and undergo exchange. This behavior reflects the tendency of Au(I) to form structures with linear or trigonal coordination. The exceptions occur in cases where chelate structures, for example, $[(diars)_2Au]^+I^-$,[27] or unusual cage structures, such as $[(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2]_3(AuI)_2$[28] or $[(C_6H_5)_3P]_7Au_{11}X_3$,[29] are involved.[30] We suggest, then, that the failure to isolate $[(C_6H_5)_2PCH_3]_4Au_2WS_4$ is a consequence of the preference of Au(I) for trigonal coordination and the lability of the phosphine ligands. The net-like structure of $[(C_6H_5)_2PCH_3]_2Au_2WS_4$, as opposed to a dimeric cage structure similar to that found for I, may be explained by the same considerations.

Supplementary Material Available: Final values of $|F_o|$ and F_c (in electrons) for $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$ (19 pages). Ordering information is given on any current masthead page.

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Excited-State Behavior of Polypyridyl Complexes of Chromium(III)[1]

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Abstract: Flash photolysis and luminescence techniques have been used to investigate the properties and the behavior of the ^2E excited states of Cr(III) complexes of 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′,2″-terpyridine (terpy), and some of their methyl, phenyl, and chloro derivatives. The specific complexes used in the study have been the ClO_4^- salts of $Cr(bpy)_3^{3+}$, $Cr(4,4'\text{-}Me_2bpy)_3^{3+}$, $Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$, $Cr(phen)_3^{3+}$, $Cr(5\text{-}Clphen)_3^{3+}$, $Cr(4,7\text{-}Me_2phen)_3^{3+}$, $Cr(4,7\text{-}Ph_2phen)_3^{3+}$, $Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$, and $Cr(terpy)_2^{3+}$. The following aspects of the nature of the metal-centered ^2E states have been examined and comparisons made with the behavior of the MLCT excited states of analogous polypyridyl complexes of Ru(II) and Os(II): (a) excited-state absorption and emission spectra; (b) excited-state lifetimes in aqueous solution at room temperature and in methanolic ice at 77 K; (c) solution medium effects on the excited-state lifetimes; (d) relative phosphorescence quantum yields; (e) quenching by O_2, Fe_{aq}^{2+}, and I^-. O_2 quenches ^2E predominantly via energy transfer and Fe_{aq}^{2+} and I^- quench via reductive electron transfer. An estimate of the $(^2E)Cr(NN)_3^{3+}$–$Cr(NN)_3^{2+}$ self-exchange rate yields the value of $4 \times 10^7\ M^{-1}\ s^{-1}$ in 1 M HCl at 25 °C.

Introduction

Investigations in recent years have demonstrated that excited states of transition-metal complexes can engage in electron transfer and energy transfer in solution.[3] The lowest excited states of polypyridyl complexes of Ru(II) and Os(II) can undergo oxidative and reductive electron transfer reactions and are phosphorescent.[4] These complexes are viewed as having potential applicability in solar energy storage and conversion schemes.[5,6]

The lowest excited state of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) (^2E) is phosphorescent,[7] is remarkably long lived (63 μs) in deaerated aqueous solution at room temperature,[8] and is highly reactive toward redox quenchers.[9-12] In this paper we examine in detail the excited-state behavior of polypyridyl complexes of chromium(III), $Cr(NN)_3^{3+}$, containing substi-

Table I. Elemental Analysis of Polypyridyl Complexes of Chromium(III)

complex	calcd C	calcd H	calcd N	calcd Cl	calcd Cr	found C	found H	found N	found Cl	found Cr
$Cr(bpy)_3(ClO_4)_3\cdot ½H_2O$	*a*									
$Cr(4,4'\text{-}Ph_2bpy)_3(ClO_4)_3\cdot 2H_2O$	60.44	4.00	6.41	8.11	3.96	60.52	3.97	6.28	8.02	4.93
$Cr(4,4'\text{-}Me_2bpy)_3(ClO_4)_3\cdot 2H_2O$	46.24	4.31	8.99		5.56	46.33	4.40	8.90		5.35, 5.36[b]
$Cr(phen)_3(ClO_4)_3\cdot 2H_2O$	46.64	3.04	9.07			46.93	3.02	9.11		
$Cr(5\text{-}Clphen)_3(ClO_4)_3\cdot 2H_2O$	41.97	2.44	8.16	20.64	5.05	41.60	2.20	8.07	20.60	5.09
$Cr(4.7\text{-}Me_2phen)_3(ClO_4)_3\cdot 2H_2O$	49.86	3.99	8.31	10.51	5.14	49.51	4.00	8.26	11.44	5.30
$Cr(4,7\text{-}Ph_2phen)_3(ClO_4)_3\cdot 4H_2O$	60.91	3.98	5.92	7.49	3.66	60.70	3.84	5.80	7.70	3.59
$Cr(3,4,7,8\text{-}Me_4phen)_3(ClO_4)\cdot 2.5H_2O$	52.23	4.79	7.61		4.71	52.25	4.88	7.59		4.91
$Cr(terpy)_2(ClO_4)_3\cdot 2.5H_2O$	41.80	3.16	9.75			41.88	2.83	9.97		

[a] This complex was analyzed earlier (see ref 18) and the purity of the present product was verified by absorption spectral comparisons. [b] In an earlier analysis on the same sample Cr was 4.51; the discrepancy may be due to the ashing method. This may explain the discrepancy also in the Cr analysis of the 4,4'-Ph_2bpy complex.

tuted bpy and phen (phen = 1,10-phenanthroline) ligands. Previous studies[13,14] of ligand substituent effects on the photophysical properties of polypyridyl complexes of Ru(II) and Os(II) have shown that, for complexes with charge transfer excited states ($d\pi^*$ MLCT), substitution on the polypyridyl ligands produces relatively minor variation in the lifetimes of the states. Inasmuch as the ^2E state of $Cr(NN)_3^{3+}$ complexes is metal centered, it becomes important to examine the effects of ligand substitution for Cr(III) in comparison to those reported for Ru(II) and Os(II). The aspects of the excited-state behavior that are discussed are (a) absorption and emission spectra of the ^2E species, (b) lifetimes of the ^2E species, (c) solution medium effects on the lifetimes, (d) relative phosphorescence quantum yields, and (e) quenching of ^2E by I^-, Fe_{aq}^{2+}, and O_2.

Experimental Section

Reagents and Solvents. The following materials were used without further purification as received from commercial sources: anhydrous $CrCl_2$ (98%, Alfa), 2,2'-bipyridine (bpy, Eastman), 1,10-phenanthroline monohydrate (phen, Sigma), 5-chloro-1,10-phenanthroline (5-Clphen), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me_2bpy) and 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me_4phen, G. F. Smith), 4,4'-diphenyl-2,2'-bipyridine (4,4'-Ph_2bpy) and 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen, Eastman), and 2,2',2''-terpyridine (terpy, K & K). The following chemicals were reagent grade quality: $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, NaI, $NaClO_4$, THF, CH_3OH (anhydrous), C_2H_5OH (95%), HCl (0.1 ppm Fe), H_2SO_4 (0.2 ppm Fe), and $HClO_4$ (60%, 0.2 ppm Fe). Water was monodistilled.

