, are (with some exceptions) relatively substitution inert. If redox processes occur, oxidation of the central metal ion would be an expected reaction pathway for the MLCT state.

### *(i) Rhodium(III) and iridium(III)*

#### *(a) Amine complexes*

In contrast to the first row congener cobalt, the +2 oxidation state is virtually unknown for iridium or rhodium[26]. Consequently, while irradiation of LMCT bands of $Co^{III}$ amine complexes normally results in relatively efficient formation of $Co^{II}$ products, photolysis of analogous rhodium(III) complexes in aqueous solution leads only to $Rh^{III}$ products[23]. Nevertheless $Rh^{II}$ intermediates have been invoked in interpreting flash photolysis studies at LMCT excitation wavelengths. Another feature distinguishing $Rh^{III}$ photochemistry is the relative reactivity of $Rh^{III}$ LF states[30] compared to the apparent inertness of LF excited states of $Co^{III}$ complexes. It has been suggested that the differences between the apparent reactivities of $Rh^{III}$ LF states and those of $Co^{III}$ may lie not in the intrinsic reactivities of the LF states but in the efficiency of intersystem crossing to the reactive LF triplets from singlet states produced by initial excitation. Intersystem crossing from LF singlets to triplets occurs with nearly unitary efficiency with $Rh^{III}$ complexes but with markedly lower efficiency for $Co^{III}$ complexes. These differences may be attrib-

TABLE 1

Quantum yields from irradiation of rhodium(III) ammine complexes in aqueous solution at 25°

| Complex | Type of absorption band irradiated | λ, nm | $\Phi_X$ | $\Phi_{NH_3}$ | Ref. |
|---|---|---|---|---|---|
| $Rh(NH_3)_5Cl^{2+}$ | LF | 254 | $0.11 \pm 0.01$ | $\leq 10^{-3}$ | 30 |
| | LF | 230 | $0.12 \pm 0.01$ | $\leq 10^{-3}$ | |
| | LF | 350 | $0.16 \pm 0.01$ | $\leq 10^{-3}$ | |
| | LF | 380 | $0.14 \pm 0.01$ | $< 10^{-3}$ | |
| $Rh(NH_3)_5Br^{2+}$ | LF | 360 | $0.019 \pm 0.001$ | $0.18 \pm 0.02$ | 30 |
| | LF | 420 | $0.019 \pm 0.001$ | $0.17 \pm 0.02$ | |
| $Rh(NH_3)_5I^{2+}$ | CTTM | 214 | – | $0.41 \pm 0.02$ | 30, 23 |
| | CTTM | 254 | – | $0.43 \pm 0.04$ | |
| | CTTM | 280 | – | $0.52 \pm 0.08$ | |
| | CTTM + LF | 350 | – | $0.58 \pm 0.03$ | |
| | LF | 385 | – | $0.82 \pm 0.08$ | |
| | LF | 420 | – | $0.87 \pm 0.07$ | |
| | LF | 470 | – | $0.85 \pm 0.05$ | |
| $Rh(NH_3)_5N_3{}^{2+}$ | LF | 350–400 | 0.025 | – | 45b |
| *trans*-$Rh(NH_3)_4I_2{}^+$ | CTTM | 254 | $0.20 \pm 0.02$ | – | 23 |
| | CTTM | 280 | $0.32 \pm 0.03$ | – | |
| | CTTM | 340 | $0.33 \pm 0.03$ | – | |
| | LF | 470 | $0.48 \pm 0.01$ | – | |
| *trans*-$Rh(NH_3)_4Cl_2{}^+$ | ? | 254 | 0.031 | – | 39 |
| | LF | 350 | $0.04 \pm 0.02$ | – | 39 |
| | LF | 358 | 0.17 | – | 35 |
| | LF | 407 | $0.13 \pm 0.02$ | $< 2 \times 10^{-3}$ | |
| *trans*-$Rh(en)_2Cl_2{}^+$ | ? | 254 | 0.03 | | 39 |
| | LF | 350 | $0.1 \pm 0.05$ | | |
| | LF | 407 | $0.047 \pm 0.002$ | $< 3 \times 10^{-3}$ | 35 |
| *trans*-$Rh(en)_2Br_2{}^+$ | ? | 254 | 0.054 | | 39 |
| | LF? | 350 | $0.1 \pm 0.05$ | | |
| *trans*-$Rh(en)_2I_2{}^+$ | CTTM | 254 | 0.23 | | 39 |
| | CTTM | 350 | $0.3 \pm 0.15$ | | |
| *cis*-$Rh(en)_2Cl_2{}^+$ | ? | 254 | $0.1 \pm 0.05$ | | 39 |
| | LF | 350 | 0.056 | | 39 |
| *trans*-$Rh(cyclam)Cl_2{}^+$ | LF | 407 | $0.011 \pm 0.001$ | $< 10^{-4}$[a] | 35 |
| $Rh(NH_3)_6{}^{3+}$ | LF | 254 | $\sim 0.07$ | | 32 |
| | LF | 313 | $0.075 \pm 0.007$ | | 32 |
| $Rh(NH_3)_5py^{3+}$ | LF | 313 | $0.12 \pm 0.02$ | $< 0.02$ | 32 |
| $Rh(NH_3)_5(CH_3CN)^{3+}$ | LF | 254 | $0.45 \pm 0.07$ | – | 32 |
| | LF | 313 | $0.47 \pm 0.04$ | $< 10^{-2}$ | 32 |
| $Rh(NH_3)_5(C_6H_5CN)^{3+}$ | LF | 313 | $0.35 \pm 0.04$ | $\leq 10^{-3}$ | 32 |

[a] Actually $\Phi_{H^+}$, a measure of amine group aquation.

utable[30] to the much larger spin–orbit coupling for the heavier rhodium atom.

Kelly and Endicott[23,30] and Moggi[31] have studied the photochemistry of the halopentaaminerhodium(III) ions $Rh(NH_3)_5X^{2+}$ ($X = Cl^-$, $Br^-$ or $I^-$) in aqueous solution. Photoaquation results when ligand field bands are irradiated; however, quantum yields and the course of the reactions were both found to depend upon the identity of X (Table 1). Ligand field excitation of $Rh(NH_3)_5Cl^{2+}$ leads to chloride aquation,

$$Rh(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{3+} + Cl^- \qquad (1)$$

LF excitation of the iodo complex leads to aquation of *trans*-$NH_3$,

$$Rh(NH_3)_5I^{2+} \xrightarrow{h\nu} trans\text{-}Rh(NH_3)_4(H_2O)I^{2+} + NH_3 \qquad (2)$$

while if X is $Br^-$ both pathways are observed.

$$Rh(NH_3)_5Br^{2+} \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{3+} + Br^- \qquad (3)$$

and

$$trans\text{-}Rh(NH_3)_4(H_2O)Br^{2+} + NH_3$$

In sensitization experiments at room temperature[30] it has been shown that all three of these complexes quench the phosphorescence of biacetyl but do not affect the fluorescence. Since the same products and quantum yields were obtained from the sensitized and the direct ligand field photolyses, it was concluded that the products arise from triplet ligand field excited states and that intersystem crossing from singlet LF states populated by direct excitation to the reactive triplet states is highly efficient (i.e., $\Phi_{isc} = 1.0$).

The mechanism proposed[30] to account for the product distributions (eq. 1, 2, 3) involves two reactive, triplet LF excited states (Fig. 1), $^3X$ leading to *trans*-$NH_3$ aquation and $^3Y$ leading to halide aquation. The geometry of these states was suggested to be strongly distorted along the labile bond axis (nearly dissociative); and the energy separation to be a function of the halogen. The product distributions would be explained if the separation is large for $Rh(NH_3)_5Cl^{2+}$ so that $^3Y$ is the only reactive state with significant population, small for $Rh(NH_3)_5Br^{2+}$, and very small (or perhaps the order of the states reversed) for $Rh(NH_3)_5I^{2+}$. The orbital character of the proposed states $^3X$ and $^3Y$ is not obvious. However, the idea of two reactive states is consistent with the suggestion[22b], based on spectral data from pentaamine rhodium(III) complexes, that for strong tetragonal distortion by the sixth ligand a $B_2$ state of $T_{2g}$ parentage (from the octahedral field) could have an energy comparable to the $E$ state of $T_{1g}$ parentage normally expected to be lowest in energy.

Quantum yields have also been measured for ligand field excitation of pentaamine rhodium(III) complexes of the uncharged ligands $NH_3$, pyridine, acetonitrile and benzonitrile. Like the chloro complex, these predominantly undergo photoaquation of the sixth ligand[32], (Table 1)

$$Rh(NH_3)_5L^{3+} \xrightarrow{h\nu} Rh(NH_3)_5H_2O^{3+} + L$$

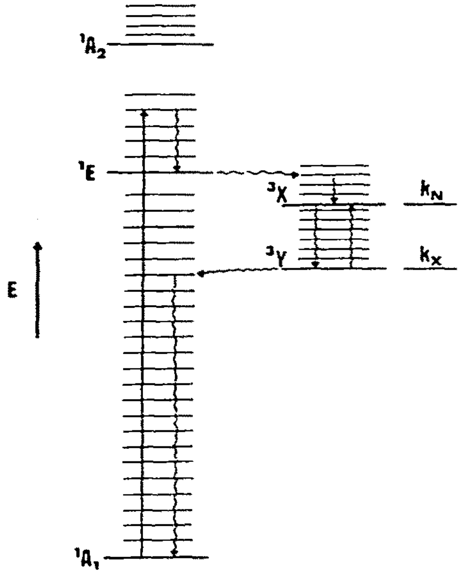


Fig. 1. Qualitative energy level scheme and mechanism for the photochemistry of halopentaamminerhodium (III) complexes, $Rh(NH_3)_5X^{2+}$. Initial excitation is followed by efficient intersystem crossing to give the lowest triplet states ($^3X$ and $^3Y$) proposed to be in thermal equilibrium. Competitive aquation of *trans* $NH_3$ ($k_N$) or the halide ($k_X$) and nonradiative deactivation to ground state determines the product mixture and quantum yields. (Adapted from ref. 30)

A simple spectrochemical series[33,34] for these Rh(III) complexes based upon the energy of the first LF band ($^1T_1 \leftarrow {}^1A_1$ in octahedral symmetry) gives the following order for the various halide and uncharged ligands $I^- < Br^- < Cl^- < NH_3 \simeq py \simeq CH_3CN \simeq C_6H_5CN$. This series suggests that unlike the iodo and bromo complexes, the electronic distortion of the various $Rh(NH_3)L^{3+}$ complexes away from the octahedral microsymmetry of the hexaamine is small. Despite this, the sixth ligand L is selectively photoaquated[32]. One explanation may lie in examining ligand base strength. The photoaquation quantum yields follow the order $NH_3 < py < C_6H_5CN \sim CH_3CN$, the approximate inverse of the Brönsted basicities of the free ligands: $NH_3 > py \gg CH_3CN \sim C_6H_5CN$. The relatively high ligand field strength of the nitriles must in large part be due to their polarizability (softness)[34].

The lowest $Rh^{III}$ LF excited state will have the configuration $t_{2g}{}^5e_g{}^1$. Not only should this be dissociation labile owing to population of the $\sigma^*$ *d*-orbital, but also the excited state might be considerably less polarizable (harder) owing to the angular redistribution of charge, thus reducing the bonding interaction relative to the ground state more for the unsaturated organic base than for $NH_3$. This explanation not only rationalizes the relative values of $\Phi_L$ but also the essentially exclusive aquation of the sixth ligand L from the pentaamine complexes. An alternative and not completely exclusive explanation is to take $\pi$-bonding between the unsaturated ligand and the rhodium atom into account. Metal-to-ligand $\pi$-backbonding in the ground state serves to place a ligand at position higher on the spectrochemical series than would be expected from $\sigma$-donor ability alone. Thus although such $\pi$-backbonding in systems as the acetonitrile and benzonitrile complexes has been demonstrated to be at least relatively minor[11], it may be enough to place the nitrile and perhaps pyridine at anomalously high positions. Such $\pi$-bonding would be less important in a LF excited state, thus competitive lability of $NH_3$ or ligand L in that condition may depend primarily on relative $\sigma$-donor strengths.

Recently, Zink[36] has presented a molecular orbital model for the photoreactions of $d^6$ complexes and applied this to rationalize the product distributions resulting from the photolyses of the halopentaammine rhodium(III) complexes. However, as this model does not treat non-radiative deactivation processes (see below) it has limited application for the prediction of quantum yields.

