plified somewhat because, due to the structural similarities of these ligands and the absence of steric effects, K_s must be due entirely to electronic effects. Let us consider the effects of electrostatic attraction and repulsion on bond length between the positively charged iron and ligand A, B, or C. Ligand A is neutral whereas B and C carry negative charges. No electrostatic interactions exist between A and Fe nor between A and the neighboring ligands, so the A–Fe bond lengths should be nearly identical in all of the mixed complexes for a single oxidation state of iron. However, the C–Fe bond length should increase (or the bond strength should decrease) in going from A_2CFe to AC_2Fe to C_3Fe because of the increasing electrostatic repulsion between the negatively charged C ligands. For the mixed complexes A_2CFe and AC_2Fe, this results in stabilities that are greater than would be predicted from simple ligand additivity and entropic effects, and positive values of log K_s are anticipated for both the iron(II) and iron(III) derivatives. The data in Table I, however, give us only the *ratio* of stabilization constants. The positive values for log $(K_{s,o}/K_{s,r})$ show that the stabilization effect is greater for the iron(III) derivatives, which is not surprising given that a negatively charged ligand C should interact more strongly with iron(III) than with iron(II). The same arguments apply to the A–B–Fe system. For the B–C–Fe complexes, however, no significant stability enhancement is anticipated for either the iron(II) or the iron(III) complex because all ligands in these complexes are negative charged. This would result in values of $K_{s,o}$ and $K_{s,r}$ that are both close to unity. The values of log $(K_{s,o}/K_{s,r})$ for B_2CFe and BC_2Fe in Table I are both approximately zero, which is consistent with this argument.

It should be emphasized that the arguments presented above are based on the assumption that only electrostatic interactions contribute to K_s for the mixed complexes and, as a corollary to this assumption, that values of log K_s are positive for mixed complexes containing at least one neutral ligand and at least one negatively charged ligand. While the values of log $(K_{s,o}/K_{s,r})$ are consistent with these assumptions, knowledge of the absolute values of K_s for the mixed complexes is desirable. Due to the kinetic instability of the iron(III)–phenanthroline complexes to hydrolysis, direct determination of the formation constants of the complexes (from which the mixing constants are readily calculated) would be extremely difficult. If, however, the formation constants of the iron(II) derivatives were measured, eq 11, 19, and 21 could then be applied to calculate the formation constants, mixing constants, and stabilization constants of the iron(III) derivatives.

Conclusion

The relationship between the reduction potential of a mixed-ligand complex and the reduction potentials of the parent binary complexes, in which the electronic spin states of all complexes are the same and no significant spin equilibrium exists, has been established. As demonstrated by the discussion on the mixed complexes of iron phenanthrolines, the relationships involving K_m and K_s provide a convenient and sound basis to account for the observed reduction potentials of the mixed-ligand-complex couples. These relationships also provide a means to calculate the mixing constants and stabilization constants for one oxidation state of a mixed-ligand complex couple, provided that the corresponding constants for the other oxidation state are known.

Contribution from the Department of Chemistry and Quantum Institute,
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Synthesis and Excited-State Properties of Rhodium(III) Terpyridine Complexes

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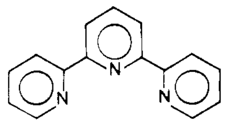
Reported are the photophysical properties of several previously known and newly synthesized rhodium(III) complexes of 2,2′:6′,2″-terpyridine: $Rh(trpy)_2^{3+}$, $Rh(trpy)(bpy)(py)^{3+}$, and $Rh(trpy)(bpy)Cl^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine). The absorption spectrum of each of these complexes in aqueous solution is dominated by intraligand π_L–π_L* transitions that obscure the regions where ligand field (LF) bands would be expected. However, the luminescence spectra both in ambient-temperature fluid solutions and in 77 K glasses show broad, Gaussian-shaped bands interpreted to be the result of emission from the lowest energy triplet ligand field states. Photolysis of $Rh(trpy)(bpy)Cl^{2+}$ in aqueous solution leads to photolabilization of Cl^-, as seen with other Rh(III) chloro amine complexes; however, the quantum yield proved to be quite small (0.002 mol/einstein), a feature that can be attributed to an unusually small rate constant for Cl^- labilization from the ^{3}LF* state.