Syntheses. The preparations of the $Cr(NN)_3^{3+}$ complexes were carried out under a N_2 atmosphere in a glovebag using N_2-purged (45 min) solvents. $Cr(bpy)_3(ClO_4)_3\cdot ½H_2O$ was prepared by a slightly modified procedure of that of Baker and Mehta.[15] The absorption spectrum of that complex was in agreement with that reported by König and Herzog.[16] The other complexes were prepared by an analogous procedure in which anhydrous $CrCl_2$ was reacted with a stoichiometric amount (solution or suspension) of the appropriate polypyridine ligand. The resulting mixture was oxidized with Cl_2(g), and the product was collected, recrystallized (as ClO_4^- salt) at least twice, and dried in vacuo. The elemental analyses (Galbraith Laboratories, Inc., Knoxville, Tenn.) of the complexes are given in Table I.

Apparatus. Absorption spectra of the complexes were recorded with an Aminco-Bowman DW-2 UV-vis spectrophotometer. Room temperature luminescence spectra were taken with a Perkin-Elmer MPF-2A spectrofluorimeter equipped with a R-446 photomultiplier tube and high-intensity accessory; low-temperature (77 K) emission lifetimes were determined using the phosphorescence accessory. The flash kinetic and flash spectroscopic experiments were carried out with an apparatus described previously.[17] Emission lifetimes in air-equilibrated solutions were determined with an apparatus consisting of the following components: Lambda Physik pulsed 1 MW N_2 laser, Bausch & Lomb high-intensity monochromator, and Tektronix R7912 transient digitizer.

Table II. Ground-State Absorption Spectra of $Cr(NN)_3^{3+}$ Complexes[a]

bpy	4,4'-Ph_2bpy[b]	4,4'-Me_2bpy
∼235[c] (4.62)	268 (4.92)	240 (4.78)
265 (4.24)	∼320 (4.83)	278 (4.38)
276 (4.22)	332 (4.84)	307 (4.44)
∼305 (4.36)	∼404* (3.73)	342 (3.96)
313 (4.40)	∼422* (3.56)	∼354 (3.86)
346 (3.95)	∼445* (3.24)	∼394* (2.97)
∼360 (3.76)		∼418* (2.80)
∼402* (2.97)		∼446* (2.43)
∼428* (2.83)		
∼458* (2.43)		
phen	**5-Clphen**	**4.7-Me_2phen[b]**
∼225 (4.93)	∼238 (4.87)	230 (4.86)
269 (4.81)	275 (4.79)	∼237 (4.80)
∼285 (4.57)	∼368 (3.56)	269 (4.85)
∼323 (4.10)	∼436* (2.85)	∼308 (4.40)
∼342 (3.90)	∼466* (2.59)	∼340 (3.94)
358 (3.61)		357 (3.77)
∼405* (2.94)		∼402* (3.02)
∼435* (2.78)		∼424* (2.95)
∼454* (2.51)		∼450* (2.70)
4,7-Ph_2phen[b]	**3,4,7,8-Me_4phen**	**terpy**
∼220 (5.05)	∼234 (4.95)	225 (4.79)
283 (4.90)	274 (4.90)	∼238 (4.64)
308 (4.91)	∼295 (4.65)	267 (4.49)
∼362 (4.43)	∼310 (4.42)	∼286 (4.32)
∼380 (4.29)	∼327 (4.27)	315 (4.04)
∼445* (3.31)	∼400* (3.13)	327 (4.12)
∼484* (3.09)	∼428* (3.06)	348 (4.22)
	∼456* (2.87)	364 (4.23)
		422* (3.31)
		443* (3.35)
		473* (3.15)

[a] λ, nm (log ϵ, $M^{-1}\ cm^{-1}$); in aqueous HCl solutions. unless otherwise noted; positions marked with an asterisk are assigned to the lowest energy spin-allowed quartet transition, $^4A_2 \rightarrow {}^4T_2$ (see text). [b] In methanol (spectroquality). [c] Shoulders.

Procedures. Unless otherwise noted, experiments were carried out in 1 M HCl aqueous solutions at 23–24 °C. Deoxygenation of the solutions was effected by bubbling with a stream of purified N_2 for 30 min or longer. Low-temperature (77 K) emission spectra and lifetimes were taken in a 50% v/v mixture of aqueous $HClO_4$ (pH 3.1) and spectroquality CH_3OH. Steady-state luminescence experiments were carried out on 10^{-5}–10^{-6} M solutions of the complexes with right-angle illumination. The exciting wavelength was chosen such that the absorbance of the solution (1-cm path length) was <0.8. In the case of the Ph_2bpy and Ph_2phen complexes, their slightly solubility in acidic aqueous solutions necessitated the use of small amounts of CH_3OH (<2% v/v) to effect dissolution.

Table III. Photophysical Data of Polypyridyl Complexes of Chromium(III)

complex	τ_0,[a] ms	τ_{77},[b] ms	ϕ_{rad}[c]	$^2T_1$, $\times 10^{-3}$ cm^{-1}	^2E, $\times 10^{-3}$ cm^{-1}	E^0,[d] V	$^*E^0$, V	ΔE^f,[e] V
$Cr(terpy)_2^{3+}$	$\ll 0.03$		<0.01	14.1	13.0	−0.17	1.44	0.08
$Cr(bpy)_3^{3+}$	0.063	6.5	1.0	14.4	13.7_4	−0.26	1.44	
$Cr(4,4'-Ph_2bpy)_3^{3+}$	0.14		0.58	14.0	13.4_7			
$Cr(4,4'-Me_2bpy)_3^{3+}$	0.23		1.7	14.3	13.6_8	−0.45	1.25	
$Cr(5-Clphen)_3^{3+}$	0.13	5.4	0.95	14.3	13.7_4	−0.17	1.53	0.125
$Cr(phen)_3^{3+}$	0.27	5.3	1.7	14.3	13.7_4	−0.28	1.42	0.000
$Cr(4,7-Me_2phen)_3^{3+}$	0.34	4.3	1.0	14.2	13.6_2	−0.45	1.24	−0.140
$Cr(4.7-Ph_2phen)_3^{3+}$	0.37	3.5	0.91	14.0	13.4_6			
$Cr(3,4,7.8-Me_4phen)_3^{3+}$	0.47		0.76	14.1	13.5_7	(−0.54)[f]	(1.15)[f]	−0.175

[a] N_2-purged aqueous solutions; 23-24 °C; 1 M HCl. [b] Aqueous $HClO_4$(pH 3.1) and CH_3OH (spectroquality), 50% v/v, 77 K. [c] Phosphorescence quantum yields relative to $Cr(bpy)_3^{3+}$. [d] Standard reduction potential vs. NHE in 1.0 M LiCl (ref 18), unless otherwise noted. [e] $E^f(Cr(NN)_3^{3+}/Cr(NN)_3^{2+}) - E^f(Cr(phen)_3^{3+}/Cr(phen)_3^{2+})$ (ref 42). [f] Formal reduction potential, E^f vs. SCE in ethanol-water (ref 42).

In the flash photolysis experiments, the xenon flash (1/*e* decay time = 30 μs) was filtered through acetone (λ >330 nm) or pyridine (λ >305 nm) contained in the outer jacket of a quartz cell (path length = 22 cm). The analyzing light was filtered through a monochromator (400-700-nm range) or 6 mm of Pyrex (320-400-nm range). The N_2-purged solutions in the cell were replaced after every second flash; no changes in the behavior of the solutions were observed as a result of the flash under the experimental conditions used. Solutions (10^{-4}-10^{-6} M) were prepared and purged with N_2 immediately prior to use.