Kutal and Adamson[35] have examined the ligand field photochemistry of aqueous dichlorotetraamine rhodium(III) complexes $RhA_4Cl_2^+$, where A = $NH_3$, ethylenediamine/2 or cyclam/4. In each case, chloride aquation was the only observed pathway, and the reaction proceeded with retention of configuration.

$$trans\text{-}RhA_4Cl_2^+ \xrightarrow{h\nu} trans\text{-}RhA_4(H_2O)Cl^{2+} + Cl^-$$

Quantum yields (Table 1) were dependent on the identity of the equatorial amines; however, the overall decrease in $\Phi_{Cl}$ in going from *trans*-$Rh(NH_3)_4Cl_2^+$ to *trans*-Rh(cyclam)$Cl_2^+$ was a relatively small factor of about 10. These results contrast rather sharply with the ligand field photochemistry of the analogous chromium(III) complexes[37], where *trans*-$Cr(NH_3)_4Cl_2^{2+}$ and *trans*-$Cr(en)_2Cl_2^{2+}$ photoaquate $Cl^-$ with high quantum yields to give the isomerized products, *cis*-$CrA_4(H_2O)Cl^{2+}$, but the stereorigid cyclam complex is at least a factor of 400 less photoactive. Reactions of the excited state consistent with these Cr(III) results would be either a dissociative pathway involving collapse to a trigonal bipyramidal intermediate concerted with loss of $Cl^-$ or an associative pathway involving attack of solvent $H_2O$ to form a pentagonal-bipyramidal intermediate. The stereochemistry and relative insensitivity to the nature of the equatorial ligands in $Rh^{III}$ ligand field photochemistry has been interpreted[35] in terms of a dissociative pathway *via* a pentacoordinate square pyramidal intermediate. Evidence for the ability of such an intermediate to maintain its stereochemical integrity has been reported for thermal substitution reactions of isoelectronic ruthenium(II) amine complexes[38].

Muir and Huang[39] have also reported studies of several *trans*-$Rh(en)_2X_2^+$ complexes. These workers also reported *trans*-$Rh(en)_2(H_2O)X^{2+}$ as the only product of photoaquation of $X^-$ ($X^- = Cl^-, Br^-, I^-$) thus indicating that photoisomerization is not an accompanying process. However, photolysis of *cis*-$Rh(en)_2Cl_2^+$ was shown by spectral techniques to result in substantial *cis*- to *trans*-isomerization with quantum yields (0.38 at 350 mm) exceeding photosubstitution (0.1). Thus, stereorigidity is not a general photochemical characteristic of all $Rh^{III}$ amine complexes and the failure of the *trans*-$Rh(en)_2X_2^+$ to undergo photoisomerization may, in fact, simply result from greater stability of *trans* products. Table 1 shows certain discrepancies in quantum yield data for the *trans*-$RhA_4Cl_2^+$ between refs. 35 and 39. However, since these were measured using rather different apparatus and since ref. 39 reported quantum yields on a relative basis it is not clear that the differences, though large, are significant.

An understanding of the rates and mechanisms of radiationless deactivation of excited states is of fundamental importance to understanding photochemical reactions[40]. Thomas, Watts and Crosby[22a] have considered this question in relation to the luminescence spectroscopy of rhodium(III) amine complexes in methanol–water glasses at 110°K. These complexes each phosphoresce from a LF state, found at a very low energy relative to the lowest energy absorption band (large Stokes shift). Radiative lifetimes depend on the ligand field and are short for complexes of heavier ligands, a phenomenon attributed to greater spin–orbit coupling. Despite the large Stokes shift, the radiationless deactivation process has been assigned to a weak coupling mechanism, where deactivation of the electronic excited state occurs via vibrational activation of the N–H bonds (the highest frequency vibrational modes of the complex). This conclusion is primarily based on the observation that excited states of the perdeuterated complexes, $Rh(ND_3)_5X^{2+}$ are significantly longer lived (a factor of 62 larger for $Rh(ND_3)_6{}^{3+}$) than those of the corresponding perprotio complexes, $Rh(NH_3)_5X^{2+}$. Since the longer lifetimes are accompanied by larger emission quantum yields, they must result from decreases in the radiationless deactivation rates.

On the basis of photochemical observations, Kelly and Endicott[30] have argued that in aqueous solution at 25° radiationless deactivation occurs predominantly *via* a strong coupling mechanism, one which involves large horizontal displacement of the potential well of the excited state relative to the ground state owing to major distortion along a metal–ligand bond axis. This conclusion is based on the observation of high quantum yields for photoaquation (presumably by a dissociative mechanism) and the apparent insensitivity of photoaquation quantum yields to perdeuteration of the ammines. Since photochemistry is not observed under the luminescence conditions, it is argued that the temperature and medium change from 110–300°K results in an apparent change of the dominant deactivation mechanism. Surely this is almost a trivial conclusion for the iodo complex, $Rh(NH_3)_5I^{2+}$, which undergoes photoaquation with a quantum yield near unity, so that deactivation occurs nearly exclusively by photoreaction. On the other hand, perdeuteration of coordinated amines has been shown to enhance the photoaquation quantum yields of $Rh(NH_3)_5Cl^{2+}$ by about 40%[30] and of $Rh(NH_3)_6{}^{3+}$ by about 100%[32] in aqueous solution at 25°. Since the deuteration effect is apparently due to decreases in the radiationless deactivation rates, a weak coupling deactivation mechanism must in those cases remain competitive with dissociation and other deactivation pathways. Further examination of the hexaammine complex has shown that photoaquation quantum yields for the perdeuterio have a significantly smaller apparent activation energy than for the perprotio complex. This result has been interpreted[33] as suggesting that $k_n$ under the photolysis experimental conditions is composed of two components: a deuteration sensitive but temperature insensitive weak coupling contribution and a temperature sensitive but deuteration insensitive strong coupling contribution.

Examination of Table 1 points out that, although irradiation of the LMCT bands of $Rh(NH_3)_5I^{2+}$ and *trans*-$Rh(NH_3)_4I_2^+$ gives the same net photoaquation products as irradiation of LF bands, quantum yields are lower for charge transfer excitation. Decreased quantum yields at higher energy excitation can only mean that the efficiency of the interconversion from LMCT states to the lowest LF state is less than unity. Consequently, direct radiationless deactivation from the LMCT states is competitive with intersystem crossing.

Flash photolysis of $Rh(NH_3)_5I^{2+}$ in the LMCT region when traces of $I^-$ are present produced a transient identified as $I_2^-$. Since $I_2^-$ was produced only when the LMCT bands were irradiated, it was concluded[23] that a redox pathway must be responsible for a major fraction of the $NH_3$ photoaquation under these conditions:

$$Rh(NH_3)_5I^{2+} \xrightarrow{h\nu\,(\text{LMCT})} Rh(NH_3)_4^{2+} + NH_3 + I^{\cdot}$$

$$I^{\cdot} + I^- \longrightarrow I_2^-$$

$$Rh(NH_3)_4^{2+} + I_2^- + H_2O \longrightarrow \textit{trans}\text{-}Rh(NH_3)_4(H_2O)I^{2+} + I^-$$

or

$$Rh(NH_3)_4^{2+} + I^{\cdot} + H_2O \longrightarrow \textit{trans}\text{-}Rh(NH_3)_4(H_2O)I^{2+}$$

Since only *trans*-tetraamminerhodium(III) products were observed, the proposed $Rh^{II}$ intermediate must maintain its integrity over the course of its lifetime, presumably as a tetragonally distorted six-coordinate or square planar, low-spin $d^7$ species. For LMCT irradiation, if one corrects for the redox contribution to the $NH_3$ aquation quantum yield, aquation occurring directly from the lowest LF states is about one fourth that occurring from irradiation of LF bands.

Amine complexes of iridium(III) have been shown to be photoreactive but so far have been subject to relatively little quantitative study. Broad band irradiation of the complexes *trans*-$Ir(en)_2X_2^+$ ($X = Cl, Br, I$) in aqueous solution leads to stereospecific aquation[41]

$$\textit{trans}\text{-}Ir(en)_2X_2^+ + H_2O \xrightarrow{h\nu} \textit{trans}\text{-}Ir(en)_2(H_2O)X^{2+} + X^- \qquad (4)$$

Since the haloaquo product reacts stereospecifically with excess ligand $Y^-$, this photoreaction provides a useful route for preparation of mixed diacidobis(ethylenediamine) complexes, *trans*-$Ir(en)_2XY^+$. The $Rh^{III}$ analogs can be synthesized in a like manner. The photochemistry of the *cis*-complexes has also been examined, and while photosubstitution of the halide ions occurred, isomerization to the *trans*-complex was also observed[42]. The quantum yield of eqn. (4) for $X = Cl$ has been measured[43] and found to be approximately 0.1 for 350 nm irradiation. A similar value has been observed[32b] for the photoaquation of chloride from $Ir(NH_3)_5Cl^{2+}$ using 313 nm light.

Photolysis of the azido complex $Ir(NH_3)_5N_3^{2+}$ in aqueous hydrochloric acid leads not to substitutional behavior but to reaction of the coordinated azide[44]. The products isolated are $Ir(NH_3)_5(NH_2Cl)^{3+}$ and molecular nitrogen. The chloramine products have been attributed to the intermediate formation of coordinated nitrenes, e.g.,

$$(NH_3)_5IrN_3^{2+} \xrightarrow{h\nu} (NH_3)_5IrN\!:^{2+} + N_2$$

$$(NH_3)_5IrN\!:^{2+} \xrightarrow{H^+, HCl} (NH_3)_5Ir(NH_2Cl)^{3+}$$

Quantum yields for the formation of $Ir(NH_3)_5(NH_2Cl)^{3+}$ are large (0.6–0.8) and essentially wavelength independent over the range 250–400 nm. Although the longer wavelengths correspond to direct excitation of bands assigned as ligand field transitions, it was proposed[44b] that the observed reaction takes place from an internal ligand excited state of the azide ion lower in energy than the ligand field excited states. The principal basis for this argument[44] is the expectation that a LF state would undergo photoaquation of $N_3^-$ rather than decomposition of the coordinated ligand.

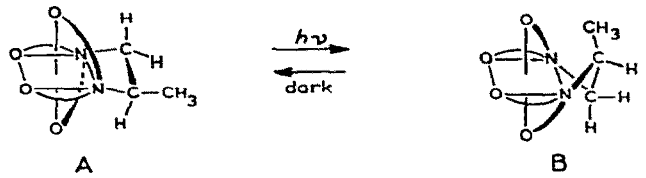
The analogous rhodium(III) complex, $Rh(NH_3)_5N_3^{2+}$, shows somewhat different photochemical behavior[44a,45]. Excitation at $\lambda > 285$ nm (LF transitions) leads to photoaquation of $N_3^-$ with a quantum yield of 0.02–0.03. However higher energy photolysis leads to decomposition of the coordinated azide to give $N_2$ and products consistent with intermediate coordinated nitrene formation. At 254 nm this is reflected in a quantum yield of 0.2 for $Rh(NH_3)_5(NH_2Cl)^{3+}$ formation[45c]. No evidence for primary photoaquation was found at this lower wavelength, thus the states initially populated apparently do not efficiently interconvert to the ligand field excited states. Flash photolysis studies[45a] of the azido complex have been reported to show formation of a transient in solution believed to be the nitrene intermediate which may undergo dimerization. Ferraudi and Endicott have attributed nitrene formation to the reactions of a LMCT excited state[45c].

The differences observed for the photochemistries of the $Ir^{III}$ and $Rh^{III}$ azido complexes are somewhat puzzling. First, irradiation of "ligand field" bands at wavelengths such as 400 nm leads to azide aquation at a relatively low quantum yield from $Rh(NH_3)_5N_3^{2+}$ but nitrene formation at a high quantum yield from $Ir(NH_3)_5N_3^{2+}$. If a ligand excited state is responsible for the reaction of the $Ir^{III}$ complex a similar state should be present in the $Rh^{III}$ excited state manifold, and (assuming the various +3 charged metals do not make a major perturbation of the ligand states) this state should have comparable energy to the ligand state of the $Ir^{III}$ complex. If, however, a LMCT state is responsible for the nitrene formation from $Rh(NH_3)_5N_3^{2+}$, there is no reason to expect a similar state (based on the similar optical electronegativities of $Rh^{III}$ and $Ir^{III}$)[4] to have a significantly lower energy in the $Ir^{III}$ analog. Thus, reactivity differences may result from differences in metal–ligand interactions for the two metals in the ground and/or excited states.