The polypyridyl complexes of d^6 metal ions have been the subjects of considerable interest in recent years, especially with regard to their extraordinarily rich photochemical and photophysical properties. Much of this attention has focused on complexes of 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and their substituted derivatives; however, some examples of 2,2′:6′,2″-terpyridine (trpy) complexes have also been the objects of photochemical/physical investigations.[3-5] The present investigation is concerned with such properties of rhodium(III) trpy complexes, the goals being to compare these to similar Rh(III) complexes of other amines and to characterize the manner in which changes in ligand fields influence the energies and dynamics of relevant excited states (ES).


trpy

Experimental Section

Syntheses. Trichloro(terpyridine)rhodium(III), $Rh(trpy)Cl_3$, was prepared from $RhCl_3{\cdot}xH_2O$ plus terpyridine (Aldrich) according to the

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(1) Taken in part from the Ph.D. dissertations of M.E.F. (1984) and S.D.S. (1984), University of California, Santa Barbara.

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(3) (a) Wichramasinghe, W. A.; Bird, P. H.; Serpone, N. *Inorg. Chem.* **1982**, *21*, 2694–2698. (b) Wichramasinghe, W. A.; Bird, P. H.; Jamieson, M. A.; Serpone, N. *J. Chem. Soc., Chem. Commun.* **1979**, 798–800.

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Table I. Electronic Absorption Spectra of Rhodium(III) Terpyridine Complexes[a]

complex	λ_{max}, nm	ϵ, 10^4 M^{-1} cm^{-1}
$Rh(trpy)_2^{3+}$	244	3.4
	268	2.8
	324	0.93
	338	1.5
	355	1.7
$Rh(trpy)(bpy)(py)^{3+}$	284	2.5
	310	2.5
	340	0.72
	358	0.5
$Rh(trpy)(bpy)Cl^{2+}$	283	2.2
	309	2.5
	339	0.79
	356	0.64
$Rh(trpy)(bpy)(H_2O)^{3+}$	282	2.1
	308	2.4
	338	0.81
	355	0.64

[a] Spectra of the ClO_4^- salts in 10^{-3} M $HClO_4$ aqueous solution at 298 K.

published method.[6] Bis(terpyridine)rhodium(III) chloride, $[Rh(trpy)_2]Cl_3$, was prepared via reaction of trpy with $Rh(trpy)Cl_3$ as reported.[7] The chloride salt was then dissolved in aqueous solution and the solid perchlorate $[Rh(trpy)_2](ClO_4)_3$ obtained by adding $NaClO_4$. Each of these materials was purified by recrystallization.

Chloro(bipyridine)(terpyridine)rhodium(III) chloride, $[Rh(trpy)(bpy)Cl]Cl_2 \cdot 3H_2O$, was prepared via the following procedure. A solution of $Rh(trpy)Cl_3$ (0.26 g) and 2,2′-bipyridine (0.095 g) in dimethylformamide (5 mL) plus ethanol (15 mL) was refluxed gently for 6 h to give a pale yellow solution. The cooled mixture was filtered, and then ether (20 mL) was added to the filtrate, from which a pale yellow solid precipitated. The product was dried in vacuo. Anal. Calcd for $RhC_{25}H_{25}N_5Cl_3O_3$: C, 46.00; H, 3.80: N, 10.72. Found: C, 46.13; H, 3.85; N, 10.94. This compound was soluble in water and ethanol and was converted to the perchlorate salt by dissolving it in hot water and adding aqueous sodium perchlorate. Upon cooling, $[Rh(trpy)(bpy)Cl](ClO_4)_2 \cdot H_2O$ crystallized from the solution. The crystals were washed with cold water and then dried in vacuo. Anal. Calcd for $RhC_{25}H_{21}N_5Cl_3O_9$: C, 40.32; H, 2.84; N, 9.40. Found: C, 40.65; H, 2.72; N, 9.30.

