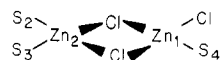We shall consider the matter from the statistical point of view. We assume that the third chloride substitutes S_1

Then the following three cases are considered for the substitution by the fourth chloride: (1) all remaining solvent molecules, S_2, S_3, and S_4, have the same possibility of substitution; (2) the fourth chloride substitutes only S_2 or S_3 bonded to the zinc ion, Zn_2; (3) only the trans solvent, S_3, is available for substitution. Then, statistical factors of K_{23}/K_{24} for these cases are calculated as 8/3, 4, and 8, respectively.[28] All reactants being noncharged ion pairs, the electrostatic interaction between them is negligible in this system. The observed ratio, therefore, indicates that the second case is most probable. It is considered reasonable that the substitution of S_2 or S_3 by chloride is neither sterically nor electrostatically affected by the third chloride already attached to Zn_1. The statistical factor of $K_{25}/K_{26} = 4$, calculated on the above assumption (2), is in good agreement with the observed value, $\log(K_{25}/K_{26}) = 0.57$ ($K_{25}/K_{26} = 3.7$).

The observed value of $\log(K_{24}/K_{25}) = 1.37$ is much larger than that calculated statistically by using the above assumption, $(K_{24}/K_{25})_{stat} = 1$. This difference may be attributable to the effect on neighboring terminal chloride already attached. Then we can estimate the equilibrium constant of the following equilibrium to be $10^{1.4}$

$$Zn_2Cl_4(S_2)(S_3) \rightleftharpoons Zn_2Cl_4(S_2)(S_4) \text{ or}$$
$$Zn_2Cl_4(S_3)(S_4)$$
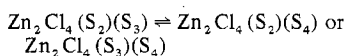
Monomeric cadmium complexes are considered to have an octahedral configuration, and the difficulties in taking the tetrahedral configuration would prevent the formation of dimeric species.

Although the formation constants of halogeno complexes with group 2B elements increase considerably with increasing atomic number in aqueous solution,[2] the formation constants of monochloro complexes of zinc and cadmium, β_{11}, differ little in acetic acid. The formation enthalpies of the complexes in the gaseous phase are similar for these ions, while the hydration enthalpies of the ions decrease with the atomic number of the central metal ion. Therefore, the difference in the formation constants of halogeno complexes in the aqueous solution is mainly due to the difference in hydration energy. On the other hand, in a solvent of low solvating power such a acetic acid, it seems reasonable that the formation energy of the halogeno

complex differs little for zinc and cadmium.

Registry No. $Zn(ClO_4)_2$, 13637-61-1; $Cd(ClO_4)_2$, 13760-37-7; $[ZnCl(S)_5]^+,ClO_4^-$, 59448-52-1; $[Zn_2Cl_2(S)_4]^{2+},2(ClO_4^-)$, 59448-54-3; $[Zn_2Cl_3(S)_3]^+,ClO_4^-$, 59448-56-5; $[Zn_2Cl_4(S)_2]$, 59448-57-6; $Li^+,[Zn_2Cl_5(S)]^-$, 59448-58-7; $2Li^+,[Zn_2Cl_6]^{2-}$, 59448-59-8; $[CdCl(S)_5]^+,ClO_4^-$, 59448-61-2; $CdCl_2$, 10108-64-2; $Li^+,[CdCl_3(S)_3]^-$, 59448-62-3; $[Cd_2Cl_2(S)_4]^{2+},2(ClO_4^-)$, 59448-64-5; $LiClO_4$, 7791-03-9; $LiCl$, 7447-41-8.