### *(b) Other $Rh^{III}$ and $Ir^{III}$ complexes*

Given the recent contributions in the luminescence spectroscopy of other $Rh^{III}$ and $Ir^{III}$ complexes (e.g., ref. 6b, 10, 12, 19, 21, 24, 25) and the known photosensitivity of some[43,46–51], the photochemistry of these systems will no doubt receive increasing attention in the near future. Most observed photoactivity involves simple ligand substitution reactions, both for $Rh^{III}$ and for $Ir^{III}$, and some photoreactions have proved useful for the synthesis of new compounds. However, a redox reaction, photoelectron production has been reported[51] for the 254 nm irradiation of $IrCl_6{}^{3-}$. Delépine's complexes, mixed pyridine–halo complexes of $Rh^{III}$ and $Ir^{III}$, $M(py)_nX_{6-n}{}^{(3-n)-}$, have been shown to undergo ligand labilization of the stoichiometrically predominant ligand when irradiated with white light[49,50]. Similarly, white light irradiation of complexes such as $Ir(phen)Cl_4{}^-$ and $M(phen)_2X_2{}^+$ in aqueous solution labilizes the halide ion and provides a route for the synthesis of various aquo and diaquo complexes[47]. Recent quantitative studies have been reported by Muir and Huang[39,43] for complexes of the type *cis*-$M(bipy)_2X_2{}^+$, *cis*-$M(phen)_2X_2{}^+$ and *trans*-$M(py)_4X_2{}^+$ ($X = Cl$, Br, or I; $M = Rh$ or Ir) in aqueous solution. All the complexes studied underwent photosolvation of halide when irradiated at 254 nm (internal ligand $\pi$–$\pi^*$ absorption region) or 350 nm (d–d for the $Rh^{III}$ complexes[13] but MLCT for the $Ir^{III}$ complexes[21]). In general, the reactivity order was $I^- > Br^- > Cl^-$ for halide photosubstitution from analogous complexes. Photoaquation of a nitrogen ligand was noted only for the *trans*-$M(py)_4X_2{}^+$ complexes where $X^-$ and py aquation are competitive. None of these complexes underwent photoisomerization. The similarity in photoreactivity between analogous $Rh^{III}$ and $Ir^{III}$ complexes is puzzling given that the luminescent (therefore lowest) states are of different nature, $Ir(phen)_2X_2{}^+$ and $Ir(bipy)_2X_2{}^+$ emit from MLCT states while $Rh(bipy)_2X_2{}^+$ and $Rh(phen)_2X_2{}^+$ emit from d–d states. The ligand field excited states would be expected to be substitution labile; however, given that $Ir^{IV}$ complexes are not labile it is unclear that MLCT states of $Ir^{III}$ should be (see Sec. C(iii)).

The rhodium(III) complex of optically active 1,2-propylenediaminetetraacetate (PDTA) provides an interesting example of photoisomerization. Dwyer and Garvan in 1961[52] first reported that the complex $(-)_{546}Rh^{III}$-D-$(-)$-PDTA (A) loses optical activity when exposed to ultraviolet light but regains it after several days in the dark. As the reaction was carried out in aqueous solution, this phenomenon was attributed to a photoaquation reaction in which one carboxylate was replaced by water in the coordination sphere. Recent work[48] utilizing CD and NMR to identify the photogenerated intermediate led to the conclusion that the photoproduct was the complex B, an isomer with a coordination sphere geometry diasteromeric to that of A:



B, however, has an axial methyl group and, as a result, reverts slowly to A which has an equatorial methyl group and should be about 3 kcal/mole more stable.

### *(ii) Platinum(IV)*

#### *(a) The hexahalo complexes, $PtX_6^{2-}$*

The photosensitivity of the hexahaloplatinum(IV) complexes was reported as early as 1832, and ref. 2 (p. 258) summarizes studies of historical interest. Here, we will be concerned with the results and conclusions of recent quantitative investigations. However, even these studies are burdened with ambiguities which need resolving before the relevant photochemistry of the hexahalo-complexes is understood.

Aqueous hexachloroplatinate(IV), $PtCl_6^{2-}$, undergoes both photoaquation and photocatalyzed exchange with chloride ion in the solution.

$$PtCl_6^{2-} + H_2O \xrightarrow{h\nu} PtCl_5(H_2O)^- + Cl^- \tag{5}$$

$$PtCl_6^{2-} + \overset{*}{Cl}{}^- \xrightarrow{h\nu} Pt\overset{*}{Cl}{}_6^{2-} + Cl^- \tag{6}$$

Rich and Taube[53] studied the latter reaction and also thermal processes which lead to exchange. They observed that exchange is greatly accelerated even by diffuse room light, and that both thermal and photochemical exchange are inhibited by oxidizing agents as $Fe(CN)_6^{3-}$, $IrCl_6^{2-}$ and $Cl_2$. Thus, these workers concluded that a chain mechanism involving a catalytic intermediate such as $PtCl_5^{2-}$ was responsible. This $Pt^{III}$ intermediate presumably is produced by a photoredox process:

$$PtCl_6^{2-} \xrightarrow{h\nu} PtCl_5^{2-} + Cl\cdot \tag{7}$$

$$PtCl_5^{2-} + \overset{*}{Cl}{}^- \rightleftharpoons Pt\overset{*}{Cl}{}_5^{2-} + Cl^- \tag{8}$$

$$Pt\overset{*}{Cl}{}_5^{2-} + PtCl_6^{2-} \rightleftharpoons Pt\overset{*}{Cl}{}_6^{2-} + PtCl_5^{2-} \tag{9}$$

The $Pt^{III}$ intermediate apparently can also be generated by adding $PtCl_4^{2-}$ to a dark solution of $PtCl_6^{2-}$

$$PtCl_4^{2-} + PtCl_6^{2-} \longrightarrow 2PtCl_5^{2-}$$

Inhibition by oxidizing agents purportedly is due to the oxidation of $PtCl_5^{2-}$ to $Pt^{IV}$. The chain character of the photocatalyzed chloride exchange is confirmed by the magnitude of quantum yields (from about 15 to 1312) measured for a variety of experimental conditions[54].

A recent study[55] of the photoaquation of $PtCl_6^{2-}$ (eq. 5) in 1 M perchloric acid has shown that irradiation at 270 or 365 nm results in overall quantum yields for this reaction substantially higher than unity. The presence of dissolved $Cl_2$ suppresses the photoaquation almost completely. It was concluded that a chain mechanism involving a labile platinum(III) species would account for this behavior. If $PtCl_5^{2-}$ is produced according to eq. (7), the following reactions could serve as the chain propagation steps for the photoaquation.

$$PtCl_5^{2-} + H_2O \rightleftharpoons PtCl_4(H_2O)^- + Cl^- \tag{10}$$

$$PtCl_4(H_2O)^- + PtCl_6^{2-} \rightleftharpoons PtCl_5(H_2O)^- + PtCl_5^{2-} \tag{11}$$

Conceivably, redox reaction (11) (and (9) as well) could proceed via a chloride bridged electron transfer step. Inhibition by $Cl_2$ would again be explained as due to oxidation of $Pt^{III}$ catalytic intermediates.

Irradiation at 270 nm and at 365 nm corresponds to direct excitation of bands assigned[27] to a LMCT transition and to a LF-transition on the shoulder of a LMCT band respectively, and reaction (7) is consistent with the chemistry expected for a LMCT state. In addition, trapping experiments[55] indicated the generation of free chlorine atoms in the photolysis experiments. Irradiation ($\lambda > 330$ nm) of aqueous $PtCl_6^{2-}$ solutions containing free $Cl^-$ and methylacrylate (a vinyl monomer) gave an organic polymer which exhibited a positive test for terminal halogen groups. Irradiation at 450 nm, exciting a band identified as ligand field in character (assigned[27] to the transition ${}^1A \rightarrow {}^3T$), also gives photoaquation but at smaller quantum yields. A puzzling aspect is that this process is also largely suppressed by the presence of $Cl_2$, thus indicating a redox type mechanism. It was suggested that the photoreactivity even at this wavelength is the consequence of the charge transfer band tailing to long wavelengths.

A flash photolysis study[56] of $PtCl_6^{2-}$ has now confirmed the presence of a redox reaction. A continuum flash of aqueous $Na_2PtCl_6$, with light absorption predominantly by the LMCT band at 262 nm ($\epsilon$ 24,500), gives a transient absorption band in the wavelength range 350–450 nm ($\lambda_{max} \sim 410$ nm). The spectrum of this transient is virtually identical to that of the $Pt^{III}$ species obtained by pulse radiolysis[57] of $PtCl_4^{2-}$ and of $PtCl_6^{2-}$. The $Pt^{III}$ transient of the flash experiment decayed with a lifetime of about 100 msec according to a second order process:

$$2\,Pt^{III} \xrightarrow{k_1} Pt^{IV} + Pt^{II} \tag{12}$$

The relatively slow rate of disproportionation ($k_1 = (4.6 \pm 0.4) \times 10^6\ M^{-1}\,sec^{-1}$ at 20°) makes it virtually certain that $Pt^{III}$ is the chain carrier responsible for the large quantum yields of photoexchange with $Cl^-$ and of photoaquation. In the presence of excess $Cl^-$, the flash photolysis also produced $Cl_2^-$ radicals, presumably from reaction of $Cl\cdot$ (eq. (7)) with $Cl^-$. Ionic strength dependence for rates of reduction by $Fe^{2+}$ was used to assign[56] the ionic charge of the $Pt^{III}$ transient as $-1$, and it was concluded that the most likely formulation is $PtCl_4^-$, arguing that low-spin $d^7$ $Pt^{III}$ would favor a square planar configuration. However, a square pyramidal structure with a labile apical ligand is equally consistent with the $d^7$ configuration. The $-1$ charge could be explained by an equilibrium such as eq. (10), with $PtCl_4(H_2O)^-$ being favored in the absence of excess chloride.

The redox intermediates $Cl_2^-$ and $Pt^{III}$ are not the only products of flash photolysis. The decrease in $[PtCl_6^{2-}]$ resulting from the flash was much larger than the $Pt^{III}$ produced. Apparently, photoaquation by direct heterolysis of Pt–Cl bonds is also a primary reaction pathway[56]. However, it should be questioned whether this may be due to catalysis by $Pt^{III}$, since efficient $Pt^{III}$ catalysis apparently allows the chain mechanism to dominate product formation under continuous photolysis conditions.

Recently Shagisultanova and co-workers[58] reported that broad band UV–vis photolyses of aqueous $PtCl_6{}^{2-}$ leads as well to the formation of $Pt^{II}$ complexes. However, since the presence of chloride in solution strongly inhibits the photodecomposition, it is likely that the $Pt^{II}$ results primarily from secondary photolysis of $PtCl_4(OH)_2{}^{2-}$, the principal product under the experimental conditions. It was shown independently that this product undergoes facile photoreduction[58].

The photosubstitutions of other halide ions for the chlorides of $PtCl_6{}^{2-}$ have also been studied[59]. Reactions with $Br^-$ occurred with quantum yields ranging from 30 to 1000, and chain mechanisms were proposed. The exchange of $I^-$ with $PtCl_6{}^{2-}$ is inhibited by the oxidizing agent $IrCl_6{}^{2-}$, which is often found as an impurity in $PtCl_6{}^{2-}$ preparations. These data were interpreted[59b] as indicating the existence of a $Pt^{III}$ chain carrying intermediate in a mechanism such as that proposed by Rich and Taube.

Hexabromoplatinate(IV), $PtBr_6{}^{2+}$, also undergoes both photoaquation and photoexchange. However, photoaquation of aqueous $PtBr_6{}^{2-}$ apparently occurs via direct heterolysis of the $Pt^{IV}$–Br bond and does not involve a chain carrying intermediate[60,61].

$$PtBr_6{}^{2-} + H_2O \xrightarrow{h\nu} PtBr_5H_2O^- + Br^- \qquad (13)$$

In contrast, the exchange of free $Br^-$ in aqueous solution with coordinated bromide occurs with quantum yields greatly exceeding unity (10–500 moles/einstein at 540 nm, dependent on light intensity), a clear indication of chain reaction[62]. A mechanism analogous to eqns. (7)–(9) was originally proposed to account for this photoexchange, although subsequent flash photolysis results[63] were interpreted to be inconsistent with this pathway. Since neither free bromine atoms nor $Br_2{}^-$ were detected in the flash experiments, an alternate pathway was proposed involving the photochemical generation of a chain carrying tetrabromoplatinum(II) intermediate by concerted departure of two *cis*-bromine atoms:

$$PtBr_6{}^{2-} \rightarrow [PtBr_4{}^{2-}] + Br_2$$

The intermediate $[PtBr_4{}^{2-}]$ was proposed to have an unstable geometry and be relatively long lived to account for its reactivity in the chain mechanism. The validity of $[PtBr_4{}^{2-}]$ acting as a chain carrier has been questioned[64] on the basis that this species, if generated, could be expected to react with $Pt^{IV}$ to produce $Pt^{III}$ intermediates. In this context, it is particularly interesting that flash photolysis[63] of $PtBr_6{}^{2-}$ did produce a transient absorption between 400 and 450 nm with a halflife of about 100 msec. These characteristics are remarkably similar to those of the $Pt^{III}$ transient detected[56] in the flash photolysis of $PtCl_6{}^{2-}$. On these bases, it appears that regardless of the method of production, $Pt^{III}$ species are probably present in the photolysis solutions of $PtBr_6{}^{2-}$ under conditions which lead to bromide exchange, and

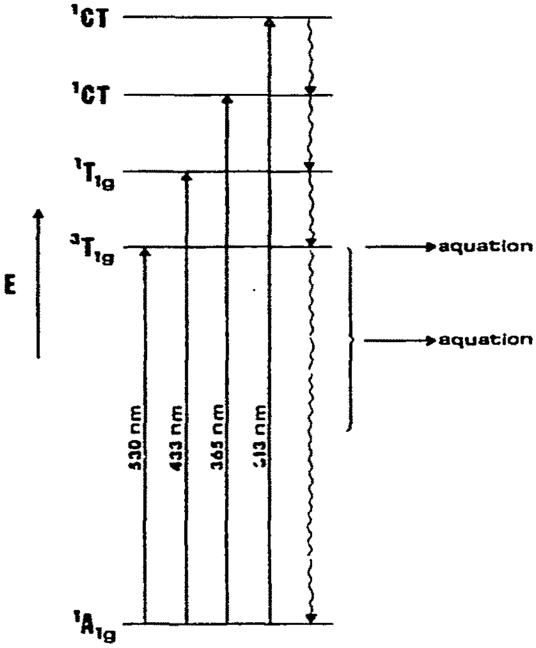


Fig. 2. Energy level diagram and photoaquation mechanism for $PtBr_6^{2-}$ (from reference 61).

that the mechanism utilizing the $Pt^{III}$ chain carrying intermediate is more likely to be the correct explanation[62].