Aqua(bipyridine)(terpyridine)rhodium(III) perchlorate, $[Rh(trpy)(bpy)(H_2O)](ClO_4)_3$ was prepared by dissolving $[Rh(trpy)(bpy)Cl](ClO_4)_2 \cdot H_2O$ (0.2 g) in hot water (25 mL) and adding $AgNO_3$ (0.2 g in 5 mL of H_2O). The solution immediately became cloudy. This mixture was heated at 100 °C for 15 min and then filtered while hot. Dilute (10%) $HClO_4$ was added to the filtrate, from which, upon cooling, precipitated a very pale cream-colored crystalline solid. The solid was washed with cold water and dried in vacuo. Anal. Calcd for $RhC_{25}H_{21}N_5Cl_3O_{13}$: C, 37.13; H, 2.62; N, 8.66. Found: C, 37.68; H, 2.73; N, 9.18.

(Bipyridine)(pyridine)(terpyridine)rhodium(III) perchlorate monohydrate, $[Rh(trpy)(bpy)(py)](ClO_4)_3 \cdot H_2O$ was prepared as follows. A mixture of $[Rh(trpy)(bpy)Cl](ClO_4)_2 \cdot 3H_2O$ (0.14 g), pyridine (1 g), and ethanol (15 mL) was refluxed for 10 h. This mixture was filtered and then the volume reduced to 10 mL by boiling. Excess ether addition to the cooled solution led to the formation of pale yellow crystals. These were collected, washed several times with ether, dried, and dissolved in warm water. The hot solution was filtered, and aqueous $NaClO_4$ was added, whereupon the pale yellow product crystallized. Anal. Calcd for $RhC_{30}H_{26}N_6Cl_3O_{13}$: C, 40.56; H, 2.95; N, 9.46. Found: C, 40.59; H, 2.75; N, 9.57.

Photochemical Procedures. The photolyses of $Rh(trpy)(bpy)Cl^{2+}$ were carried out at 313 nm in dilute aqueous solutions (10^{-3} M $HClO_4$) by using the apparatus and actinometry procedures described previously.[8] The quantum yield for Cl^- aquation (ϕ_{Cl}) was calculated from the change in the concentration of the free chloride in solution by using a Gam Rad chloride ion electrode sensitive to 1×10^{-6} M and a Gam Rad double-junction reference electrode on a Radiometer PHM 84 pH meter. Standard chloride ion solutions were used to prepare calibration curves.

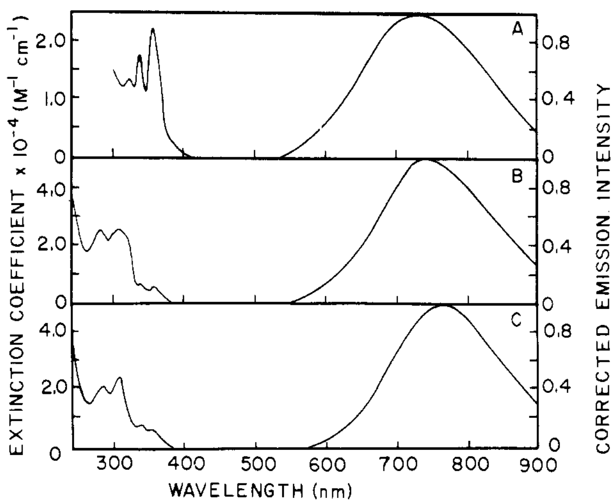

Figure 1. Absorption spectra in 298 K aqueous solution (left) and emission spectra in 77 K ethanol glass of $Rh(trpy)_2^{3+}$ (A), $Rh(trpy)(bpy)(py)^{3+}$ (B), and $Rh(trpy)(bpy)Cl^{2+}$ (C) (ClO_4^- salts in each case).