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Notes

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106

Photochemical Studies of Iridium(III)–Ammine Complexes. Ligand Field Excitation of $Ir(NH_3)_6^{3+}$, $Ir(NH_3)_5H_2O^{3+}$, and $Ir(NH_3)_5Cl^{2+}$ in Aqueous Solution

Andrew W. Zanella, Mehdi Talebinasab-Sarvari, and Peter C. Ford*[1]

The photochemistry resulting from ligand field excitation of hexacoordinate d^6 transition metal complexes has been an active area of mechanistic study in recent years.[2-4] Systems investigated include Werner type complexes of Co(III), Rh(III), Ru(II), Fe(II), and Pt(IV), as well as several metal

carbonyl systems. Iridium(III) complexes have been shown to be photoactive, and photolytic techniques have been employed for some syntheses.[4] However, the *only* amine complexes for which quantum yields have been reported for the direct excitation of ligand field bands are *trans*-$Ir(en)_2Cl_2^+$ and of $Ir(NH_3)_5N_3^{2+}$. The former complex undergoes photoaquation of Cl^- with a quantum yield of ~ 0.1 mol/einstein when irradiated at 350 nm.[5] In contrast, ligand field excitation of the azide complex leads not to substitution reactions but to efficient decomposition of the coordinated azide to give $Ir(NH_3)_5(NH_2Cl)^{3+}$ and N_2 as the products in aqueous HCl.[6] It is unlikely that these products represent a reaction of a ligand field excited state.

Reported here is a quantitative investigation of the photoreactions of $Ir(NH_3)_6^{3+}$, $Ir(NH_3)_5H_2O^{3+}$, and Ir-

Table I. Spectral and Photochemical Properties of Iridium(III)–Ammine Complexes in Aqueous Solution (25 °C)

Complex	λ_{max},[a] nm (ϵ)	Assignment[a]	λ_{irr},[b] nm	Φ_X,[c] mol/einstein	Φ_{NH_3},[d] mol/einstein
$Ir(NH_3)_6^{3+}$ [e]	~315 sh (14)	f	313	0.09 ± 0.02 (3)	0.093 ± 0.006 (9)
	251 (92)	$^1T_1 \leftarrow {}^1A_1$	254	0.083 ± 0.001 (2)	0.082 ± 0.001 (4)
	214 (160)	$^1T_2 \leftarrow {}^1A_1$			
$Ir(NH_3)_5H_2O^{3+}$ [g]	~333 sh (12)	f	313	0.42 ± 0.02 (2)	<0.002 (1)
	258 (86)	$(^1E, {}^1A_2) \leftarrow {}^1A_1$	254	h	<0.03 (1)
	213 (128)	$(^1E, {}^1B_2) \leftarrow {}^1A_1$			
$Ir(NH_3)_5Cl^{2+}$ [i]	~365 (10)	f	313	0.13 ± 0.02 (3)	0.021 (1)
	286 (73)	$(^1E, {}^1A_2) \leftarrow {}^1A_1$	254	0.15 ± 0.02 (4)	0.026 ± 0.01 (2)
	227 (333)	$(^1E, {}^1B_2) \leftarrow {}^1A_1$		0.14 ± 0.01 (2)[j]	

[a] Reference 7. [b] Wavelength of photolysis light. [c] Quantum yield for L aquation as determined by spectrophotometry for L = NH_3 or Cl^- and by mass spectral techniques for L = H_2O. [d] Quantum yield for NH_3 aquation as determined from pH changes (initial pH 2.8–3.7), standard deviations and number of determinations (in parentheses) reported. [e] ClO_4^- salt; [Ir] ≅ 5 × 10^{-3} M. [f] Singlet → "triplet" band. [g] ClO_4^- salt; [Ir] = 5.5 × 10^{-3} M at 254 nm, 8.8 × 10^{-3} M at 313 nm. [h] Not determined. [i] Cl^- salt; [Ir] = 7 × 10^{-3} M at 254 nm, 1.2 × 10^{-3} M at 313 nm. [j] Φ_{Cl^-} determined by potentiometric titration of chloride photoaquated from the perchlorate salt.

$(NH_3)_5Cl^{2+}$ in aqueous solution. These iridium(III)–ammine complexes were studied as an extension of our interests in the photochemistry of similar Rh(III) and Ru(II) species with the goal of establishing the threads of generality which extend from one metal ion system to another.