Unlike photocatalyzed exchange, photoaquation of $PtBr_6^{2-}$ occurs with reproducible quantum yields less than unity and is not quenched[60] by the oxidizing agents $H_2O_2$ or $IrCl_6^{2-}$. These observations led to the conclusion[60,61] that a redox reaction is not involved in the photoaquation mechanism, but instead the reaction proceeds by direct heterolysis of the platinum(IV)–bromide bond (eqn. 13). In addition, quantum yields for this process measured in aqueous acid solutions for irradiations at 313, 365, 433 and 530 nm (corresponding to CTTM and LF bands) proved to be independent of wavelength (0.4 moles/einstein). The conclusion drawn was that photoaquation does not take place from the various excited states reached directly by irradiation since these should display different reactivities. Instead radiationless processes of unitary efficiency lead from the higher states to the lowest, the ligand field "triplet" state (Fig. 2). Aquation would occur from this state, having a $t_{2g}^5e_g^1$ configuration, or from a "vibrationally hot" ground electronic state produced by radiationless deactivation of the LF triplet.

A comparison[2] of the photoaquation and photoexchange processes for $PtBr_6^{2-}$ clearly shows that the two reactions display different behaviors and that their respective mechanisms cannot be coupled. The failure to detect photochemical products not attributable to the photoaquation pathway (noting the $Br^-$ exchange cannot be detected except by isotope methods) indicates that the principal direct photoreaction is heterolytic aquation and that other primary photolysis pathways including those responsible for $Br^-$ exchange are minor. This conclusion is consistent with the proposed redox chain mechanism for photoexchange since only very small primary yields of the chain carrying intermediate may be required to give very large overall quantum yields.

Somewhat more puzzling is the constrast between the photoaquation mechanisms for $PtBr_6^{2-}$ and for $PtCl_6^{2-}$, particularly since bromide would be expected to be more easily oxidized than chloride in a reaction such as eqn. (7). Cox et al.[55] have suggested (with reservation) that perhaps the different behavior of these two complexes may be attributed to more rapid intersystem crossing for $PtBr_6^{2-}$, an expected consequence of the heavy atom effect on spin–orbit coupling. However, the argument is less attractive given that spin selection rules for Pt complexes are likely to have only marginal validity. In this context the following points should be considered. First, since $PtBr_6^{2-}$ undergoes photoexchange by a chain mechanism, it is probable that, under the conditions reported for the photoaquation study[60], some chain carrying intermediate, presumably $Pt^{III}$, is also produced. Second, interpretation[56] of the flash photolysis of $PtCl_6^{2-}$ suggested that heterolytic photoaquation may be the dominant primary photolysis pathway and that generation of the $Pt^{III}$ intermediate may be a relatively minor primary pathway. Consequently, the differences in the photoaquation pathways may not be due either to the unique generation of $Pt^{III}$ intermediates in $PtCl_6^{2-}$ photolysis or to the unique predominance of heterolytic dissociation in $PtBr_6^{2-}$ photolysis, but may be due to differences in the ability of the $Pt^{III}$ intermediates produced to act efficiently as a chain carrier in a redox pathway photoaquation. The key might lie in the proposed unsymmetrical redox step which for the $Cl^-$ and $Br^-$ systems would be:

$$PtCl_4(H_2O)^- + PtCl_6^{2-} \rightleftharpoons PtCl_5(H_2O)^- + PtCl_5^{2-}$$

or

$$PtBr_4(H_2O)^- + PtBr_6^{2-} \rightleftharpoons PtBr_5(H_2O)^- + PtBr_5^{2-}$$

The affinity of $Br^-$ (vs. $H_2O$) for $Pt^{IV}$ relative to that for $Pt^{III}$ might be sufficient to make this reaction much less favorable for the bromide system. Similarly for the $Br^-$ analog of eqn. (10) the relative affinity of

$$PtBr_5^{2-} + H_2O \rightleftharpoons PtBr_4(H_2O)^- + Br^-$$

the halide ion for $Pt^{III}$ in comparison to $H_2O$ might be enough greater for $Br^-$ than for $Cl^-$ to make this process less favorable for the $Br^-$ system. Clearly, if these chain steps are slow relative to the chain termination processes, the reduced $Pt^{III}$ intermediate can not contribute significantly to the bromide photoaquation yields.

Photochemical studies of hexaiodoplatinate(IV) are subject to difficulties imposed by the relatively rapid thermal decomposition of this ion in aqueous solution. However, it has been shown[60] that irradiation at wavelengths ranging from 254 to 530 nm (all corresponding to LMCT bands) accelerated the aquation of $I^-$. Flash photolysis of $PtI_6^{2-}$ solutions gives a transient absorbing at 410 nm with a halflife of about 100 msec[63]. As with $PtBr_6^{2-}$, these characteristics are very similar to those of the transient observed when $PtCl_6^{2-}$ was subjected to flash photolysis. The duplication of these characteristics despite the differences in the starting complex $PtX_6^{2-}$ is somewhat unsettling, and major interpretation based on these observations should await better identification of the transient in each case.

### *(b) Other $Pt^{IV}$ complexes*

Although numerous other $Pt^{IV}$ complexes are photosensitive[1,2,27], only a few have been subject to careful scrutiny. One of the latter is nitroamidotetraammineplatinum(IV), $Pt(NH_3)_4(NH_2)(NO_2)^{2+}$. In aqueous solution, irradiation[65] at 254 nm and at 313 nm, on the high and low sides of a $NO_2^-$-to-$Pt^{IV}$ charge transfer band, causes photoisomerization to the nitrito linkage isomer, $Pt(NH_3)_4(NH_2)(ONO)^{2+}$. Aquation (of $NO_2^-$) and a redox reaction were also photoinduced pathways. Quantum yields for isomerization are wavelength dependent as are quantum yields for decomposition (the sum of aquation and redox processes) with $\Phi_i = 0.11$ and $\Phi_d = 0.54$ at 254 nm and $\Phi_i = 0.29$ and $\Phi_d = 0.23$ at 313 nm. At 254 nm the irradiated solutions were found to contain $NO_2^-(\Phi_{NO_2^-} \simeq 0.4)$; $NO_3^-(\Phi_{NO_3^-} \simeq 0.2)$, a redox product; and a cationic reducing species presumed to be a platinum(II) complex ($\Phi_{Pt^{II}} \simeq 0.4$), also the product of a redox reaction. The experimentally found ratio of $Pt^{II}$ to $NO_3^-$ of 2 (rather than 1 which would be expected if the redox reaction was a simple two electron transfer to give $Pt^{II}$ plus $NO_3^-$) was interpreted as indicating that the $NO_2^-$ ligand contributes one electron to reduction of the platinum(IV) ion. It was suggested that the photoredox reaction involved one electron transfer from $NO_2^-$ to the metal followed by disproportionation of the $NO_2$ radical and reduction of $Pt^{III}$ by some other species in the solution. The fact that $\Phi_d$ is larger than $\Phi_{Pt^{II}}$ and $\Phi_{NO_2^-}$ is larger than $\Phi_{NO_3^-}$ led to the conclusion that some $NO_2^-$ photoaquation was also occurring with a quantum yield about 0.1–0.2.

Irradiation of *trans*-$Pt(NH_3)_4Br_2^{2+}$ in aqueous solution gives photoaquation of $Br^-$ as the net reaction[66].

$$trans\text{-}Pt(NH_3)_4Br_2^{2+} + H_2O \xrightarrow{h\nu} Pt(NH_3)_4(H_2O)Br^{3+} + Br^-$$

The quantum yields are wavelength dependent with values of 0.11 at 305 nm and 0.06 at 350 nm. Flash photolysis experiments have revealed that the actual mechanism is more complicated than a simple primary heterolytic photoaquation of the $Pt^{IV}$–bromide bond. Flashing $Pt(NH_3)_4Br_2^{2+}$ in the presence of bromide ion produced a transient absorption identified as being due to the presence of $Br_2^-$, thus indicating a redox reaction mode. When the reaction was carried out in a 10% methanol aqueous solution, formaldehyde was a product. The yields of both $Br_2^-$ and formaldehyde were coupled to bromide concentration, a result interpreted as indicating that these products were related to the concentration of a $Pt(NH_3)_4Br_2^{2+} - Br^-$ ion pair in solution. On the basis that $Br_2^-$ does not react with sufficient efficiency with $CH_3OH$ to explain the formation of formaldehyde, it was suggested that the photolysis proceeds via the redox reaction where water rather than Pt(IV) is reduced.

$$Pt(NH_3)_4Br_2^{2+} \cdot Br^- + H_2O \xrightarrow{h\nu} Pt(NH_3)_4Br^{3+} + Br_2^- + H\cdot + OH^-$$

The pentacoordinate $Pt^{IV}$ species, $Pt(NH_3)_4Br^{3+}$ would react rapidly with $H_2O$ to form the photoaquation product and the H· radical can abstract a hydrogen atom from $CH_3OH$. The ensuing $\cdot CH_2OH$ radical can react with oxygen to form formaldehyde. This mechanism is certainly a novel one and the primary photochemical step appears too energetic for the wavelengths used. The mechanism no doubt will be subjected to future tests.

Broad band UV–vis irradiation of the complexes $Pt(en)_3^{4+}$ and $Pt(gly)_3^+$ in aqueous solution has been shown to result in $Pt^{II}$ products in each case[67]. Formation of $Pt^{II}$ is accompanied by oxidative decomposition of ethylenediamine in the former system[67a] and this presumably is the result of ligand to metal charge transfer. Similar photolytic oxidative decomposition of coordinated ethylenediamine has been noted [67a,68] for the cobalt(III) analog $Co(en)_3^{3+}$. Different behavior was observed[67b] for $Pt(gly)_3^+$, photolysis of which leads to a 2 to 1 mixture of *cis* and *trans* $Pt(gly)_2$. Redox decomposition of coordinated glycine was not detected and since the reaction occurred more readily when $Br^-$ was present in solution rather than $Cl^-$, it was proposed that the reduction of $Pt^{IV}$ is accompanied by oxidation of outersphere halide. Low temperature ESR studies have shown the formation of $Cl_2^-$ when $Pt(gly)_3^+$ was irradiated in 10 M LiCl solution.

### *(iii) Ruthenium(II)*

#### *(a) Ammine complexes*

Ruthenium(II) complexes of $\pi$-unsaturated ligands characteristically display MLCT bands in their electronic spectra[13,29]. The pentaammineruthenium(II) complexes, $Ru(NH_3)_5L^{2+}$, are not exceptions; when L is an aromatic nitrogen heterocycle[69], an organonitrile such as benzonitrile or acetonitrile[70], or even dinitrogen $(N_2)$[71], prominent and intense MLCT bands appear in the absorption spectra. Other spectral features observed with various heterocycle complexes include ligand $\pi$–$\pi^*$ transitions[69,70] and in the case of $Ru(NH_3)_6^{2+}$ less intense absorptions which have been assigned to the two spin-allowed LF transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$; $^1A_{1g} \rightarrow {}^1T_{2g}$) predicted for octahedral symmetry[29].

Studies[72,73] of the photochemistry of ruthenium(II) ammine complexes first appeared in 1969. These observed that broad band UV and visible range irradiation (high pressure mercury sources) of $Ru(NH_3)_5L^{2+}$ complexes results in several reactions including oxidation of $Ru^{II}$ to $Ru^{III}$ [72,73] and aquation of one or more ligands[73]. For example, irradiation of the dinitrogen complexes, $Ru(NH_3)_5N_2^{2+}$ or $[Ru(NH_3)_5]_2N_2^{4+}$ in deaerated aqueous solution was reported[72] to give a redox pathway:

$$Ru(NH_3)_5N_2^{2+} + X^- \xrightarrow{h\nu} Ru(NH_3)_5X^{2+} + ? \qquad (14)$$

where $X^- = Cl^-$ in dilute HCl or $OH^-$ in neutral water without chloride. The appearance of the product $Ru(NH_3)_5X^{2+}$ does not necessarily imply involvement of

$X^-$ in the primary photochemical step, since if $Ru(NH_3)_5H_2O^{3+}$ were the initial $Ru^{III}$ product, reaction of this species to form $Ru(NH_3)_5X^{2+}$ would be rapid under the experimental conditions[29].