Table II. Photoluminescence Data in 77 K Glasses for Terpyridine and Related Complexes of Rhodium(III)

complex[a]	ν_{max}, μm^{-1}	τ, μs	ϕ_{em}	$\Delta\nu_{1/2}$, μm^{-1}	ν_{00}, μm^{-1} [b]
$Rh(trpy)_2^{3+}$	1.36	8.0	0.09	0.37	1.84
$Rh(trpy)(bpy)(py)^{3+}$	1.37	16.5	0.08	0.35	1.82
$Rh(trpy)(bpy)Cl^{2+}$	1.31	9.3	0.10	0.37	1.78
$Rh(bpy)_2Cl_2^+$ [c]	1.42	27.2	0.04	0.35	1.86
$Rh(NH_3)_5Cl^{2+}$ [d]	1.42	17.2	0.002	0.38	1.91
$Rh(NH_3)_6^{3+}$ [e]	1.64	18.7	$<10^{-3}$	0.37	2.12
$Rh(NH_3)_5(py)^{3+}$ [e]	1.63	17.1	[f]	0.37	2.10
$Rh(bpy)_3^{3+}$ [c]	2.22[g]	2.2×10^3	[f]	[f]	2.22[g]

[a] Perchlorate salts in EtOH/MeOH or MeO/H_2O glasses. [b] Calculated from the approximation $\nu_{00}(calcd) = \nu_{max} + 1.29\Delta\nu_{1/2}$.[9] [c] Reference 11. [d] Bergkamp, M. A. Ph.D. Dissertation, UCSB, 1980. [e] Reference 9. [f] Not determined. [g] Highest frequency band of a structured emission from a π_L/π_L^* ES.

Luminescence Procedures. Emission spectra at 77 K were measured in ethanol/methanol (4/1) glasses on a red-sensitive lock-in amplifier apparatus in this laboratory as described in earlier publications.[9] A dry-ice-cooled RCA 7102 photomultiplier tube (S-1 spectral response) was used. The emission intensities were corrected for monochromator and PMT spectral response on a Digital PDP 11 computer by using a correction program. Emission quantum yields were determined on the same apparatus calibrated by using fluorescein as a standard. Lifetime measurements were carried out at 77 K in ethanol glasses and at near-ambient temperatures in aqueous solutions by using the Nd/YAG pulse laser system reported previously.[10,11] Experimental uncertainties for lifetime measurements in ambient-temperature solutions are <±10%, while those in 77 K glasses are <±5%. For emission quantum yields, the estimated experimental uncertainties are ±10%.

Results

The absorption spectra of the trpy Rh(III) complexes $Rh(trpy)_2^{3+}$ (I), $Rh(trpy)(bpy)(py)^{3+}$ (II), and $Rh(trpy)(bpy)Cl^{2+}$ (III) are summarized in Table I. These spectra are dominated by the intense intraligand transitions that obscure the near-UV region where ligand field bands for Rh(III) amine complexes would be expected to fall. However, the 77 K emission spectra in alcohol glasses gave, in each case, broad Gaussian-shaped bands

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[6] Bhayat, I. I.; McWhinnie, W. R. *Spectrochim. Acta, Part A* **1972**, *28A*, 743.

[7] Harris, C. M.; McKenzie, E. D. *J. Inorg. Nucl. Chem.* **1963**, *25*, 171.

[8] (a) Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549-4554. (b) Petersen, J. D.; Ford, P. C. *J. Phys. Chem.* **1974**, *78*, 1144-1149.

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(Figure 1 and Table II) similar in shape and energy to those described for Rh(III) complexes of saturated amines and assigned as originating from lowest energy ligand field triplet states.[9,12] Time-resolved spectra recorded by using pulsed excitation and a boxcar averager indicated only a single emitting state in each case. Luminescence lifetimes were measured in 77 K alcohol glasses and found to be 8.0, 16.5, and 9.3 μs with emission quantum yields of 0.09, 0.08, and 0.10 for I, II, and III, respectively. These data are given in Table II.