In the luminescence quenching experiments with Fe_{aq}^{2+} and I^-, the solutions were air equilibrated; stock solutions of Fe_{aq}^{2+} were prepared just prior to use. In other experiments, the solutions were N_2 purged or O_2 saturated for ~20 min.

The quantum yields of phosphorescence (ϕ_{rad}) relative to that of $Cr(bpy)_3^{3+}$ were measured under conditions of constant total light absorption at the excitation wavelength (band-pass 20 nm) and the area under the emission spectral curve was determined by weight.

Results

The absorption spectra of the ground-state complexes are shown in Figure 1; details of the spectra are presented in Table II. Also depicted in Figure 1 are the absorption spectra of the flash photolysis transients which are identified as arising from the ^2E state of the complexes.

The flash photolysis transients decay via first-order kinetics from which are calculated their lifetimes in N_2-purged 1 M HCl solutions at 23 ± 1 °C ($\tau_0 = 1/k$; see Table III). Also given in Table III are the emission lifetimes for selected complexes at 77 K (τ_{77}); the standard deviation of the values of τ_0 and τ_{77} is <10%. The emission lifetimes at 25 °C for some of the complexes have been measured by others[18] and are in fair agreement with our values in Table III. In the case of $Cr(terpy)_2^{3+}$, no flash photolysis transient is observed within the lifetime of the flash. Table III also includes values of ϕ_{rad} relative to that of $Cr(bpy)_3^{3+}$ taken as unity, as well as the energies of the emission maxima; the spectra all resemble closely the phosphorescence spectrum of $Cr(bpy)_3^{3+}$ which has been published before.[8]

The effect of solution medium on the lifetimes of the ^2E states of the complexes, determined from the decay of the flash photolysis absorption or the phosphorescence emission, is presented in Table IV. Here are tabulated values of τ_{air}, the lifetimes of ^2E in air-equilibrated solutions, τ_{HClO_4}, the lifetimes in solutions containing 5 M $HClO_4$, and $\tau_{H_2SO_4}$, the lifetimes in solutions containing 1 M H_2SO_4. In all cases, except for the 4,7-Me_2phen complex, the presence of 5 M $HClO_4$ causes a prolongation of the lifetimes of the ^2E states. A value of τ_{HClO_4} for $Cr(3,4,7,8-Me_4phen)_3^{3+}$ could not be determined owing to the very slight solubility of the complex in this medium even with CH_3OH as the solvent.

The quenching of the phosphorescence of the complexes by Fe_{aq}^{2+}, I^-, and O_2 results in linear Stern-Volmer plots of I_0/I vs. [quencher]. For Fe_{aq}^{2+} quenching, absorption of the radiation by the Fe_{aq}^{2+} at the excitation wavelength used was accounted for by suitable corrections. The concentrations of O_2 in air-equilibrated and O_2-saturated 1 M HCl solutions were taken[18] as 2.5×10^{-4} and 1.2×10^{-3} M, respectively. A least-squares analysis of the slopes of the Stern-Volmer plots yielded K_{sv} from which were obtained values of k_q; $k_q = K_{sv}/\tau_{air}$ for Fe_{aq}^{2+} and I^- and $k_q = K_{sv}/\tau_0$ for O_2. The values of k_q are given in Table V; values for $Cr(bpy)_3^{3+}$ have been previously reported.[8]

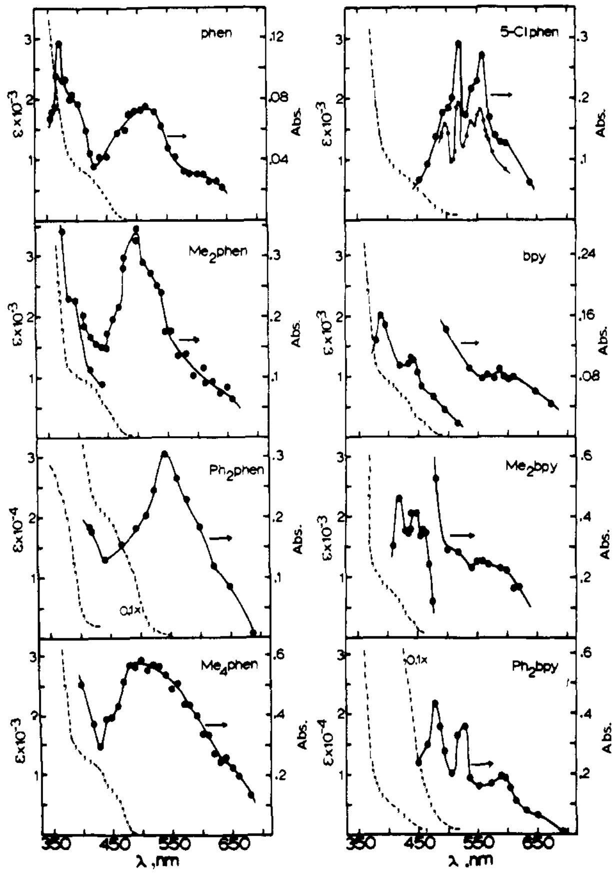


Figure 1. Absorption spectra (λ > 350 nm) of the ground-state $Cr(NN)_3^{3+}$ complexes (dashed line), and of the primary transient species (^2E)-$Cr(NN)_3^{3+}$ (solid line and points) obtained by flash photolysis absorption in N_2-purged acidic media (1 M HCl); concentration of complexes ~10^{-4}-10^{-6} M. Spectra were measured 40 μs after the flash, except for the bpy and phen complexes, for which the spectra were taken 150 μs after the flash.

Table IV. Solution Medium Effects on the Lifetimes of (^{2}E)-$Cr(NN)_3^{3+}$ Complexes

complex	τ_{HClO_4},[a] ms	τ_{HClO_4}/τ_0	τ_{air},[b] ms	$\tau_{H_2SO_4}$,[c] ms
$Cr(bpy)_3^{3+}$	0.29	4.6	0.055	
$Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$	0.36	2.7	0.017	
$Cr(4,4'\text{-}Me_2bpy)_3^{3+}$	0.40[d]	1.8	(0.077)[e]	0.26
$Cr(5\text{-}Clphen)_3^{3+}$	0.19	1.4	0.050	
$Cr(phen)_3^{3+}$	0.30	1.1	0.071	
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	0.17	0.5[f]	0.037	0.45
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	0.52	1.4	0.016	
$Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$	[g]		(0.026)[e]	0.38

[a] N_2-purged aqueous solutions; 23–24 °C; 1 M HCl, 5 M $HClO_4$. [b] Air-equilibrated aqueous solutions, 1 M HCl; 25 °C. [c] N_2-purged aqueous solutions; 23–24 °C; 1 M H_2SO_4. [d] With 10% methanol present, $\tau = 0.42$ ms. [e] Estimated from O_2-quenching experiments. [f] For $Cr(phen)_3^{3+}$ in 1 M HCl + 1 M $HClO_4$, $\tau = 0.22$ ms; $\tau_0/\tau = 0.8$. [g] Complex insoluble under these conditions.