When photooxidation of a metal complex is observed, a question of major importance is the identity and eventual fate of the species which was the recipient of the electron transferred. Two possibilities proposed[72] for the reduction product which must accompany eqn. 14 are $H_2$ from reduction of solvent water or some reduced form of dinitrogen. The former possibility appears reasonable since certain $Ru^{II}$ aquo complexes have been reported[74] to slowly reduce solvent $H_2O$ in the dark. However, the second has appeal in the context that the $N_2$ complexes have MLCT bands in the spectrum region irradiated[71] and since such a product would represent a nitrogen fixation process. No $H_2$ was found in the mass spectrometric analysis of gases above the photolysis solution[72], but besides this negative result, there has been no published evidence supporting ligand reduction as the fate of the eqn. (14) reducing equivalents. The mass spectrometric analyses did indicate small amounts of $O_2$ in the gas above the photolysis solution, and $O_2$ could surely serve to accept the electron equivalents produced in eqn. 14.

In another study[73], similar photooxidation of $Ru^{II}$ to $Ru^{III}$ was noted as the result of broad band irradiation of deaerated aqueous solutions of $Ru(NH_3)_5py^{2+}$, $Ru(NH_3)_5CH_3CN^{2+}$, $Ru(NH_3)_5H_2O^{2+}$ and $Ru(NH_3)_6{}^{2+}$. Mass spectral analysis was carried out on the gas above the product solution of $Ru(NH_3)_5py^{2+}$ photolysis, and, in contrast to the results for the dinitrogen complex, $H_2$ is a product of this reaction[73]. Furthermore, analysis of product solutions showed that aquation to give various $Ru^{II}$–aquo products is a major photoreaction mode.

$$Ru(NH_3)_5L^{2+} \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_4(H_2O)L^{2+} + Ru^{III}\text{ products}$$

In addition, the complexes $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ do not display CTTL bands in their electronic spectrum, yet do undergo photooxidation to $Ru^{III}$ under the broad-range photolysis conditions. This observation suggests that, at least in these cases, a metal-to-solvent charge transfer (CTTS) may be responsible for the photooxidation behavior.

The electronic spectrum of $Ru(NH_3)_5py^{2+}$ is shown in Fig. 3. Two absorption bands are apparent, a MLCT transition with a $\lambda_{max}$ at 408 nm ($\epsilon = 7.78 \times 10^3$) and a $\pi_L - \pi_L{}^*$ band at 244 nm ($\epsilon = 4.58 \times 10^3$). The internal ligand band is slightly higher energy than analogous ones in pyridinium ion (a multiplet centered at 255 nm), an observation suggesting $d\pi - p\pi$ orbital interaction[69]. The spectrum of the benzonitrile complex, $Ru(NH_3)_5bz^{2+}$, follows a similar pattern[70]. Photoaquation is the principal reaction mode resulting from irradiation[73,75] of scrupulously deaerated aqueous solutions of $Ru(NH_3)_5py^{2+}$ at 366 nm, 405 nm and 436 nm, all three wavelengths corresponding to excitation of the MLCT band. No photooxidation of $Ru^{II}$ to $Ru^{III}$ was observed as a result of irradiation of the MLCT band. Similarly, photoaquation is the principal reaction mode resulting from irradiation of the CTTL band of the benzonitrile complex. For $Ru(NH_3)_5bz^{2+}$, pH independent benzonitrile aqua-

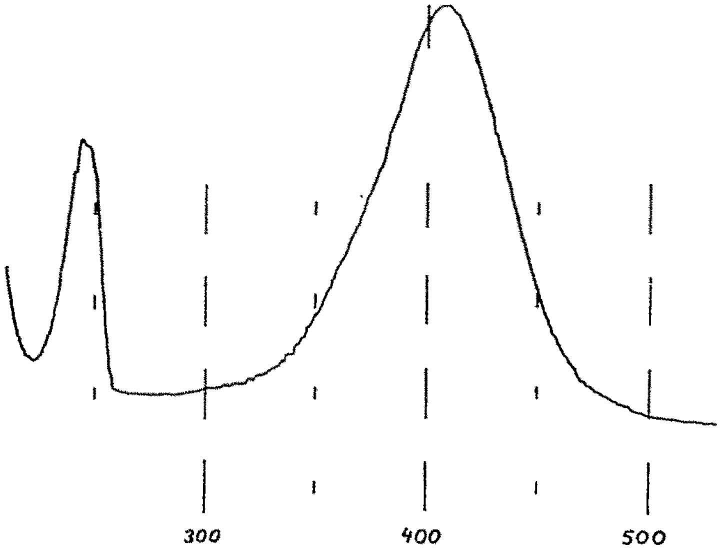
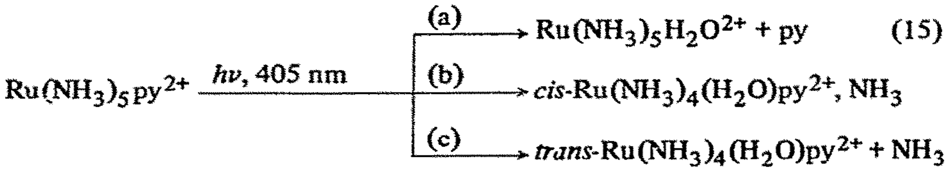


Fig. 3. Electronic spectrum of $Ru(NH_3)_5py^{2+}$ in aqueous solution.

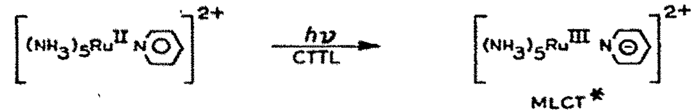
tion is the principal pathway, but for $Ru(NH_3)_5py^{2+}$ competitive aquation of the ammonias is also observed[75].



$$Ru(NH_3)_5py^{2+} \xrightarrow{h\nu,\ 405\ nm} \begin{cases} \text{(a)} \rightarrow Ru(NH_3)_5H_2O^{2+} + py \\ \text{(b)} \rightarrow \textit{cis}\text{-}Ru(NH_3)_4(H_2O)py^{2+}, NH_3 \\ \text{(c)} \rightarrow \textit{trans}\text{-}Ru(NH_3)_4(H_2O)py^{2+} + NH_3 \end{cases} \tag{15}$$

The ruthenium products of ammonia are found in a roughly statistical *cis*/*trans* ratio of 3.5 ± 1. Interestingly, the quantum yield of pyridine aquation, $\Phi_{py}$, has pH-dependent (increasing at low pH's) and pH-independent contributions while that for ammonia aquation, $\Phi_{NH_3}$, is independent of pH. Figure 4 shows the pH dependence of the pyridine aquation quantum yields ($\Phi_{py}$). At pH 4.6 the ratio of ammonia photoaquation ($\Phi_{NH_3}$) to $\Phi_{py}$ is about 1.5, however, pyridine aquation is much more important at lower pH's[75].

A metal-to-ligand charge transfer transition can be conceptualized as leading to an excited state (MLCT*) having an oxidized metal ion and a radical ion ligand in a coordination complex, e.g.,



The chemical reaction properties of such an excited state are not obvious. One potential consequence suggested by the formulation MLCT* is photooxidation of the

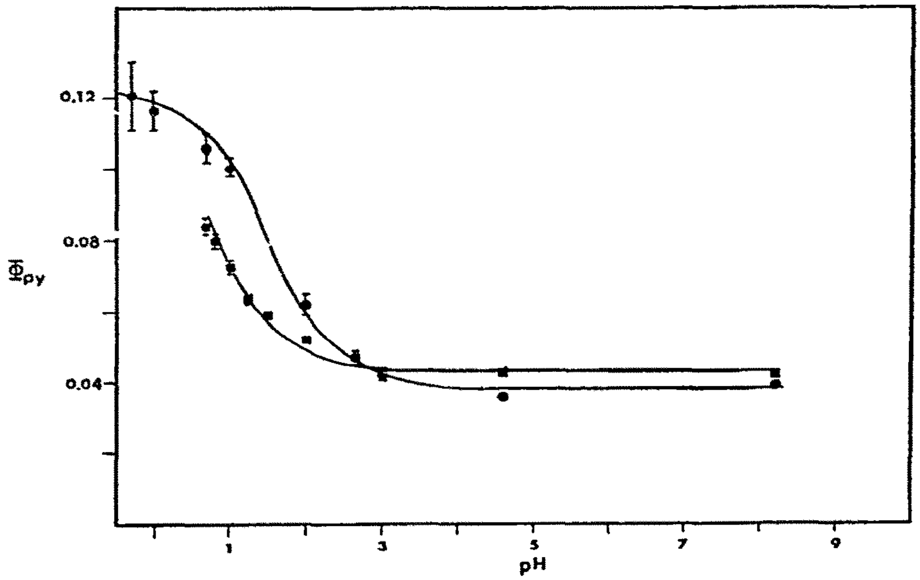


Fig. 4. Plot of $\Phi_{py}$ vs. pH for the 405 nm photolyses of $Ru(NH_3)_5py^{2+}$ in aqueous chloride solution (25°, initial complex concentration ca. $1 \times 10^{-4}$ M). Circles: $\Phi_{py}$ (spectroscopic) for $\mu = 2.00$ M. Squares: $\Phi_{py}$ (spectroscopic) for $\mu = 0.20$ M (from reference 75a).

ruthenium(II). However, no photooxidation is observed as the result of monochromatic irradiation of the $Ru(NH_3)_5py^{2+}$ MLCT band in deaerated aqueous solution. The formulation MLCT* for the pyridine complex, suggests that the aromatic ring in the MLCT excited state may be more susceptible than the ground state to electrophilic reactions. In acidic $D_2O$ solutions, electrophilic H/D exchange of pyridine protons indeed was observed as a photochemical pathway[75a]. However, the quantum yield $\Phi_D$ for deuteration is small (~ 0.001), indicating that a carbon protonated species is not a necessary intermediate in the acid-dependent pyridine photoaquation pathways (see below). Nonetheless, the photo-induced H/D exchange implies that a MLCT excited state of undetermined multiplicity has sufficient lifetime for bimolecular solution reactions.

It is unlikely that MLCT* should be aquation labile. The electron promoted from the low spin $d^6$ $Ru^{II}$ has $\pi$-symmetry with respect to the metal ligand bond, and the $\sigma$ metal–ammonia bonds and the $\sigma$ component of the Ru–py bond should be unaffected or perhaps enhanced owing to the more positive nature of the ruthenium in the excited state. The $\pi$-component of the Ru–py bond is, no doubt, less important in the excited state. However, since metal-to-ligand $\pi$-backbonding is relatively insignificant to the stability of ruthenium(III) complexes[69,70], it is improbable that a ligand in a charge transfer state such as MLCT* would be noticeably more substitution labile than in the corresponding $Ru^{III}$ compound. Under the photolysis conditions, neither $NH_3$ nor pyridine of $Ru(NH_3)_5py^{3+}$ are substitution labile. It has been proposed[75a] that if a single excited state is responsible for the competitive aquation of py and $NH_3$ from $Ru(NH_3)_5py^{2+}$, this state is probably a ligand field

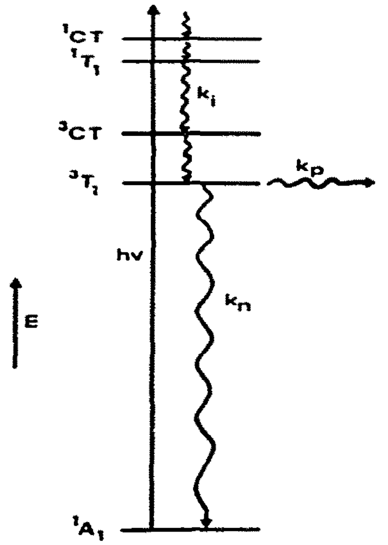


Fig. 5. Excited state diagrams for the proposed mechanism for photoaquation of $Ru(NH_3)_5py^{2+}$; $k_i$ represents internal conversion/intersystem crossing to the lowest triplet state, $k_p$ represents reactions leading to aquation products and $k_n$ represents nonradiative deactivation to the ground state.

excited state generated by interconversion from the manifold of MLCT states. Estimates of the energies of the lowest triplet MLCT and LF states[75a] suggest that the LF triplet may have the lower energy (Fig. 5).