In aqueous solutions (10^{-3} M) at near-ambient temperature, emission lifetimes for II and III were found to be nearly 3 orders of magnitude lower (14.2 and 14.9 ns, respectively, at 298 K) and emission intensities proved to be very weak (too weak to determine accurate emission quantum yields). A modest temperature effect on τ in fluid solutions (275–308 K) was noted with E_a(apparent) values of about 1.4 and 1.8 kcal/mol (0.05 and 0.06 μm^{-1}, respectively). Lifetimes were unaffected by increasing the $HClO_4$ concentration to 1.0 N or by using 1.0 N HCl as the medium. However, τ was lengthened in D_2O solution (298 K) to 17.9 and 19.8 ns for II and III with the respective E_a(apparent) values of 1.8 and 2.1 kcal/mol (0.06 and 0.07 μm^{-1}). For $Rh(trpy)_2^{3+}$, no emission was observable in aqueous solution over the temperature range 278–298 K.

The photolysis of $Rh(trpy)(bpy)Cl^{2+}$ in dilute aqueous solution (pH 3) with 313-nm light led to the aquation of Cl^- with a quantum yield of 0.002 ± 0.0005 mol/einstein as measured with the use of a chloride ion selective electrode. This process was accompanied by virtually no spectral changes; however, given that III and $Rh(trpy)(bpy)(H_2O)^{3+}$ have virtually the same spectra (see Table I), these observations are consistent with the occurrence of the reaction shown in eq 1. The absence of pH changes in

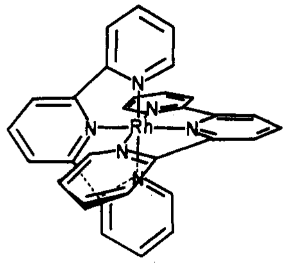
$$Rh(trpy)(bpy)Cl^{+} + H_2O \xrightarrow{h\nu} Rh(trpy)(bpy)(H_2O)^{3+} + Cl^- \qquad (1)$$

the solution implies that little or no amine was aquated under these conditions. No spectral changes were noted on photolysis of aqueous $Rh(trpy)_2^{3+}$; however, the photochemical properties of neither I nor II were examined in detail.

Discussion

Emission Properties. The microsecond lifetimes and broad Gaussian-shaped bands with low-energy ν_{max} values recorded in the 77 K alcohol glasses for the perchlorate salts of I, II, and III point strongly to the assignment of the luminescence spectra of these Rh(III) terpyridine complexes, each being from a lowest energy triplet ligand field state ($^3LF^*$). For $Rh(trpy)_2^{3+}$, the obvious comparisons are to other Rh(III) complexes in which all coordination sites are occupied by nitrogens. Examples quantitatively investigated include $Rh(bpy)_3^{3+}$, $Rh(dmbp)_3^{3+}$ (dmbp = 3,3′-dimethyl-2,2′-bipyridine), $Rh(phen)_3^{3+}$, and $Rh(NH_3)_6^{3+}$.[9,11,13] For the first three, the 77 K emission is from ligand-centered $^3(\pi_L-\pi_L^*)$ states with ν_{00} values (estimated from the position of the highest energy vibrational feature in the structured emission) at 2.22, 2.22, and 2.07 μm^{-1}, respectively, while the 77 K emission of $Rh(NH_3)_6^{3+}$ is unambiguously from a metal-centered $^3T_{1g}$ LF state with an estimated energy of 2.12 μm^{-1}.[9] For $Rh(dmbp)_3^{3+}$, there is also evidence of 77 K emission from a second, slightly higher energy ES, a $^3LF^*$ state estimated to have the ν_{00} energy 2.15 μm^{-1} according to a Gaussian band shape analysis described previously.[9,14] For this complex the steric repulsion between the methyl groups in the 3- and 3′-positions forces the two pyridyl rings of the coordinated dmbp about 30° out of coplanarity.[15] The result is a lower field strength relative to unsubstituted bipyridine, thus a lower $^3LF^*$ energy for $Rh(dmbp)_3^{3+}$ than for $Rh(bpy)_3^{3+}$, which must have an energy >2.22 μm^{-1}. For comparison, the $^3LF^*$ of $Rh(trpy)_2^{3+}$ has an estimated ν_{00} of 1.84 μm^{-1}, a feature that suggests the effective field strength of terpyridine to be substantially smaller than that of bpy, phen, dmbp, or NH_3.