Discussion

The similarity of the behavior of the complexes suggests that the general energy level diagram and mechanism developed[8] for the excited states of $Cr(bpy)_3^{3+}$ can also be applied, at least qualitatively, to the $Cr(NN)_3^{3+}$ (and $Cr(terpy)_2^{3+}$) complexes. Excitation into the spin-allowed quartet manifolds results in the rapid formation (reaction 1) of the lowest excited quartet state, $^4T_2$. With a lifetime of $\ll$1 ns,[19] the $^4T_2$ state undergoes (reactions 2a–c) nonradiative decay back to the ground ($^4A_2$)

$$(^4A_2)Cr(NN)_3^{3+} \xrightarrow{h\nu} (^4T_2)Cr(NN)_3^{3+} \qquad (1)$$

$$(^4T_2)Cr(NN)_3^{3+} \rightarrow (^4A_2)Cr(NN)_3^{3+} \text{ (nonradiative)} \qquad (2a)$$

$$\xrightarrow{\text{solvent}} \text{product} \qquad (2b)$$

$$\rightarrow (^2E)Cr(NN)_3^{3+} \text{ (intersystem crossing)} \qquad (2c)$$

state, reaction with solvent, or intersystem crossing into the doublet manifold with formation of the ^2E and $^2T_1$ states in thermal equilibrium; no fluorescence from $^4T_2$ has been observed.[20] For $Cr(bpy)_3^{3+}$ in H_2O, the quantum yield of formation of ^2E is ~1; for $Cr(phen)_3^{3+}$, the corresponding value is ~0.2.[21] According to the model, the ^2E state undergoes nonradiative and radiative return to the ground state (reactions 3a and 3b) and reacts with solvent to yield a seven-coordinate intermediate (reaction 3c) which is the direct precursor of the

$$(^2E)Cr(NN)_3^{3+} \xrightarrow{k_{rad}} (^4A_2)Cr(NN)_3^{3+} + h\nu' \qquad (3a)$$

$$\xrightarrow{k_{nr}} (^4A_2)Cr(NN)_3^{3+} \text{ (nonradiative)} \qquad (3b)$$

$$\xrightarrow[H_2O]{k_{rx}} Cr(NN)_3(H_2O)^{3+} \qquad (3c)$$

final aquation product; back intersystem crossing to $^4T_2$ has been ruled out on experimental and theoretical grounds.[8] The seven-coordinate intermediate has been proposed to account for the pH-dependent photoaquation quantum yield (Φ) which for $Cr(bpy)_3^{3+}$ reaches low (0.007)[22] and high (0.20)[23] limiting values in acidic and alkaline solutions, respectively. Because the stoichiometry and pH dependence of the photochemical[8] and thermal aquation[24,25] processes are identical, the same seven-coordinate intermediate can be invoked in both mechanisms. Owing to the relative photochemical and thermal stability of the complexes in acid solution, all experiments, unless otherwise noted, were performed at [H+] = 1 M. The stability of the complexes was evident from the lack of any permanent spectral changes upon flashing.

Table V. Quenching Rate Data of the Phosphorescence Emission of (^{2}E)$Cr(NN)_3^{3+}$ Complexes by I^-, Fe_{aq}^{2+}, and O_2[a]

NN	$k_q \times 10^{-8}$, $M^{-1}\,s^{-1}$		
	I^-	Fe_{aq}^{2+}	O_2
4,4'-Ph_2bpy	22	0.20	1.7
bpy	14	0.37	0.17
4,4'-Me_2bpy	0.40	0.022	0.34
5-Clphen	80	1.2	0.37
4.7-Ph_2phen	59	0.25	3.1
phen	21	0.32	0.27
4,7-Me_2phen	1.5	0.060	1.9
3,4,7,8-Me_4phen	0.47	0.0092	1.5

[a] Air-equilibrated aqueous solutions; 1 M HCl; 25 °C.

Ground-State Absorption Spectra. Typically, the ligand field absorption spectrum of Cr(III) complexes of octahedral symmetry consists of three spin-allowed quartet bands:[26] $^4A_{2g} \rightarrow {}^4T_{2g}$, a^4T_{1g}, and b^4T_{1g} with ϵ values of ~10–100 $M^{-1}\,cm^{-1}$. The lowest energy band ($^4A_{2g} \rightarrow {}^4T_{2g}$) gives the value of the ligand field parameter Δ. Assuming an octahedral microsymmetry for $Cr(bpy)_3^{3+}$, König and Herzog[16] assigned the three spin-allowed quartet bands at 23.4, 28.9, and 35.5 × 10^3 cm^{-1} (center of gravity of band maxima) to transitions to $^4T_2$, a^4T_1 and b^4T_1, respectively; ligand-centered bands were identified at 32.7 and 42.1 × 10^3 cm^{-1}. The three unresolved shoulders centered at 23.4 × 10^3 cm^{-1} were assigned to vibrational components of the octahedral $^4A_2 \rightarrow {}^4T_2$ transition. Inasmuch as the actual symmetry of the $Cr(NN)_3^{3+}$ complexes is D_3, the triply degenerate O_h excited states are split as $^4T_{1g} \rightarrow {}^4A_2 + {}^4E$ and $^4T_{2g} \rightarrow {}^4A_1 + {}^4E$.[26] The extent of this splitting is often too small to be resolved in solution spectra.

As illustrated in Figure 1, all of the absorption spectra reveal a steep drop in absorption in the 350–400-nm region. The first ligand field band often appears as two or three unresolved shoulders on the low-energy side of the very intense intraligand band. This makes it difficult to assess the positions and intensities of the ligand field band (Table II). Observation of more than two components is probably the result of coexcitations of some appropriate vibrational modes of the very complex structure of the $Cr(NN)_3^{3+}$ cations. Such interactions suggest some degree of electron delocalization. That there exists some degree of back-π-bonding from NN ligands to Cr(III) has also been suggested by Josephsen and Schäffer,[27] who separated the parameter Δ into its σ and π components ($\Delta = \Delta_\sigma - \Delta_\pi$). They concluded that $\Delta^\sigma_{bpy} - \Delta^\sigma_{phen} = 300$ cm^{-1} in the Cr(III) complexes studied. Comparison of the centers of gravity of the lowest energy band of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ (Table II) indicates that $\Delta_{bpy} \sim \Delta_{phen}$.

Adopting the approach of König and Herzog,[16] the lowest energy multicomponent band of the complexes is assigned to the $^4A_2 \rightarrow {}^4T_2$ transition (denoted by an asterisk in Table II). The center of gravity of the vibrational components yields the energies of the $^4T_2$ manifold resulting from the $t_{2g}{}^2e_g$ configuration; Δ varies in the order, 4,4'-Me_2bpy (23.9 × 10^3 cm^{-1}) $\gtrsim$ 4,4'-Ph_2bpy (23.6 × 10^3 cm^{-1}) $\gtrsim$ bpy (23.4 × 10^3 cm^{-1}). Substituents on the bpy framework slightly blue shift the low-energy band in the bpy complexes. Methyl substituents on the phen ligand blue shift the low-energy band while the 5-Cl and 4,7-Ph_2 substituents cause a red shift: 4,7-Me_2phen (23.6 × 10^3 cm^{-1}) $\gtrsim$ 3,4,7,8-Me_4phen (23.4 × 10^3 cm^{-1}) $\gtrsim$ phen (23.3 × 10^3 cm^{-1}) > 5-Clphen (22.2 × 10^3 cm^{-1}) > 4,7-Ph_2phen (21.6 × 10^3 cm^{-1}). Similar to the substituent effects on the absorption maxima of MLCT states of $Ru(NN)_3^{2+}$ complexes,[13,14,28] phenyl substitution in Cr^{III}-phen complexes has a marked effect on metal-centered states. An additional general feature of phenyl substitution is the increase in the value of ϵ (Figure 1 and Table II).