The latter suggestion is strongly reinforced by the observed quantum yields[76] for py–X aquation from a series of complexes $Ru(NH_3)_5(py{-}X)^{2+}$ (where py–X is a substituted pyridine or related aromatic nitrogen heterocycle). The energy of the MLCT band (and presumably the MLCT thermally equilibrated states) is very sensitive to the nature of the substituent X. Although it is uncertain how ligand field excited state energies are affected by ligand substituents, they should be much less sensitive to this perturbation than are the CTTL states. Therefore if the lowest ligand field state lies lower in energy than the lowest MLCT state for the pyridine complex, it should be possible by appropriate choice of substituents to modify the ordering so that the lowest state of the triplet manifold is $^3CT$. If there is rapid interconversion of higher states to the lowest, then a change in the nature of the lowest state should be reflected as a significant perturbation in the photoreactivity of $Ru(NH_3)_5py{-}X^{2+}$. Such a perturbation was observed for the photoaquation of py–X[76]. The relative quantum yields for the pyridine ($\lambda_{max}$ 408 nm), *p*-trifluoromethylpyridine (454 nm), pyrazine (472 nm), methylisonicotinate (495 nm) and *N*-methylpyrazinium (540 nm) are 1.00, 0.49, 0.033, 0.0062 and $< 0.0009$ respectively, and these results have been interpreted to imply that modification of the MLCT energy with appropriate substituents leads to a reversal in the state ordering, with appropriate changes in the photochemical properties. The related conclusion is that a lowest lying ligand field state is responsible for at least the acid independent photoaquation pathway[76].

For photoaquations resulting from irradiation of the MLCT band of $Ru(NH_3)_5py^{2+}$, the pH dependence of $\Phi_{py}$ and the pH independence of $\Phi_{NH_3}$ require a mechanism where the role of $H^+$ in pyridine photoaquation occurs after the $NH_3$ aquation and the $[H^+]$-dependent py aquation pathways have branched. Several mechanistic schemes have been proposed. In the first, photolysis generates a relatively longlived intermediate capable of competitive acid-dependent and -independent pathways to aquation products and acid-independent return to substrate (eq. 16–18). The implicit assumption in this scheme is that pyridine aquation occurs via an intermediate (A) which can undergo bimolecular

$$[Ru(NH_3)_5(py)]^{2+} \underset{k_3}{\overset{h\nu,\ \Phi_A}{\rightleftharpoons}} \underset{(A)}{\{(NH_3)_5Ru^{II} \ldots py\}} \tag{16}$$

$$H_2O + A \xrightarrow{k_1} [Ru(NH_3)_5(H_2O)]^{2+} + py \tag{17}$$

$$H_3O^+ + A \xrightarrow{k_2} [Ru(NH_3)_5(H_2O)]^{2+} + pyH^+ \tag{18}$$

$$\Phi_{py} = \Phi_A \left( \frac{k_1 + k_2[H^+]}{k_1 + k_3 + k_2[H^+]} \right)$$

reaction with $H^+$. In discussing the possible character of A it was suggested that the pyridine ring could turn 90° with respect to the normal $Ru^{II}$–N bond axis and enter into a weak $\pi$ complex with the $Ru(NH_3)_5^{2+}$. It was also proposed that a ligand field excited state would be the precursor for both ammonia aquation and formation of A.

In another proposed scheme[75a], two excited states would be responsible for the aquations: a ligand field state for $NH_3$ and acid-independent py aquation and a lower energy CT state capable of reversible protonation for the acid-dependent py aquation. An additional requirement imposed by the pH independence of $\Phi_{NH_3}$ is that the higher LF state cannot be significantly populated from the low CT state (Fig. 6). This scheme does not appear to be consistent with the pyridine substituent studies[76] (see above) given the conclusion that interconversion to the lowest excited state is rapid compared to aquation of that state.

Recent flash photolysis experiments[77] with $Ru(NH_3)_5py^{2+}$ have shown transient Bleaching of the MLCT band followed by relatively slow decay to substrate and products at a rate, in part inversely proportional to $[H^+]$. This observation was interpreted[77] in terms of an intermediate having a free radical coordinated to a ruthenium(III) center with the pyridine nitrogen assuming an "insulating" tetrahedral configuration capable of reversible protonation.

(19)

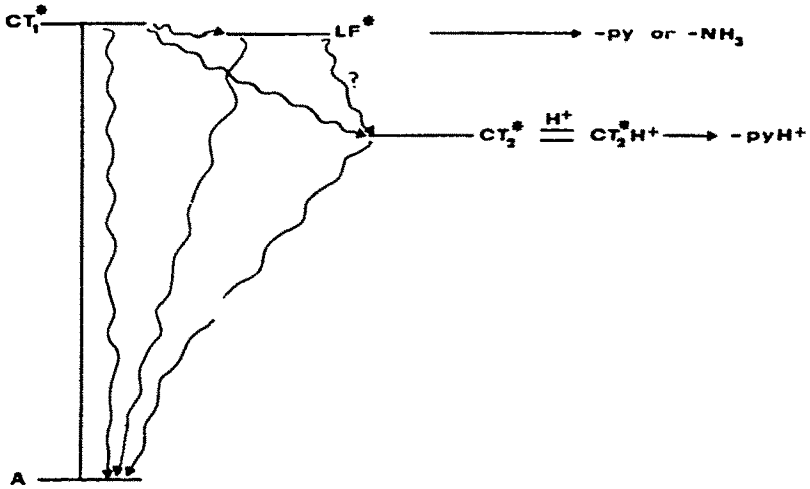


Fig. 6. A possible scheme leading to acid catalyzed photoaquation of pyridine from a charge transfer excited state of $Ru(NH_3)_5py^{2+}$ (from reference 75a).

An analogy was drawn to the report[78] of the transient $Co^{III}$ coordinated radical anion of *p*-nitrobenzoate produced by reaction of the hydrated electron $e^-_{aq}$ with $(p\text{-}O_2NC_6H_4CO_2)Co(NH_3)_5^{2+}$. Even better analogy can be drawn to the recent report[79] of transients resulting from one electron reduction of $Co(bipy)_3^{3+}$ and $Cr(bipy)_3^{3+}$. This suggestion is more or less compatible with the second mechanistic scheme proposed above (except that the lifetime requires the transient be considered an intermediate) but alone is insufficient to describe the other photochemistry of the complex. These data can also be reconciled with a scheme similar to eq. 16–18 where the intermediate A is instead reversibly protonated and is thus stabilized relative to substrate or products but capable of independent decomposition to products, e.g.,

$$A + H^+ \xrightleftharpoons{K} AH^+ \qquad (20)$$

$$AH^+ + H_2O \xrightarrow{k_4} Ru(NH_3)_5H_2O^{2+} + pyH^+ \qquad (21)$$

Eqs. 16, 17, 20 and 21 would give a quantum yield dependent on $[H^+]$ in a manner consistent with experimental observations:

$$\Phi_{py} = \Phi_A \left( \frac{k_1 + k_4K[H^+]}{k_1 + k_3 + k_4K[H^+]} \right)$$

Support for the possible stability of a species such as $AH^+$ comes from the observation of Toma and Malin[80] of an associative intermediate of unusual stability occurring in the thermal reaction of $Ru(NH_3)_5H_2O^{2+}$ with *N*-methyl-pyrazinium ($CH_3pz^+$) to form $Ru(NH_3)_5(CH_3pz)^{3+}$. Transient bleaching has also been observed[77] in the flash photolysis of $Ru(NH_3)_5bz^{2+}$, but the lifetime is pH independent. The pH independence of the benzonitrile photoaquation[75] and of the transient lifetime is consistent with the suggestion that the nitrogen atom is the site of protonation of transients produced by the photolysis of the pyridine complex.

Irradiation of $Ru(NH_3)_5py^{2+}$ in pH 3 aqueous solution at 334 nm, 313 nm and 254 nm gives quantum yields[81] for reaction 15a (pyridine aquation) comparable to those observed for irradiation of the MLCT band. This result suggests that there is relatively efficient interconversion from the higher states (254 nm corresponds to the $\pi_L - \pi_L{}^*$ transition) to a lowest energy reactive state. However, while photooxidation of $Ru^{II}$ to $Ru^{III}$ is not observed for a wavelength of irradiation 366 nm or greater, photooxidation is found with a small quantum yield (~0.01) at 334 nm and with increasing quantum yields for lower wavelength[81]. This suggests that at these high energies, another excited state, perhaps CTTS in nature, is showing some reactivity. A similar wavelength dependence of photoredox behavior is also observed for the acetonitrile complex $Ru(NH_3)_5CH_3CN^{2+}$ in aqueous solution[81].

### *(b) Other Ru$^{II}$ complexes*

The chemistry resulting from the irradiation of MLCT absorption bands has also been examined for some $Ru^{II}$ complexes of chelating nitrogen aromatic heterocycle ligands. For example, irradiation of *cis*-bis(bipyridine)-bis(4-stilbazole)ruthenium(II) or *cis*-chloro-bis(bipyridine)(4-stilbazole)-ruthenium(II)

T (for *trans*-stilbazole)

C (for *cis*-stilbazole)

T′ (for *trans*-stilbazole)

C′ (for *cis*-stilbazole)

in butyronitrile solution leads to isomerization about the 4-stilbazole carbon—carbon double bond as the only observed photoreaction[82]. No photosubstitution was observed. Photolysis of these complexes at different wavelengths gave the following results. Irradiation at 313 nm, a wavelength corresponding closely to the $\pi - \pi^*$ transition of the free stilbazole ligand, causes efficient *trans* to *cis* isomerization of the olefinic linkage (i.e., T → C). In contrast, irradiation in the visible region (405, 436 and 546 nm), corresponding to excitation of the MLCT bands, causes nearly complete conversion of C to T and C′ to T′. Even when the differences in the extinction coefficients are taken into account, it is clear from the photostationary ratios that the $\pi_L - \pi_{L^*}$ state has a reactivity distinctly different from that of the MLCT states with regard to isomerization of the ligand double bond. An additional conclusion based on the observation that quantum yields are less than unity is that interconversion of the $\pi - \pi^*$ state to the lower MLCT states is slow in comparison to photoreaction and radiationless deactivation directly to the ground state It should be noted that this latter conclusion contrasts with the observation of unitary interconversion of higher states to emitting lowest states in the luminescence spectroscopy[10] of $Ru(bipy)_3{}^{2+}$.

Another feature of these complexes is that T and C show only very weak luminescence in room temperature solutions (under conditions where both free 4-stilbazole and $Ru(bipy)_3{}^{2+}$ emit)[82b]. This emission is much stronger for excitation into the MLCT state than for excitation of the $\pi_L-\pi_L{}^*$ bands.

The efficient photoisomerization T → C at 313 nm (*trans* to *cis* for the double bond) is comparable to the photochemical behavior of free stilbazole under the influence of $\pi-\pi^*$ excitation. Thus in this case the ligand excited state reactivity seems little perturbed by complexation. The *cis* to *trans* isomerization from MLCT excitation parallels the behavior observed for thermal isomerization using iodine as a catalyst. This behavior is consistent with that which might be expected for a charge transfer state where an electron has been transferred to the lowest antibonding orbital of the 4-stilbazole ligand and where the ligand in the excited state can be thought of as having radical-anion character.

Tris(bipyridyl)ruthenium(II), $Ru(bipy)_3{}^{2+}$, does not undergo permanent changes in either coordination sphere or oxidation state when irradiated. However, its photochemistry is relatively rich though by no means fully understood. For example, it has been shown that $Ru(bipy)_3{}^{2+}$ can be used as a sensitizer for the photoreactions of $PtCl_4{}^{2-}$ (ref. 19) and as a sensitizer or quencher with other transition metal complexes[20,83–86]. The $Ru(bipy)_3{}^{2+}$ luminescence is also quenched by $O_2$ with simultaneous formation of singlet oxygen[86b]. However, several intriguing complications with the sensitization process have turned up. For example, flash photolysis[77] of $Ru(bipy)_3{}^{2+}$ has been reported to lead to formation of a transient, with an acid concentration dependent lifetime, which decays back to the starting complex. This behavior is analogous to the flash photolysis behavior of $Ru(NH_3)_5py^{2+}$ (above), but occurs in much smaller quantum yields (~ 0.001), quantum yields small enough that formation of this transient should not significantly affect the photosensitization properties[83].