Experimental Section

Reagent grade materials and doubly distilled water were used throughout. $[Ir(NH_3)_6][ClO_4]_3$,[8] $[Ir(NH_3)_5H_2O][ClO_4]_3$,[9] and $[Ir(NH_3)_5Cl]Cl_2$[10] were synthesized and purified according to published procedures. The uv spectra quantitatively agreed with reported values.[7]

Photolyses were carried out in 2-cm path length cylindrical quartz spectrophotometer cells using apparatus and procedures described previously.[11-13] Reaction solutions were prepared from dilute perchloric acid (pH 3.0–3.7) with iridium complexes in the concentration range (1.2–6.7) × 10^{-3} M. Quantum yields for ammonia aquation (Φ_{NH_3}) were determined from changes in the solution pH. In addition, spectral changes were used to evaluate the quantum yields (Φ_L) for photoaquation of NH_3 from $Ir(NH_3)_6^{3+}$ and of Cl^- from $Ir(NH_3)_5Cl^{2+}$. The quantum yields for chloride photoaquation were confirmed independently by potentiometric titration with silver nitrate solution. Typical irradiation intensities were 1.4 × 10^{-7} einstein/(l. s) (254 nm) and 1.8 × 10^{-6} einstein/(l. s) (313 nm) as determined by ferrioxalate actinometry. Corrections were not made for thermal reactions since control solutions in the dark displayed no spectral or pH changes, thus confirming the very low thermal reactivity of the pentaammineiridium(III) complexes.[10,14] Product study photolyses were carried to completion by irradiating reaction solutions with an Ultraviolet Products Model PCQ-X1 low-pressure mercury lamp (principally 254-nm irradiation). The extent of reaction was evaluated by periodic measurement of the photosolution spectrum.

Quantum yields for the photoexchange between solvent and coordinated water for solutions of $Ir(NH_3)_5H_2O^{3+}$ in oxygen-18-enriched water were carried out using the apparatus and procedures identical with those described[13] for the analogous reactions of $Rh(NH_3)_5H_2O^{3+}$. Reaction solutions were prepared by dissolving accurately weighed $[Ir(NH_3)_5H_2O][ClO_4]_3$ (66–80 mg) in 5.5 ml of the enriched water (1.6% oxygen-18). These solutions were irradiated in a 2-cm cylindrical quartz spectrophotometer cell with 313-nm light. The reactions were carried out at 25.0 °C. The thermal exchange reaction has been studied previously[10] and is negligible under the condition of the photolysis experiments.[10]

Results and Discussion

Quantum yields measured in this study are summarized in Table I. Extensive irradiation of $Ir(NH_3)_5H_2O^{3+}$ in pH 3.0–3.7 aqueous solution with either 254- or 313-nm light leads to minimal changes in the absorption spectrum and solution pH. Ammonia aquation is therefore at most a minor pathway and the small upper limits listed for Φ_{NH_3} (Table I) are based on the estimated uncertainty of the pH measurements. The larger value for 254 nm is the result of lower irradiation intensities and thus gives higher uncertainties. Aqueous $Ir(NH_3)_5H_2O^{3+}$ is photoactive, however, and exchanges coordinated and solvent water (eq 1) under 313-nm irradiation

$$Ir(NH_3)_5H_2O^{3+} + H_2{}^{18}O \xrightarrow{h\nu} Ir(NH_3)_5(H_2{}^{18}O)^{3+} + H_2O \quad (1)$$
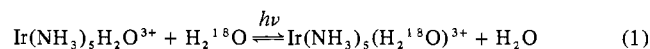
in oxygen-18-enriched solution.