The absorption spectrum of $Cr(terpy)_2^{2+}$ reveals three relatively well-resolved vibrational components of the band corresponding to the $^4A_2 \rightarrow {}^4T_2$ transition ($\Delta = 22.5 \times 10^3$ cm^{-1}).

Doublet-State Absorption Spectra. Inspection of Figure 1 reveals that the absorption spectra of the ^2E states of the bpy and substituted bpy complexes show overall similarity. Methyl substitution at the 4,4′ positions results in a red shift of the 390-nm band of $(^2E)Cr(bpy)_3^{3+}$ to 420 nm; phenyl substitution red shifts both the 390- and 445-nm bands to 480 and 525 nm, respectively. The band at 590 nm in $(^2E)Cr(bpy)_3^{3+}$ does not appear to be very sensitive to ligand substituents. Inasmuch as the ^2E excited states are $\sim 13.7 \times 10^3$ cm^{-1} above the $^4A_2$ ground state, the excited states reached by ^2E absorption are $\sim$30-40 $\times 10^3$ cm^{-1} above the ground state, as expected from the energy level diagrams.[29,30] These diagrams predict the existence of five metal-centered doublet transitions in the 20-32 $\times 10^3$ cm^{-1} (500-313 nm). Ohno and Kato[31] noted that the energy levels of the doublet states of $Cr(acac)_3$ are not far removed from the corresponding quartet states. On this basis, the upper doublet state corresponding to the a^4T_1 state, which is 28.9×10^3 cm^{-1} above the ground state for $Cr(bpy)_3^{3+}$,[16] should occur at 15.2×10^3 cm^{-1} ($\sim$660 nm) above the ^2E level. A band corresponding to such a transition ($^2E \rightarrow b^2T_1$) is observed at 16.9×10^3 cm^{-1} (590 nm). The relative insensitivity of this transition to ligand substituents indicates that the doublet manifold (b^2T_1) is predominantly metal centered. The remaining two higher energy bands, red shifted by the presence of ligand substituents, probably correspond to electronic transitions to doublet states containing some ligand character and could be described as $^2E \rightarrow {}^2$(LMCT) transitions. Furthermore, similar to the situation with the ground-state absorption spectra, some of the observed features in the ^2E excited-state spectra could correspond to vibrational components of the same electronic transition.

The ^2E absorption spectrum of $Cr(phen)_3^{3+}$ is characterized by a rather broad band centered at 515 nm. This band is insensitive to methyl substitution at the 4,7 and 3,4,7,8 positions of the phen framework; phenyl groups at the 4,7 positions and the 5-Cl substituent red shift this band slightly by $\sim$20 nm. Following the above discussion for the bpy systems, this band is ascribed to the $^2E \rightarrow b^2T_1$ transition with the corresponding a^4T_1 state situated $\sim 32 \times 10^3$ cm^{-1} above the ground state. A band at 32.6×10^3 cm^{-1} (308 nm) is observed in the ground-state spectrum of $Cr(4,7\text{-}Ph_2phen)_3^{3+}$ and is not present in the absorption spectrum of the free ligand monocation. The band at 35.2×10^3 cm^{-1} (283 nm), also present in the free ligand monocation, is attributed to a ligand-centered electronic transition.

Doublet-State Emission Spectra. The emission spectral bands, which represent the 0-0 transitions of the $^2T_1 \rightarrow {}^4A_2$ and $^2E \rightarrow {}^4A_2$ electronic transitions, are only slightly sensitive to the nature of the ligand substituents. Table III reveals that substitution varies the energy of the low-energy transition in the order bpy > 4,4′-Me_2bpy > 4,4′-Ph_2bpy. Ligand substituents on the phen complexes decrease the energy of the ^2E state in the order phen $\sim$ 5-Clphen > 4,7-Me_2phen > 3,4,7,8-Me_4phen > 4,7-Ph_2phen. Phenyl substitution on the bpy and phen ligands red shifts the emission maxima in both cases by $\sim$14 nm. It is interesting to note that the terpy ligand red shifts the emission from ^2E by $\sim$42 nm compared to the $Cr(bpy)_3^{3+}$ band at 728 nm. An additional feature in the $Cr(terpy)_2^{2+}$ emission spectrum is that, while the ^2E-$^2T_1$ energy gap is $\sim$600 cm^{-1} for all the bpy and phen complexes, the gap here is $\sim$1100 cm^{-1}.

In a similar manner, the energies of the emission bands from $Ru(NN)_3^{2+}$ complexes in fluid solutions are not markedly dependent on the nature of the ligand substituents.[13] Methyl and phenyl substituents at the 4,7 positions of the phen ring system red shift the emission. More dramatic substituent effects have recently been reported[28] for the emission from the unsymmetrically substituted $Ru(phen)_2(4,7\text{-}(OH)_2phen)^{2+}$ and its deprotonated analogue; deprotonation shifts the emission from 635 nm (15.7×10^3 cm^{-1}) to 720 nm (13.9×10^3 cm^{-1}).

Lifetimes of ^{2}E States. Investigations of $Ru(NN)_3^{2+}$ complexes containing various substituted bpy and phen ligands have shown that the lifetimes of the emitting MLCT states are sensitive to ligand substitution.[13] In both room temperature fluid[13] and low-temperature glass environments,[14,32] emission lifetimes are longer for the phen systems than for the bpy. In contrast, however, whereas phenyl substitution on both bpy and phen *decreases* both the radiative and nonradiative lifetimes at 77 K, phenyl substitution in fluid media leads to an *increase* in the luminescence lifetimes. Otherwise, lifetimes do not appear to be especially sensitive to methyl substitution on the phen ring system. Attachment of methyl groups to the 4,4′ positions of bpy decreases the emission lifetime while substitution to phen nearly doubles the values of τ_0. The Cl and Br substituents on phen (5 position) have virtually no effect on τ_0.

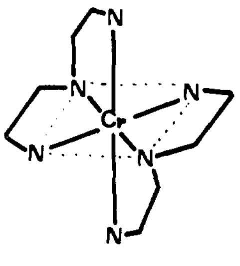
The $^*Os(NN)_3^{2+}$ emission lifetimes (9-84 ns in H_2O) are much shorter than the values for the corresponding $^*Ru(NN)_3^{2+}$ species (0.6-1.8 μs in H_2O).[4] The emission lifetimes for the *Os(II) complexes show a greater variation on the nature of the ligands than do the τ_0 values for *Ru(II).[4]

In contrast, the ^2E states of $Cr(NN)_3^{3+}$ complexes in fluid solution at room temperature are strikingly long lived. Inasmuch as the rate constants for the decays of the flash photolysis transient absorptions are the same as those for the decays of the luminescence emissions under identical experimental conditions, the transient absorption can be identified as arising from the luminescent ^2E state. The data in Table III show that, in contrast to *Ru(II),[4] the nature of the substituents on the 4,7 positions of phen has no effect on τ_0. In general, substitution on the bpy or phen ligands alters τ_0, often to a substantial extent. For example, phenyl substitution at the 4,4′ sites of bpy doubles τ_0; methyl substitution there leads to nearly a fourfold increase. Also, methyl and phenyl substitution on $Cr(phen)_3^{3+}$ prolongs the lifetime of ^2E. It is noteworthy that increased methyl substitution, as for the 3,4,7,8-Me_2phen ligand, leads to further increase in τ_0; the 5-Cl substituent, on the other hand, decreases τ_0.