In another study[87], it was proposed that $Ru(bipy)_3{}^{2+}$ when photolyzed was capable of acting as a reductant for certain pentaamminecobalt(III) complexes

$$Co(NH_3)_5X^{2+} + [Ru(bipy)_3{}^{2+}]^* \rightarrow Co^{II} + Ru(bipy)_3{}^{3+} \qquad (22)$$

This proposal was based on the observation of the $Ru(bipy)_3{}^{3+}$ product when the reaction was carried out in strongly acidic solution (1 N aqueous $H_2SO_4$). In less acidic solution the $Ru^{III}$ complex is a sufficiently strong oxidant to react with the solvent (and any $Br^-$ produced by the photoreaction) quickly to give the initial $Ru(bipy)_3{}^{2+}$ sensitizer. An alternate explanation for formation of the $Ru^{III}$ is that it results from reaction between ground state $Ru^{II}$ and a transient radical produced by the sensitized photoredox decomposition of the $Co^{III}$ complex[87,88]. Flash photolysis and quencher studies[88] appear to support the latter mechanism for formation of $Ru(bipy)_3{}^{3+}$. For example, when the $Ru(bipy)_3{}^{2+}$ sensitized photolysis of $Co(NH_3)_5Br^{2+}$ was carried out in 50% aqueous 2-propanol, the $Ru(bipy)_3{}^{3+}$ yield was greatly reduced and the $Co^{2+}$ yield increased. This suggests that a transient radical is produced which can competitively oxidize $Ru(bipy)_3{}^{2+}$ or be captured in a reaction with the alcohol. The alcohol radical produced can be depleted by reaction with $Co(NH_3)_5Br^{2+}$. The radical formed initially is apparently Br. Flash photolysis[88a] of $Co(NH_3)_5Br^{2+}$ and $Ru(bipy)_3^{2+}$ together in 1 N $H_2SO_4$ containing dilute bromide produces $Br_2^-$ which oxidizes $Ru(bipy)_3^{2+}$ at near diffusion controlled rates. The results were rationalized on the basis of the following equations:

$$Ru(bipy)_3^{2+} + h\nu \rightarrow [Ru(bipy)_3^{2+}]^*$$

$$[Ru(bipy)_3^{2+}]^* + Co(NH_3)_5Br^{2+} \rightarrow Ru(bipy)_3^{2+} + Co^{2+} + Br\cdot$$

$$Br\cdot + Br^- \rightleftharpoons Br_2^-$$

$$Br_2^- + Ru(bipy)_3^{2+} \rightleftharpoons Ru(bipy)_3^{3+} + 2\ Br^-$$

A redox method comparable to eq. 22 has also been proposed for the $Ru(bipy)_3^{2+}$ sensitized photolysis of $Co(C_2O_4)_3^{3-}$ and the possible generality of such reactions of "sensitizer" excited states discussed[86a]. Again for this system $Ru(bipy)_3^{3+}$ is produced along with the $Co^{2+}$ which would be the product of either reduction of the $Co^{III}$ substrate by $Ru^{II}$ or of sensitized decomposition of $Co(C_2O_4)_3^{3-}$. Although the latter process would also be expected to result in the formation of free radicals resulting from oxidation of the ligands, it was suggested that in this case the radicals (probably $C_2O_4^-$ or $CO_2^-$) would be reducing not oxidizing in character. Furthermore, direct photolysis of the $Co(C_2O_4)_3^{3-}$ LMCT bands with 254 nm light (conditions which lead to efficient redox decomposition of $Co(C_2O_4)_3^{3-}$ in the presence of $Ru(bipy)_3^{2+}$) gave very little $Ru^{III}$ formation; a result interpreted to indicate the inability of the ligand radicals to oxidize $Ru(bipy)_3^{2+}$. As a general conclusion it appears that neither mechanism for formation of $Ru^{III}$ in these "sensitization" experiments has an exclusive franchise, and that the specifics of each system studied need examination to establish which one may be operable under a particular set of conditions.

Another photochemical phenomenon[89] involving $Ru(bipy)_3^{2+}$ is the chemiluminescence observed when the $Ru^{III}$ analog, $Ru(bipy)_3^{3+}$, is reduced with certain reagents including hydrazine in aqueous acid solution and hydroxide ion. The light emitted in this reaction is identical to that of normal phosphorescence under comparable conditions. Similar chemiluminescence can be generated electrochemically[90].

Some other $Ru^{II}$ complexes are photosensitive. The *cis*-bis(pyridine) complexes, $Ru(bipy)_2py_2^{2+}$ and $Ru(phen)_2py_2^{2+}$, in solution have been reported[91,92] to undergo substitution of the pyridine ligands when irradiated in the visible region. This photochemistry has been confirmed[93] but in aqueous solution quantum yields measured for irradiation at 366 nm and 405 nm were relatively small. Brief observations[1] with the hexacyano complex, $Ru(CN)_6^{4-}$ show its photochemistry to parallel that of the iron analog $Fe(CN)_6^{4-}$. Photolysis in the UV region[94a] apparently gives the aquated product, $Ru(CN)_5H_2O^{3-}$, while flash photolysis studies[51] show the production of photoelectrons, an observation attributed to the presence of a CTTS band[94b]. Additional observations include the interesting photodimerization of a ruthenium(II) porphyrin complex[95], the photoisomerization[46b] of the carbonyl complexes,

$RuCl_2(CO)_2L_2$, where L is dimethylphenylphosphine or diethylphenylphosphine, and that sunlight causes isomerization of $Ru(CO)_2(PPh_3)_2I_2$ in benzene solution from the isomer having *cis* carbonyl groups to one having *trans* carbonyls[96]. The reverse occurs thermally.

### *(iv) Some carbonyl complexes of tungsten(0)*

This review has chosen not to discuss in detail the rich photochemistry[97,98] of metal carbonyl and organometallic systems. However recent studies of the photochemistry[99] and luminescence[100] of some tungsten(0) complexes $W(CO)_5L$ (metal electronic configurations $5d^6$) are of interest with respect to the reactions of other $d^6$ complexes discussed above. Of particular interest are the *N*-coordinated aromatic heterocycle complexes $W(CO)_5$(pyridine), $W(CO)_5$(*trans*-4-stilbazole) and $W(CO)_5$-(*trans*-2-stilbazole). The absorption spectra have been assigned, and for the pyridine complex two ligand field bands were reported[99]: ${}^1A_1 \rightarrow {}^3E$ (440 nm) and ${}^1A_1 \rightarrow {}^1E$ (380 nm). Luminescence of this complex was observed to occur at 516 nm (assigned to the ${}^3E \rightarrow {}^1A_1$ ligand field transition) with a lifetime of $2.5 \times 10^{-6}$ sec in hydrocarbon glass at 77°K. The short lifetime of the ligand field excited state and observation of the "singlet–triplet" transition in the absorption band (not seen for analogous Mo and Cr complexes) are attributed to large spin–orbit coupling terms for the heavy tungsten atom.

Photochemically the pyridine and stilbazole complexes undergo substitution reactions with high quantum yields when irradiated in hydrocarbon solvent:

$$W(CO)_5L + L' \xrightarrow{h\nu} W(CO)_5L' + L$$

$$\xrightarrow{\text{or}} cis\text{-}W(CO)_4L'L + CO$$

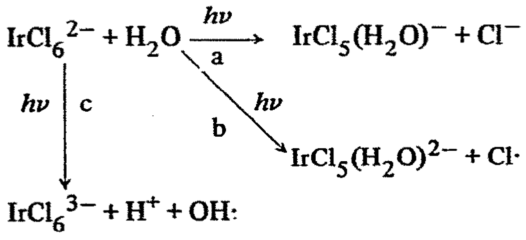
where L is py or stilbazole and L′ is isopentene in isooctane solvent. The stilbazole complexes were observed to undergo *trans* → *cis* isomerization of the stilbazole ligand as well as substitution reactions. Whrighton and co-workers[99] attributed isomerization to a $\pi_L \rightarrow \pi_L{}^*$ ligand excited state and suggested that this state results in internal conversion from the ligand field triplet state. This suggestion does not appear to be supported by their quantum yield data which shows that direct excitation of the $\pi_L \rightarrow \pi_L{}^*$ absorption band of coordinated 4-stilbazole gives an isomerization quantum yield about half that resulting from excitation of the lower energy ${}^1A_1 \rightarrow {}^3E$ ligand field band. These authors did not discuss the possible reactivity of MLCT states; however, given the high extinction coefficients of bands assigned to *d–d* transitions, it is possible that these may have some charge transfer character. MLCT states in ruthenium(II) stilbazole complexes show ligand isomerization as their principal reactivity, although in those cases *trans* to *cis* isomerization was relatively inefficient[82].

## D. OTHER HEXACOORDINATE COMPLEXES

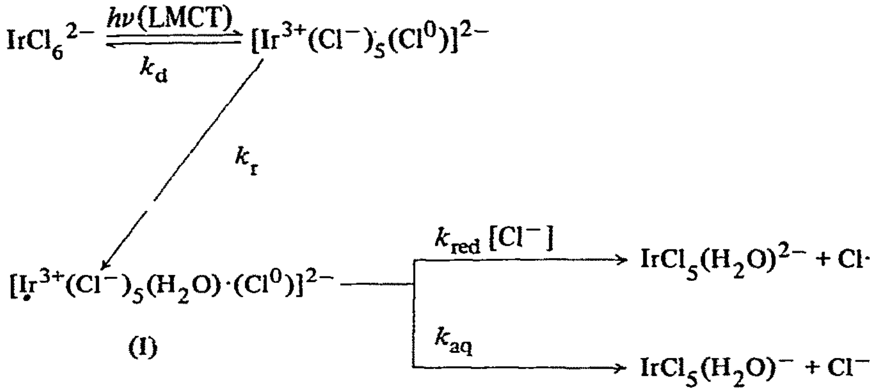
### *(i) $d^5$ Complexes: ruthenium(III) and iridium(IV)*

Ruthenium(III) and iridium(IV) complexes have the, electronic configuration $(t_{2g})^5$, thus having a vacancy in a metal $\pi$-symmetry orbital. Consequently, the spectra of these complexes are predicted to display not only ligand field ($\pi_M^*(t_{2g}) \rightarrow \sigma_M^*(e_g)$) and LMCT ($\sigma_L$ or $\pi_L \rightarrow \sigma_M^*$) absorptions but also LMCT ($\sigma_L$ or $\pi_L \rightarrow \pi_M^*$) bands. The spectrum of $IrCl_6{}^{2-}$has been assigned by Jorgensen[101] who attributed absorption maxima at 588, 488, 434 and 410 nm to $\pi_L \rightarrow \pi_M^*$ LMCT transitions, bands at 360 and 306 nm to LF transitions and a very intense band at 232 nm to a $\pi_L \rightarrow \sigma_M^*$ LMCT transition. Similarly relatively intense ($\epsilon > 10^3$) $\pi_L \rightarrow \pi_M^*$ LMCT bands are the dominant and lowest energy absorptions in the spectra of the halopentaammine ruthenium(III) complexes $Ru(NH_3)_5X^{2+}$ ($X^- = Cl^-$, $Br^-$ or $I^-$)[102]. The chemical reactivities of the $\sigma_L$ or $\pi_L \rightarrow \sigma_M^*$ LMCT excited states or of the LF excited states ($\pi_M^* \rightarrow \sigma_M^*$) would not be expected to be in general very different from those of similar states in analogous $4d^6$ or $5d^6$ complexes. However, the $\sigma_L$ or $\pi_L \rightarrow \pi_M^*$ LMCT excited states should have a pattern reactivity distinct from that of a LMCT state where a $\sigma_M^*$ ($e_g$) orbital is populated. For a $Ru^{III}$ or $Ir^{IV}$ complex, the former LMCT state can be described simplistically as a $Ru^{II}$ or $Ir^{III}$ ion coordinated to a free radical ligand. The lability of $Ru^{II}$ complexes is not particularly great (for example, the $H_2O$ of aqueous $Ru(NH_3)_5H_2O^{2+}$ has been predicted to exchange with solvent $H_2O$ with a rate constant of 1–10 $sec^{-1}$ at 25°)[38b] and that of $Ir^{III}$ is less. Therefore a species such as that described for the LMCT state would be expected to undergo internal redox to regenerate the original complex faster than dissociation to a reduced metal complex plus a free radical in solution. This expectation is borne out by the relative insensitivites of the $Ir^{IV}$ complex $IrCl_6{}^{2-}$ and of the $Ru^{III}$ species $Ru(NH_3)_5Cl^{2+}$ to photolysis of $\pi_L \rightarrow \pi_M^*$ LMCT absorption bands[103,104].

The photochemistry of aqueous $IrCl_6{}^{2-}$ is summarized in the following proposed reactions[103]:



However, the three do not occur simultaneously. Irradiation of aqueous $IrCl_6{}^{2-}$ at 254 nm ($\pi_L \rightarrow \sigma_M^*$ LMCT transition) gives $IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ in parallel zero order reactions (eqns. 23a and 23b). With respect to changes in chloride concentration, the total quantum yield for the two products is invarient ($\Phi_{sum} = 0.029$), but the ratio of the two pathways changes. Formation of the redox product $IrCl_5(H_2O)^{2-}$ is favored at higher $[Cl^-]$. The dependence of the redox/aquation ratio and the independence of $\Phi_{\text{sum}}$ has been interpreted[103] as indicating a common intermediate for these two reactions. The following mechanism was proposed:



where $[Ir^{3+}(Cl^-)_5(Cl^0)]^{2-}$ represents the $\pi_L \rightarrow \sigma_M^*$ LMCT excited state and (I) is an intermediate composed of an $Ir^{III}$ complex with a chlorine atom solvent caged in the second coordination sphere. The intermediate would be formed by an irreversible step ($k_r$) in competition with a deactivation process ($k_d$). An internal redox reaction of (I) followed by diffusion of $Cl^-$ from the solvent cage would result in aquation ($k_{aq}$) while diffusion of Cl· out of the solvent cage, in some manner assisted by free chloride ($k_{red}[Cl^-]$), would lead to a net redox reaction. It was suggested[103] that a possible role of chloride in the redox reaction could be due to an electron transfer from an outer $Cl^-$ to the solvent caged chlorine atom; however, this process appears rather unfavorable energetically. Perhaps more likely would be the reaction of (I), with $Cl^-$ to give the transient $Cl_2^-$ plus the $Ir^{III}$ product.