In comparing ligand field strengths, one should note that the symmetry of I differs from those of the other examples, which are O_h (the hexaamine) or D_3 with roughly holohedral O_h symmetry (the three tris chelates for which the six coordination sites are equivalent). In contrast, the symmetry of $Rh(trpy)_2^{3+}$ is C_{2v} but is roughly holohedral D_{4h} with the central nitrogens of the terpyridines trans to each other along one axis and the four distal pyridines in equatorial positions (see A). There is considerable evidence from the crystal structures of various $M(trpy)_2^{n+}$ complexes that the M–N bond to the center pyridine of terpyridine is generally short relative to analogous M–N bonds for other polypyridyl ligands (implying a high field strength at the center position), while the M–N bonds to the distal pyridines are longer.[3,16] Furthermore, the N–M–N angles of coordination to the two distal nitrogens of a single trpy tend to be considerably less than 180°. These two features would point to substantial splitting of the ^3A and ^3E LF states of the D_{4h} complex, the ^3A state having the lower energy. It is the energy of the latter state, primarily reflecting the metal–distal pyridine interactions, that determines the emission frequency for $Rh(trpy)_2^{3+}$. A similar argument can be applied to the LF emissions from $Rh(trpy)(bpy)(py)^{3+}$ and $Rh(trpy)(bpy)Cl^{2+}$ (see B), which appear at lower energies than those from $Rh(NH_3)_5(py)^{3+}$ and $Rh(NH_3)_5Cl^{2+}$, respectively (Table II).



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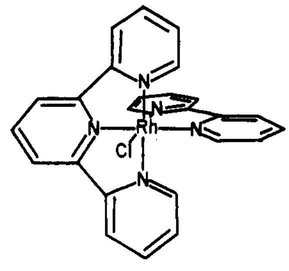

B

The ruthenium(II) complex $Ru(trpy)_2^{2+}$ displays a metal-to-ligand-charge-transfer (MLCT) emission similar to that of $Ru(bpy)_3^{2+}$; however, the lifetime of the MLCT state for the former complex is dramatically more temperature and medium sensitive than that for the latter.[4,5d] McMillin and co-workers[5b] have attributed this to the much smaller gap between the emitting MLCT state and a LF ES (from which nonradiative deactivation is more facile) in $Ru(trpy)_2^{2+}$ than in $Ru(bpy)_3^{2+}$. Since the MLCT energies are similar, the smaller gap would be the result of a lower energy $^3LF^*$ consistent with the arguments presented here for the Rh(III) terpyridine complexes. An alternative possibility has been proposed for the emission lifetime behavior of analogous Cr(III) complexes,[3] namely that the more open structure of the bis(terpyridine) complexes allows more intimate interactions with the solvent and other solution species in a manner

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(12) Thomas, T. R.; Crosby, G. A. *J. Mol. Spectrosc.* **1971**, *38*, 118–129.

(13) (a) Spectroscopic studies of $Rh(phen)_3^{3+}$ in ambient-temperature acetonitrile solution succeeded in detecting only a weak $\pi_L-\pi_L^*$ emission similar in energy and structure to that seen in 77 K glasses.[11] This observation contrasts to reports[13b–d] that under analogous conditions the emission spectrum is dominated by a Gaussian-shaped band centered at 1.73 μm^{-1}, assigned as emission from a $^3LF^*$ having an energy of about 2.2 μm^{-1}. We have no obvious explanation for this discrepancy except to note that, given the virtually identical energies estimated for the ^3LF (2.2 μm^{-1})[13] and $^3\pi_L-\pi_L^*$ (2.22 μm^{-1})[11] states, it is possible that subtle solution differences determine the identity of the emitting state. (b) Bolletta, F.; Rossi, A.; Barigelletti, F.; Dellonte, S.; Balzani, V. *Gazz. Chim. Ital.* **1981**, *111*, 155–158. (c) Indelli, M. T.; Carioli, A.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2685–2686. (d) Balzani, V., private communication.