Irradiation of aqueous $Ir(NH_3)_6^{3+}$ at either 254 or 313 nm leads to spectral and pH changes consistent with the photoaquation of one ammonia (eq 2). Quantum yields calculated

$$Ir(NH_3)_6^{3+} + H_3O^+ \xrightarrow{h\nu} Ir(NH_3)_5H_2O^{3+} + NH_4^+ \quad (2)$$
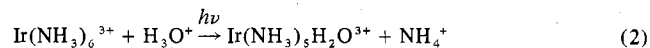
from spectral changes assuming eq 2 are matched within experimental uncertainty by those calculated from pH changes (Table I). The quantum yields are modestly wavelength dependent with the larger value at 313 nm; however, this difference may be within the experimental uncertainties given the differences in cell and photolysis lamp configuration for photolyses at these two wavelengths. Exhaustive photolysis of $Ir(NH_3)_6^{3+}$ solutions leads to product solutions having absorption spectra (λ_{max} and extinction coefficients) virtually identical with those predicted for $Ir(NH_3)_5H_2O^{3+}$ at the same concentration.

Photolysis of $Ir(NH_3)_5Cl^{2+}$ in pH 3.00 or 3.67 aqueous solution with 254- or 313-nm light, respectively, leads only to small increases in solution pH. Thus, ammonia photoaquation is a minor pathway with $\Phi_{NH_3} \simeq 0.02$ mol/einstein at both wavelengths. Initial spectral changes correspond to the formation of $Ir(NH_3)_5H_2O^{3+}$ as the principal photolysis product (eq 3). Although the spectrum of the ammonia

$$Ir(NH_3)_5Cl^{2+} + H_2O \xrightarrow{h\nu} Ir(NH_3)_5H_2O^{3+} + Cl^- \quad (3)$$
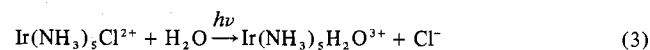
aquation product(s) is unknown, the Φ_{Cl} values reported based on the assumption that the aquation of NH_3 does not affect the spectrum dramatically are confirmed by titration of the photoaquated chloride.

For each of the complexes studied, the discernible absorption bands (Table I) can be assigned to ligand field absorptions.[7] Since Ir(III) is not easily reduced, ligand to metal charge-transfer states must lie at a relatively high energy. Consequently, the states populated by initial excitation at 313 nm and the lower energy excited states reached by subsequent internal conversion/intersystem crossing are undoubtedly ligand field in character and derived from a $(t_{2g})^5(e_g)^1$ electronic configuration. Some charge-transfer-to-metal character may contribute to the absorption at 254 nm; however, the low extinction coefficients at this wavelength (e.g., ϵ_{254} 69 for $Ir(NH_3)_5Cl^{2+}$) argues against a significant contribution. Substitution reactions would be anticipated given the general behavior resulting from population of LF states of other d^6 metal ion complexes. It has been argued[15,16] for d^6 complexes that the weak-field axis (of the three defined by the six ligands) will be the one preferentially labilized on ligand field (LF) excitation. This prediction is confirmed for the

Table II. Comparison of Quantum Yields for the Ligand Field Excitation of Rh(III) and Ir(III) Complexes[a]

$$M(NH_3)_5L^{n+} + H_2O \xrightarrow[\Phi_L]{h\nu} M(NH_3)_5H_2O^{3+} + L$$

	Ir(III)		Rh(III)	
Complex	λ_{irr}, nm	Φ_L, mol/ einstein	λ_{irr}, nm	Φ_L, mol/ einstein
$M(NH_3)_6^{3+}$	313	0.09	313	0.075[b]
	254	0.082	254	0.07[b]
$M(NH_3)_5H_2O^{3+}$	313	0.42	313	0.43[c]
$M(NH_3)_5Cl^{2+}$	313	0.13	280–380	0.12–0.16[d]
		0.02[e]		≤10⁻³ [e]

[a] In 25 °C, acidic aqueous solution. [b] Reference 12. [c] Reference 13. [d] T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, **76**, 1937 (1972). [e] Φ_{NH_3} from $M(NH_3)_5Cl^{2+}$.