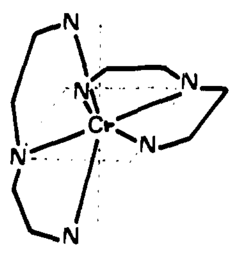
The lifetime of $(^2E)Cr(terpy)_2^{3+}$ is so short that the species cannot be seen in conventional flash photolysis; Brunschwig and Sutin[18] estimate $\tau_0 \sim 50$ ns from their emission lifetime study. Despite the apparent similarity between the bpy and terpy ligands, the Ru^{II}- and Cr^{III}-terpy excited states are extremely short lived with τ_0 = 1-5 ns for $^*Ru(terpy)_2^{2+}$.[13,33]

The lifetimes of the ^2E states of $Cr(NN)_3^{3+}$ are controlled by reactions 3a-c so that $\tau_0 = 1/(k_{rad} + k_{nr} + k_{rx})$. Inasmuch as $\phi_{rad} < 10^{-3}$ for $Cr(bpy)_3^{3+}$ [8] and is not particularly sensitive to the nature of the ligand substituents (Table III), and $\phi_{rx} \leq 0.2$,[23,34] the major contributor to the lifetimes of the ^2E states is the rate of nonradiative decay; $\tau_0 \sim 1/k_{nr}$. We proposed previously[35,36] that the nonradiative decay involves the conversion of metal-centered electronic energy to ligand-localized vibrational energy whereby the ligands act as both the oscillating perturbation dipole and the energy acceptor. The dramatic increase in τ_0 upon going from $Cr(bpy)_3^{3+}$ to $Cr(phen)_3^{3+}$ illustrates the effect of the vibrationally more rigid phen ligands on the rate of the nonradiative decay. The values of τ_0 in Table III can be rationalized in terms of this model. All the phen complexes (except 5-Clphen) have longer lifetimes than the comparable bpy complexes. In the case of the 5-Clphen complex, the Cl substituent provides an increased dipole perturbation such that k_{nr} would be increased. Interestingly, methyl and phenyl substitution increases τ_0 for both bpy and phen ligands. It must be argued that such substitution decreases the perturbation dipole through its effect on the critical ligand vibrational modes. Inasmuch as τ_0 shows no solvent isotope effect (H_2O vs. D_2O) for $Cr(bpy)_3^{3+}$,[35,36] the nonradiative decay of ^2E cannot be attributed to direct vibrational coupling between the metal-centered excited states and the solvent.

While it could be argued that the terpy complex is vibrationally stiffer than its bpy analogue, the very short lifetime of $(^2E)Cr(terpy)_2^{3+}$ is really not inconsistent with the qualitative nature of the model. Terpy is a tridentate ligand so that, in principle, the resulting Cr(III) complex can exist in two diastereomeric configurations: *fac* and *mer*. Of the two forms, the mer form will be thermodynamically more stable inasmuch as in the fac form, one of the pyridyl rings would be forced sterically to adopt a position perpendicular to the plane of the remaining two pyridyl rings; here the sp^2 character of the bond would have to be dramatically modified to accommodate ther steric distortion. In the mer structure, the N-Cr-N-angle is probably ~75-80° (by analogy with $M(bpy)_3^{n+}$ structures)[37] so that the *mer*-$Cr(terpy)_2^{3+}$ complex would possess a highly distorted structure with the distortion occurring along the direction of the two terpy planes. The Cr(III) core would now be more exposed to solvent perturbation so that direct vibrational coupling between the excited-state metal core and the solvent could occur causing k_{nr} to increase dramatically. The more open structure of $Ru(terpy)_2^{2+}$ (compared to $Ru(bpy)_3^{2+}$) has been suggested as a reason for its very short excited-state lifetime.[33]



fac



mer

The values of τ_{77} represent $1/k_{nr}$ for the ^2E states at 77 K in methanolic ice. There exists very little variation in τ_{77} as a function of the nature of the ligands and the substituents; in fact, the variations do not parallel those in fluid solution. We know that τ_0 is not affected by the presence of CH_3OH in fluid solution.[35,36]

Solution Medium Effects on the Lifetimes of ^2E States. In previous studies[35,36] we showed that high concentrations (>1 M) of anions (e.g., ClO_4^-, HSO_4^-, Cl^-) cause significant increases in the emission intensities from, and lifetimes of, the ^2E states of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ and decreases in the quantum yields of photoaquation. In the limit of 11.7 M $HClO_4$ in N_2-purged solutions, $\tau = 0.53$ and 0.67 ms for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, respectively. The prolongation of the lifetime results from a decrease in both the radiative and nonradiative decay paths (reactions 3b,c), the former from the replacement of some of the water molecules in the interligand pockets and the solvation sphere, and the latter from a decrease in the vibrational freedom of the ligands and the efficiency of intramolecular energy transfer. The magnitudes of the specific anion effects appear to result from various phenomena such as ion-pair formation, molecular events in the interligand pockets, vibrational freedom of the ligands, and the structure and activity of water. The anion effect is more pronounced for the bpy complexes than for the phen complexes.

In 5 M $HClO_4$ solutions, the lifetimes of nearly all the ^2E species are increased. The case of $(^2E)Cr(4,7\text{-}Me_2phen)_3^{3+}$ is rather peculiar; a twofold decrease in τ occurs with increasing $[HClO_4]$ up to 5 M. Such behavior does not appear to be particular to methyl substitution; $Cr(phen)_3^{3+}$ also shows a slight drop in lifetime in 1 M $HClO_4$ compared to solutions low in ClO_4^-. In 1 M H_2SO_4, the two dimethyl-substituted complexes have lifetimes slightly longer than in 1 M HCl, although the reverse situation exists for the $3,4,7,8\text{-}Me_4phen$ complex. The reasons for this behavior are the subjects of current investigations.

Quenching of ^2E States. Reactions 4a-c represent three modes of deactivation of the ^2E states upon interaction with

$$(^2\mathrm{E})\mathrm{Cr(NN)_3^{3+}} + \mathrm{Q} \xrightarrow[\text{transfer}]{\text{energy}} (^4\mathrm{A_2})\mathrm{Cr(NN)_3^{3+}} + {}^*\mathrm{Q} \qquad (4a)$$

$$\xrightarrow{\text{oxidn}} \mathrm{Cr(NN)_3^{4+}} + \mathrm{Q^-} \qquad (4b)$$

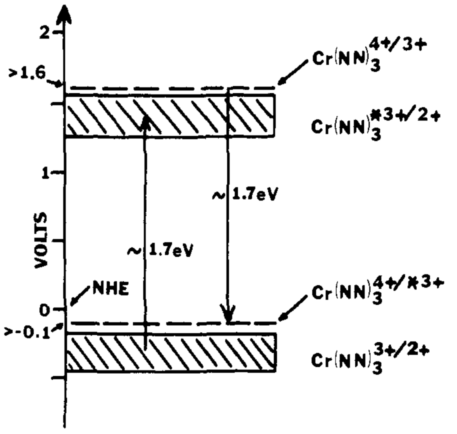
$$\xrightarrow{\text{redn}} \mathrm{Cr(NN)_3^{2+}} + \mathrm{Q^+} \qquad (4c)$$

quenchers, Q: energy transfer and oxidative or reductive electron transfer. Under favorable circumstances, it might be possible to discriminate between energy- and electron-transfer processes. In general, however, this is often difficult inasmuch as energy-transfer reactions may lead to the same oxidized or reduced products expected from electron-transfer reactions, and electron-transfer reactions may yield, in the end, nonreduced or nonoxidized products.[13,38] Knowledge of the energy of the ^2E excited state, the energy of the lowest excited state of Q, and the ground-state redox potentials of $Cr(NN)_3^{3+}$ and Q may aid in the assignment of the operative quenching pathway. Correlations between quenching rate constants, k_q, and the thermodynamic quantities involved have also afforded useful information regarding the nature of the quenching mechanism.[9] Definitive assignment of electron transfer is possible if the products of reactions 4b,c can be observed by the use of, for example, flash photolysis.[10,12]