(14) This analysis estimates the 0–0 energy as that at which the emission intensity drops to 1% of the intensity of the band maximum on the high-energy side of the band. For an idealized Gaussian band, this point is given by $\nu_{1\%} = \nu_{max} + 1.29\nu_{1/2}$ (see ref 9).

(15) Olba, S.; Miyamae, H.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1470.

(16) (a) Figgis, B. N.; Kucharski, E. S.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1563–1571. (b) Baker, A. T.; Goodwin, H. A. *Aust. J. Chem.* **1985**, *38*, 207–214.

Table III. Estimated Rate Constants for Cl^- Aquation from the Lowest Energy Ligand Field Triplet Excited States from Various Rh(III) Complexes in 298 K Aqueous Solution

complex	ϕ_{Cl}[a]	τ, ns[b]	k_{Cl}, s^{-1} [c]	k_n, s^{-1} [d]
$Rh(NH_3)_5Cl^{2+}$ [e]	0.18	14.2	1.3×10^7	5.6×10^7
$Rh(trpy)(bpy)Cl^{2+}$	0.002	14.9	1.3×10^5	6.7×10^7
cis-$Rh(NH_3)_4Cl_2^+$ [f]	0.40	1.3	3.1×10^8	4.6×10^8
cis-$Rh(bpy)_2Cl_2^+$ [g]	0.056	39	1.4×10^6	2.4×10^7

[a] Quantum yield for photoaquation of Cl^- in mol/einstein. [b] Emission lifetime of $^3LF^*$. [c] Rate constant for Cl^- aquation from $^3LF^*$ according to the equation $k_{Cl} = \phi_{Cl}\tau^{-1}$, which assumes intersystem crossing is approximately unity. [d] Rate constant for nonradiative deactivation from $^3LF^*$ according to $k_n = (1 - \phi_{Cl})\tau^{-1}$ (see text). [e] Reference 8a. [f] Reference 18. [g] Reference 10c.

facilitating nonradiative deactivation.

With regard to the Rh(III) terpyridine complexes described here, the lifetime changes for II and III between emission from glassy alcohol solutions at 77 K (Table II) and from aqueous solutions at 298 K are comparable to those seen for other Rh(III) complexes such as $Rh(NH_3)_5Cl^{2+}$ and $Rh(bpy)_2Cl_2^+$, for which a $^3LF^*$ is the lowest energy ES. In this context, it is notable that a modest, but not dramatic, enhancement of τ was noted at 298 K when D_2O was used as the solvent. Thus, there do not appear to be unusual solvation interactions dominating the photophysical properties of these trpy complexes.

Photoaquation of $Rh(trpy)(bpy)Cl^{2+}$. Although the $^3LF^*$ luminescence lifetimes of $Rh(trpy)(bpy)Cl^{2+}$ and of $Rh(NH_3)_5Cl^{2+}$ in 298 K aqueous solution are virtually the same, the Cl^- photoaquation quantum yields for these two ions differ by roughly 2 orders of magnitude. If it is assumed, as has been demonstrated for the pentaammine complex $Rh(NH_3)_5Cl^{2+}$,[17] that internal conversion/intersystem crossing from initially formed excited states to the lowest energy $^3LF^*$ has an efficiency near unity,[18] then the emission lifetimes and quantum yield are related by $\phi_{Cl} = k_{Cl}\tau$, where k_{Cl} is the rate constant for Cl^- aquation from the ligand field excited state.[8a] Thus, given the values of ϕ_{Cl} and τ, the calculated value of k_{Cl} is 1.3×10^5 s^{-1}. Table III summarizes the k_{Cl} values for the $^3LF^*$ of several similar Rh(III) complexes. In addition, these complexes are all weak emitters in ambient-temperature aqueous solutions; thus, a good approximation of the fraction of overall ES decay proceeding by nonradiative deactivation (ϕ_n) is $1 - \phi_p$, where ϕ_p is the sum of the photoreaction quantum yields. The nonradiative deactivation rate constants calculated from $k_n = \phi_n\tau^{-1}$ are also summarized in Table III.