Excitation of the LF transitions by irradiation at 313 and 365 nm in the absence of added chloride led only to $IrCl_5(H_2O)^-$ with quantum yields of 0.01 and 0.001 at these respective wavelengths. However, in 1.2 M Cl solution, irradiation at the same wavelengths gave a redox product $IrCl_6^{3-}$ (eqn. 23c) with quantum yields of 0.02 at 313 nm and 0.005 at 365 nm. Finally, irradiation at 433 nm and 495 nm ($\pi_L \rightarrow \pi_M^*$ LMCT) led to no detectable changes in the solution for the longer wavelength and only traces ($\Phi \sim 1 \times 10^{-4}$ in 1.2 M $Cl^-$) of an unidentified redox reaction for 433 nm irradiation. The observation of redox pathways under certain conditions contradicts the conclusion of an earlier report[105] that only photoaquation (eqn. 23a) occurs when $IrCl_6^{2-}$ is irradiated.

The wavelength dependence of the photoreaction modes and their quantum yields indicates that the photoreactions are characteristics of states populated by initial excitation and are competitive with decay processes. The lowest spectroscopic state, apparently a $\pi_L \rightarrow \pi_M^*$ LMCT, is essentially unreactive, as predicted by the rather naive considerations mentioned previously. In this context, it might be of interest to compare the photochemical properties of the $5d^5$ $IrCl_6^{2-}$ to those of the $5d^6$ $Pt^{IV}$ analogs $PtCl_6^{2-}$ and $PtBr_6^{2-}$. Both $Pt^{IV}$ complexes display very high quantum yield chain mechanisms ($Cl^-$ exchange and aquation for $PtCl_6^{2-}$, and $Br^-$

exchange for $PtBr_6^{2-}$) apparently as the result of charge transfer generation of chain carrying, reduced platinum intermediates. Unfortunately, chloride photoexchange with $IrCl_6^{2-}$ has not been examined; however, the quantum yields for aquation are small and reproducible and there is no indication of a chain process. This result is certainly to be expected on the basis that $Ir^{III}$, the redox product of LMCT excitation, has a $5d^6$ configuration and is not substitution labile, a prerequisite for a good chain carrying intermediate. Despite this, comparison of $IrCl_6^{2-}$ photochemistry to that of $PtBr_6^{2-}$ raises some interesting points. First, both display some form of redox behavior when $\pi_L \rightarrow \sigma_M^*$ states are irradiated, $Ir^{IV}$ being reduced in small quantum yield to $Ir^{III}$, $PtBr_6^{2-}$ undergoing chain mechanism exchange with solution $Br^-$. However, photoaquation of $IrCl_6^{2-}$ has wavelength dependent quantum yields which at their largest (< 0.03 for excitation to the $\pi_L \rightarrow \sigma_M^*$ LMCT state) are rather small, while the photoaquation of $PtBr_6^{2-}$ (not a chain reaction)[61] occurs with a relatively large, wavelength independent quantum yield (0.4). The latter observation is interpreted[60] as indicating near unitary efficiency of interconversion of higher states to the lowest excited state (presumably a ligand field triplet) responsible for this reaction. Since less than 3% of the $IrCl_6^{2-}$ higher states decay by photoreaction, there is no evidence to deny the possibility that the remainder undergo interconversion to the lowest excited state, very likely $\pi_L$–$\pi_M^*$ LMCT, which is unreactive. Thus, the mechanisms of these respective photoreactions may have the unifying feature that decay to the lowest state occurs with high efficiency in both cases, but the difference in the reactivities is due primarily to the differences in the reactivities of the lowest state.

Among $4d^5$ systems, only the photochemistries of the ruthenium(III) ammine complexes, $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5Cl^{2+}$ and *cis*-$Ru(NH_3)_4Br_2^+$ have been closely scrutinized[104,106]. The $Ru(NH_3)_5Cl^{2+}$ ion displays a moderately intense $\pi_{Cl}$–$\pi_{Ru}^*$ LMCT band ($\lambda_{max}$ 328 nm, $\epsilon \sim 2 \times 10^3$) as its most prominent spectral feature. Irradiation of $Ru(NH_3)_5Cl^{2+}$ in aqueous solution showed it to be relatively photoinsensitive. Aquation of ammonia (primarily *cis*) is the major primary photoreaction, and photolyses at 230, 254 and 321 nm gave quantum yields essentially wavelength independent (given the experimental uncertainty) in the range 0.02–0.032. Aquation of $Cl^-$ was also observed,

$$Ru(NH_3)_5Cl^{2+} \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{3+} + Cl^-$$

however, the quantum yields were small and erratic, at times falling below $10^{-2}$. Since the $Ru^{II}$ complex ion, $Ru(NH_3)_5H_2O^{2+}$, catalyzes this reaction[29] the erratic nature of $\Phi_{Cl^-}$ suggests that traces of the redox product $Ru^{II}$ may result from the CTTM excitation. If so, the quantum yields for the redox reaction must be low as no $Ru^{II}$ was detected[104]. In addition, flash photolysis ($\lambda \geqslant 300$ nm) of $Ru(NH_3)_5Cl^{2+}$ provided no evidence for the generation of a chlorine radical.

The wavelength independence of the ammonia aquation quantum yields for $Ru(NH_3)_5Cl^{2+}$ was attributed to efficient interconversion of higher states to the lowest one, presumably a $\pi_{Cl} \rightarrow \pi_{Ru}^*$ LMCT state[104]. The low quantum yields would then be explained as the result of the relatively substitution inert character of an excited state which formally can be considered to be a ruthenium(II) complex (e.g., $[Ru^{II}(NH_3)_5(Cl^0)]^{2+}$).

At wavelengths exceeding 300 nm, the spectrum of *cis*-$Ru(NH_3)_4Br_2{}^+$ is dominated by bromide to metal charge transfer bands at 370 nm and 442 nm with extinction coefficients exceeding $10^3$. In analogy to $Ru(NH_3)_5Cl^{2+}$, substitution was the only reaction detected[106] as a result of photolysis in this spectral region, and the product appeared to be exclusively *cis*-$Ru(NH_3)_4(H_2O)Br^{2+}$. However, in this case the quantum yields, though small, are somewhat wavelength dependent, with reported values ranging from $5.6 \times 10^{-3}$ at 330 nm to $1.4 \times 10^{-3}$ at 434 nm[106].

Photoaquation was the principal reaction observed[104] for 254 nm irradiation of the hexaammine complex, $Ru(NH_3)_6{}^{3+}$

$$Ru(NH_3)_6{}^{3+} \xrightarrow{h\nu} Ru(NH_3)_5H_2O^{3+}$$

The quantum yield for the aquation of ammonia was ~ 0.08, and there was no evidence for a photoredox process giving $Ru^{II}$ products. The spectral region at 254 nm has been assigned to a CTTM transition for $Ru(NH_3)_6{}^{3+}$. Interestingly, this quantum yield is close to that for the analogous photoaquation resulting from *d–d* excitation of $Rh(NH_3)_6{}^{3+}$ (Table 1). Since the $\Phi_{NH_3}$ for $Ru(NH_3)_6{}^{3+}$ is 2–3 times larger than for $Ru(NH_3)_5Cl^{2+}$ (which presumably reacts via the $\pi_{Cl} \rightarrow \pi^*_{Ru}$ LMCT state) this similarity to the $Rh^{III}$ system suggests that the reactive state resulting from 254 nm excitation of $Ru(NH_3)_6{}^{3+}$ may indeed be a ligand field excited state of some multiplicity. Such a state would have the electronic configuration $(t_{2g})^4(e_g)^1$ for $Ru^{III}$ in comparison to $(t_{2g})^5(e_g)^1$ for $Rh^{III}$. For the hexaammines the $t_{2g}$ orbitals are nonbonding and the $e_g$ orbitals are sigma antibonding. Consequently, if aquation were to occur via a limiting dissociative mechanism, there is no obvious reason why the two excited states should necessarily have remarkably different reactivities.

A recent study[107] of the far UV photochemistry of several ruthenium(III) ammine complexes has shown that 185 nm irradiation in aqueous alcohol solutions results in significant photoreduction of $Ru^{III}$ to $Ru^{II}$. The reduction is dependent on the concentration of alcohol (photoreduction quantum yields for $Ru(NH_3)_6{}^{3+}$ range from 0.05 in the absence of alcohol to 0.7 in 2 M isopropanol) but is not accompanied by primary photoaquation. Small yields (~ 0.01) of photoreduction of $Ru(NH_3)_6{}^{3+}$ were also noted with 254 nm irradiation in 0.5 M propanol in aqueous solution. The alcohol effect on the photoreduction quantum yields was rationalized on the basis that the primary photochemical act was production of a ruthenium "radical" capable of return to starting material or reaction with alcohol to give $Ru(NH_3)_6{}^{2+}$, $H^+$ and $(CH_3)_2COH$. The alcohol radical would react with $Ru(NH_3)_6{}^{3+}$ to produce acetone plus another mole of $Ru(NH_3)_6{}^{2+}$. Acetone was also produced in the reaction. The high photoreactivity at the lower wavelength was attributed to the onset of an intense LMCT absorption at $\lambda < 210$ nm[107].

### *(ii) A $4d^3$ complex, $TcCl_6{}^{2-}$*

In contrast to the extensive photochemistry of $3d^3$ complexes, principally those of chromium(III), practically nothing is known of the photochemical properties of $4d^3$ and $5d^3$ complexes. The principal reason for this state of affairs no doubt lies in the scarcity of published reports of the synthesis, characterization and thermal reactions of the latter systems[26], especially of mononuclear complexes amenable to study in homogeneous solution. As a result there have been no extensive photochemical investigations of such complexes for either $Mo^{III}$ or $W^{III}$, the second and third row congeners of $Cr^{III}$. An exception is the $4d^3$ technetium(IV) in $TcCl_6{}^{2-}$ which has been examined[108,109]. Irradiation of the thermally stable $TcCl_6{}^{2-}$ in aqueous acid at 253 nm and at 340 nm led to aquation as the only primary photoreaction detected.

$$TcCl_6{}^{2-} + H_2O \xrightarrow{h\nu} TcCl_5(H_2O)^- + Cl^-$$

Further aquation of the product occurred as a secondary photolysis and as a slow thermal reaction. The two irradiation wavelengths, which correspond to a $\pi_{Cl} \rightarrow \sigma^*_{Tc}$ LMCT transition (253 nm) and to a $\pi_{Cl} \rightarrow \pi^*_{Tc}$ LMCT transition (340 nm), gave the respective quantum yields 0.25 and 0.064 moles/einstein in 1.1 M perchloric acid. Notably the higher quantum yield is the result of populating an $e_g$ orbital. When the photolyses at 340 nm were carried out in the presence of chloride ion, the quantum yield of aquation was found to be somewhat smaller ranging down to about 0.03 in 6 M HCl. The mechanism proposed[108,109] to explain this observation involved a chloride dependent, chloride exchange step as a competitive reaction of the excited state responsible for aquation. However, there was no report concerning the effect of ionic strength on the photoreaction. Clearly the ionic strength change in going from 1.1 M $HClO_4$ to 6 M HCl is a perturbation which could be reflected in the quantum yields.

## E. SOME CONCLUDING REMARKS

From the discussions in the previous sections, it is clear that the photochemistry of the hexacoordinate complexes of the heavier transition elements is a research area of greatly expanding interest. Combined with the quantitative studies of photophysical properties, especially under comparable conditions, quantitative photochemical studies have great promise for establishing the chemical reactivities and physical properties of at least some excited states. The complexes discussed in this review run a full gamut of photoreactivities including reactions of coordinated ligands, isomerizations, redox reactions and substitutional processes. Energy transfer both to and from these heavier metal complexes has been noted, and it is clear that the range of photoproperties exhibited by these complexes is equal to or surpasses that of the more studied first transition row metal complexes.

Several important issues relating especially to the heavier transition elements were considered briefly in our discussions but should surface with greater frequency as chemists continue endeavoring to unravel photochemical reaction mechanisms. One of these is spin–orbit coupling and how it affects interconversion rates between different states and the relative energies of those states. Although photochemists have commonly used spin multiplicity terms to describe excited states, the use of such labels has been challenged[9b] as being potentially meaningless in many cases involving the heavier elements. Nonetheless, descriptions like "ligand field excited state", "metal-to-ligand charge transfer state", etc. appear to retain at least qualitative value in analyzing photoreactivities in terms of the expected character of such excited states. Another issue of utmost importance is the consideration of the rates and efficiencies of various interconversions of electronic states. This includes the internal conversion of higher energy states of one type to lower energy excited states which may have entirely different chemical reaction properties, as well as radiative and non-radiative deactivation to the ground state. These considerations raise formidable and yet unsolved theoretical problems for the practising photochemist; however, they must be approached if a quantitative theoretical framework for explaining photochemical reactivities is to be a goal.

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