From absorption and emission maxima, the excitation energy of the thermally equilibrated ^2E states of $Cr(NN)_3^{3+}$ complexes is ~1.7 eV. If entropy differences between the ground and emitting states are considered negligible,[48,49] inasmuch as the $^4A_2$ and ^2E states have the same geometry (zero Stokes shift between absorption and emission) and belong to the same t_{2g}^3 electronic configuration, the excitation energy can be considered to be a free energy so that $\Delta G^* \sim 1.7$ eV. Combining this value of ΔG^* with the ground-state reduction potentials of $Cr(NN)_3^{3+}$ [15,18,41,42] (~−0.1 to ~−0.5 V) yields the values for the reduction potentials of the ^2E states (Table III). The validity of such a procedure has been verified in the case of the MLCT state of $^*Ru(bpy)_3^{2+}$.[43] More recently, Balzani and co-workers[10] have also verified experimentally the estimation of the redox potentials of various polypyridyl species using an extensive series of quenchers of graded potentials. The $(^2E)Cr(NN)_3^{3+}$ species have reduction potentials ranging from ~1.2 to ~1.5 V; they are more powerful oxidizing agents than are the ground-state species (Scheme I). It should be noted that $(^2E)Cr(NN)_3^{3+}$ are also more powerful oxidizing agents than are the MLCT excited states of the analogous Ru(II) and Os(II) complexes.[6,10,13] With respect to excited-state donor energies, an important property in photosensitization reactions, those of the $Cr(NN)_3^{3+}$ complexes (~13.5-13.7 × 10^3 cm^{-1}) are lower than those of the corresponding Ru(II) (~18-19 × 10^3 cm^{-1})[38] and Os(II) (~15 × 10^3 cm^{-1})[44] complexes.

Direct evidence for reaction 4a has not been obtained inasmuch as the energies of the ^2E states are much lower than those of the lowest excited states of common acceptors. Evidence has been obtained for reductive quenching of $(^2E)Cr(bpy)_3^{3+}$ by Fe_{aq}^{2+} and $Ru(bpy)_3^{2+}$ from which $Cr(bpy)_3^{2+}$ is formed;[12]

Scheme I



the reduced species is rapidly reoxidized by Fe_{aq}^{3+} formed in reaction 4c. Oxidative quenching of $(^2E)Cr(bpy)_3^{3+}$ by $Fe(CN)_6^{3-}$ has been proposed but the details of reaction 4b are still subject to experimental verification.

A. Quenching by O_2. The MLCT excited states of $Ru(NN)_3^{2+}$ and $Os(NN)_3^{2+}$ are quenched by O_2 apparently via simple energy-transfer processes which produce $^1O_2$.[44,45] However, chemical generation of $^1O_2$ by electron-transfer processes has not been entirely ruled out. In fact, Sutin and co-workers[13] concluded from their study that O_2 quenching of $(MLCT)Ru(NN)_3^{2+}$ and, by analogy, $(MLCT)Os(NN)_3^{2+}$ occurs via an electron-transfer pathway in which the initially formed $M(NN)_3^{3+}|O_2^-$ pair within the solvent cage undergoes back electron transfer in a time short compared to the lifetime of the cage. Electron-transfer quenching of $(MLCT)Ru(bpy)_3^{2+}$ by O_2 has been corroborated by Hammond and co-workers.[46]

Table V shows that, for the reaction of O_2 with $(^2E)Cr(NN)_3^{3+}$, the values of k_q are two to three orders of magnitude smaller than the diffusion-controlled rate and one to two orders of magnitude smaller than the values of k_q for organic triplet states ($\sim 3 \times 10^9$ M^{-1} s^{-1} for 10.0×10^3 $cm^{-1} < E_T < 15.0 \times 10^3$ cm^{-1}); when $E_T > 16.0 \times 10^3$ cm^{-1}, k_q for the organic triplets decreases in value.[47] Inasmuch as the two lowest excited states of O_2 occur at ~ 12.9 $(^1\Sigma_g^+)$ and $\sim 7.9 \times 10^3$ cm^{-1} $(^1\Delta_g)$[48] and the energy of $(^2E)Cr(NN)_3^{3+}$ is $\sim 13.7 \times 10^3$ cm^{-1}, energy transfer to form $^1O_2$ is energetically possible and spin allowed:

$$(^2E)Cr(NN)_3^{3+} + {}^3O_2 \rightarrow (^4A_2)Cr(NN)_3^{3+} + {}^1O_2 \quad (5)$$

In Figure 2, values of k_q have been plotted as a function of the energies of the ^2E states showing that k_q is particularly sensitive to small differences in the donor energies. Consideration of these results suggests that reaction 5 generates $(^1\Delta_g)O_2$. Furthermore, to the extent that Franck-Condon factors for the $^3\Sigma_g$- $(\nu = 0) \rightarrow {}^1\Delta_g(\nu)$ and $^3\Sigma_g$- $(\nu = 0) \rightarrow {}^1\Sigma_g+(\nu)$ transitions are small (for $\nu \neq 0$)[47] and that such factors are negligible for the $^4A_2 \rightarrow {}^2E$ transition in $Cr(NN)_3^{3+}$, the variation in k_q cannot be attributed to those factors.

In his study of O_2 quenching of the ^2E states of nonpolypyridyl Cr(III) complexes, Pfeil[49] has concluded that energy-transfer quenching is a short-range interaction, the efficiency of which is sensitive to the nature and size of the ligands and to the extent of solvation of the complex. It was further suggested that energy transfer should be hindered by "insulating" ligands (e.g., NH_3, en) and enhanced by "conducting" ligands (e.g., NCS^-, CN^-). The data in Table V reveal that k_q values are dependent neither on the nature of the ligands nor on their size in any uniform way. The data also suggest that energy transfer quenching rates are not sensitive to the "insulating" or "conducting" character of the ligands. It could be argued, for example, that methyl-substituted phenanthroline ligands are "insulating" while the 5-Clphen ligand possesses "conducting" characteristics, and yet energy transfer from $(^2E)Cr(4,7\text{-}Me_2phen)_3^{3+}$ and $(^2E)Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$ donors is more efficient than energy transfer from the $(^2E)Cr(5\text{-}Clphen)_3^{3+}$ complex by almost one order of magnitude. Insofar as the insulating effect of the solvation sphere is concerned, the magnitude of k_q (relative to the diffusion-controlled limit) may arise from the tight solvation sphere about the highly charged cations which could retard the penetration of O_2 to the distance required for effective quenching. Charge effects have also been observed in the quenching of organic triplet states by Cr(III) complexes.[50] However, to the extent that the $Cr(NN)_3^{3+}$ complexes are identical in charge and shape, and somewhat similar in size, it is unlikely that the variation in k_q arises solely from the insulating effects of the solvation spheres.