The nature of the amine ligands has a profound influence not only on the quantum yield of Cl^- photoaquation but also on the apparent ES reaction rates. For both the dichloro and monochloro cases, the replacement of NH_3 with polypyridyl ligands led to a slowing of the Cl^- labilization by at least 2 orders of magnitude. The ligand effects on k_{Cl} might be the result of electronic differences between the polypyridyl and ammine ligands, but this seems unlikely given the similarities in their ligand field strengths. A more likely explanation might be drawn from the relative rigidity of these chelates toward distortions of the type that may accompany the dissociation of Cl^- to form a five-coordinate intermediate. Sheridan[19] has shown that Cl^- photoaquation from $RhA_4Cl_2^+$ complexes, where A_4 is the polydentate amine triethylenetetramine, depends strongly on the stereochemical configuration of A_4; configurations that appear to inhibit distortion of the initial coordination sphere as Cl^- dissociates display much lower ϕ_{Cl}'s. Sexton et al.[20] have noted that tetraamine complexes of this type which most readily undergo photoisomerization concomitant with photoaquation, are also those for which the $^3LF^*$ displays the faster rates for ligand labilization. Such observations suggest some synchronous nature of the ligand dissociation and isomerization mechanisms. Thus, a likely explanation of the relatively low reactivities of the ligand field ES of *cis*-$Rh(bpy)_2Cl_2^+$ and $Rh(bpy)(trpy)Cl^{2+}$ vs those of *cis*-$Rh(NH_3)_4Cl_2^+$ and $Rh(NH_3)_5Cl^{2+}$, respectively, lies in the rigidities of the bpy and trpy ligands.

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Registry No. $[Rh(trpy)_2](ClO_4)_3$, 106233-90-3; $[Rh(trpy)(bpy)(py)](ClO_4)_3$, 113132-43-7; $[Rh(trpy)(bpy)Cl](ClO_4)_2$, 113132-45-9; $[Rh(trpy)(bpy)(H_2O)](ClO_4)_3$, 113132-47-1; $Rh(trpy)Cl_3$, 35978-56-4; $[Rh(trpy)(bpy)Cl]Cl_2$, 113132-48-2.

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(17) Kelly, T. L.; Endicott, J. F. *J. Phys. Chem.* **1972**, *76*, 1937.

(18) (a) As a reviewer noted, the assumption that intersystem crossing yields are near unity is somewhat risky given that the initial excitation is to a state having a different orbital parentage than the lowest energy ES, a $^3LF^*$. However, it should be noted that this assumption is also consistent with the observation by Demas and Crosby[18b] of highly efficient π_L–$\pi_L^* \rightarrow {}^3LF^*$ intersystem crossing in 77 K emission spectra studies of the closely analogous complexes *cis*-$RhX_2Y_2^+$ (X = bpy, phen; Y = Cl, Br, I). The general (but underdocumented) experience with such heavier transition metal complexes is that, in the absence of photochemistry from the upper states, intersystem crossing/internal conversion to lowest energy excited states occurs with high efficiency.[18c] Regardless, only an intersystem crossing yield less than 10% would affect the conclusion drawn here that Cl^- aquation from the ^3LF state of $Rh(trpy)(bpy)Cl^{2+}$ is substantially slower than from that of $Rh(NH_3)_5Cl^{2+}$. (b) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262–7270. (c) Ford, P. C.; Wink, D. A.; DiBenedetto, J. *Prog. Inorg. Chem.* **1983**, *30*, 213–272.

(19) (a) Martins, E.; Sheridan, P. S. *Inorg. Chem.* **1978**, *17*, 2822–2826, 3631–3636. (b) The ϕ_{Cl} values for the A and B isomers of *cis*-$Rh(trien)Cl_2^+$ are reported as 0.21 and 5×10^{-4}, respectively. However, $^3LF^*$ lifetimes were not measured; thus, ES rates cannot be compared, since it is possible that the low ϕ_{Cl} for the latter isomer results from an increased nonradiative deactivation rate.

(20) Sexton, D. A.; Skibsted, L. H.; Magde, D.; Ford, P. *Inorg. Chem.* **1984**, *23*, 4533–4538.