Table III. Φ_{NH_3} Values for the Ligand Field Excitation of $M(NH_3)_6$[a]

$$M(NH_3)_6 + H_2O \xrightarrow{h\nu} M(NH_3)_5H_2O + NH_3$$

M	λ_{irr}, nm	Φ_{NH_3}, mol/einstein	M	λ_{irr}, nm	Φ_{NH_3}, mol/ einstein
Co(III)	514	0.0002[b]	Ir(III)	313	0.09
	488	0.0003		254	0.082
	365	0.005[c]	Ru(II)	313	~0.2[e]
Rh(III)	313	0.075[d]	Cr(III)	380–600	0.30[f]
	254	0.07[d]		320–410	0.36[f]

[a] In 25 °C, acidic aqueous solution. [b] Reference 15. [c] Reference 2, p 231. [d] Reference 12. [e] R. E. Hintze, Ph.D. Dissertation, University of California, Santa Barbara, Calif., 1974. [f] Reference 2, p 96.

photolysis of $Ir(NH_3)_5H_2O^{3+}$ and $Ir(NH_3)_5Cl^{2+}$. However, in contrast to similar cobalt(III) systems,[15] the ligand preferentially labilized is the one occupying the weaker position in the spectrochemical series (i.e., H_2O or Cl^-).

The quantitative similarity between Φ_L values for analogous Ir(III) and Rh(III) complexes (Table II) is somewhat surprising. The only difference of consequence is the modest NH_3 photoaquation noted for $Ir(NH_3)_5Cl^{2+}$. We have also observed qualitatively that, as with the Rh(III) analogues, NH_3 aquation is the dominant photoreaction resulting from LF excitation of $Ir(NH_3)_5Br^{2+}$ and $Ir(NH_3)_5I^{2+}$.

Thermal substitution reactions for iridium(III)–ammine complexes are generally much slower than for the Rh(III) analogues.[10,14] In addition, limited data suggest that the measured lifetimes of iridium(III)–ammine ligand field excited states are shorter than those of the equivalent Rh(III) states.[17] Thus, the quantum yield similarities between the Ir(III) and Rh(III) systems may be fortuitous, although moderate activity toward photoaquation is common for LF excitation of hexacoordinate metal complexes. For example, comparison of Φ_{NH_3} values for various hexaammine complexes (Table III) shows that of the systems [Ru(II), Co(III), Rh(III), Ir(III), and Cr(III)] for which quantitative data are available, Co-$(NH_3)_6^{3+}$ is the only one which does not display moderate activity toward photosubstitution under ligand field excitation in aqueous solution. One might argue that the lower energy of Co(III) LF states may provide alternative pathways for rapid nonradiative deactivation. However, while there is little evidence regarding how the mechanisms for photosubstitution differ among these ions, it is noteworthy that recent studies[18] of the tripositive metal–ammine complexes $M(NH_3)_5H_2O^{3+}$ (M = Cr(III), Co(III), Rh(III), or Ir(III)) indicate that the mechanism of the thermal substitution reaction for Co(III) is different (interchange dissociative) from those (interchange associative) of the other three. Nonetheless, the connecting

points between excited-state and ground-state reaction mechanisms are poorly understood, and it is not unlikely that the low photoactivity of cobalt(III)–ammine complexes to ligand field excitation is little related to those properties which differentiate the ground-state substitution mechanisms.

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Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Photochemistry of Dithiocarbamato Complexes. 1. Photolysis in Chlorine-Containing Solvents

G. L. Miessler, G. Stuk,[1a] T. P. Smith,[1b] K. W. Given, M. C. Palazzotto, and L. H. Pignolet*

There have been only two reports on the photochemistry of metal dithiocarbamato complexes.[2] One of these involved the reversible photobleaching of tris(*N,N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, [Ni(Bu₂dtc)₃]Br, in acetonitrile solution according to eq 1.[2a] This reaction which also

$$2Ni(Bu_2dtc)_3^+ + 2Br^- \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} Ni(Bu_2dtc)_2 + NiBr_2 + 2(Bu_2dtc)_2 \quad (1)$$
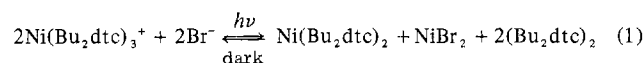
occurs thermally suggests that photoreduction of the metal