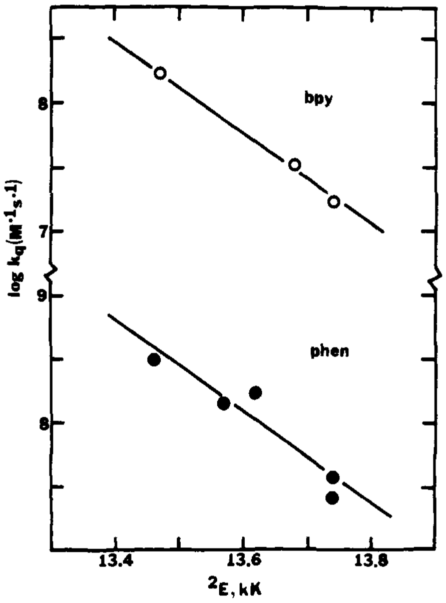


Figure 2. Plots of the logarithm of the quenching rate constant, k_q, for the reaction between $(^2E)Cr(NN)_3^{3+}$ and O_2 vs. the energy of the ^2E states; $\mu = 1.0$ M HCl, aqueous solutions, 25 °C.

A close examination of the data in Table V reveals that k_q exhibits some functionality toward the redox potentials of the complexes (Table III). The reduction potential for the reaction

$$Cr(bpy)_3^{4+} + e^- \rightarrow Cr(bpy)_3^{3+} \quad (6)$$

is > 1.6 V (and, by analogy, also for the other polypyridyl species) and therefore the corresponding redox potential for the couple $Cr(bpy)_3^{4+}/(^2E)Cr(bpy)_3^{3+}$ is >-0.1 V (see Scheme I and ref 9 and 21). If ligand substituent effects on the potentials of the $Cr(NN)_3^{4+}/Cr(NN)_3^{3+}$ couples paralleled those variations (0.1-0.5 V) in the potentials of the $Cr(NN)_3^{3+}/Cr(NN)_3^{2+}$ couples[42,51] (and, by analogy, transmitted to the corresponding excited-state redox potentials),[52] it would be reasonable to expect some variations in the values of k_q as a function of the ligand substituents. The values of k_q for the phen complexes have been plotted against ΔE^f [$= E^f(Cr(NN)_3^{3+}/Cr(NN)_3^{2+}) - E^f(Cr(phen)_3^{3+}/Cr(phen)_3^{2+})$; Table III] in Figure 3, which shows a small, but definitive, dependence of O_2 quenching on redox potentials. Such a dependence has been previously taken as evidence for an electron-transfer pathway in the quenching of the MLCT states of $Ru(NN)_3^{2+}$ by Eu(III)[13] and Eu(II).[53]

The variations of k_q with ΔE^f, however, do not support reductive quenching inasmuch as the stronger oxidant, (^2E)-

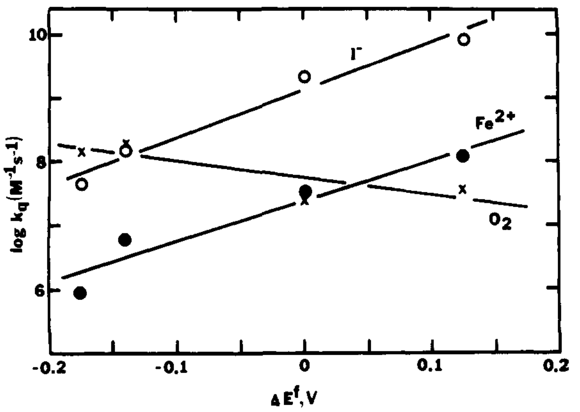


Figure 3. Plots of the logarithm of the rate constant k_q for the quenching of $(^2E)Cr(NN)_3^{3+}$ species by O_2, I^-, and Fe_{aq}^{2+} vs. ΔE^f (see text); μ = 1.0 M HCl, air-equilibrated solutions, 25 °C.

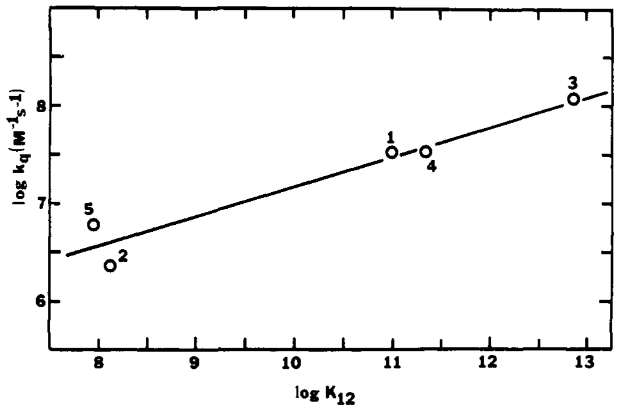


Figure 4. Plot of the logarithm of the quenching rate constant, k_q, for the reaction between Fe_{aq}^{2+} and $(^2E)Cr(NN)_3^{3+}$ (μ = 1.0 M HCl, air-equilibrated aqueous solutions, 25 °C) against the logarithm of the equilibrium constant, K_{12}, for the electron-transfer reaction (reaction 25; see text): (1) phen, (2) 4,4′-Me$_2$bpy, (3) 5-Clphen, (4) bpy, and (5) 4,7-Me$_2$phen.

$Cr(5\text{-}Clphen)_3^{3+}$, has the smaller quenching rate, contrary to expectations. In fact, the variations in Figure 3 suggest an oxidative electron transfer mode. Direct oxidative electron transfer between O_2 and $(^2E)Cr(NN)_3^{3+}$ in acidic solution to form $Cr(NN)_3^{4+}$ and HO_2 radicals is expected to be endoergic ($\Delta G > 0.2$ eV); and O_2/O_2^- potential is −0.33 V,[54] and the pK_a of HO_2 is 4.8.[55] As noted earlier, an oxidative electron transfer mode has also been inferred in the quenching of $(^2E)Cr(bpy)_3^{3+}$ by $Fe(CN)_6^{3-}$.[9] Electron transfer quenching by O_2 could occur via reactions 7-12 where | denotes encounter pairs; if $k_9 \gg k_{11}$, the redox products of reaction 11 would never be detectable. From the evidence, we conclude that the reaction of $(^2E)Cr(NN)_3^{3+}$ with O_2 occurs principally via an energy-transfer mechanism.[56]

$$(^2E)Cr(NN)_3^{3+} + O_2 \rightleftarrows (^2E)Cr(NN)_3^{3+}|O_2 \qquad (7)$$

$$(^2E)Cr(NN)_3^{3+}|O_2 \rightarrow Cr(NN)_3^{4+}|O_2^- \qquad (8)$$

$$Cr(NN)_3^{4+}|O_2^- \rightarrow Cr(NN)_3^{3+}|O_2 \qquad (9)$$

$$Cr(NN)_3^{3+}|O_2 \rightarrow Cr(NN)_3^{3+} + O_2 \qquad (10)$$

$$Cr(NN)_3^{4+}|O_2^- \rightarrow Cr(NN)_3^{4+} + O_2^- \qquad (11)$$

$$O_2^- + H^+ \rightarrow HO_2 \qquad (12)$$

B. Quenching by I^- and Fe_{aq}^{2+}. The parallel quenching of the phosphorescence emission, flash photolysis absorption, and photochemical aquation of $Cr(bpy)_3^{3+}$ by I^- led to the identification[8] of the ^2E state as that which leads to the observed products. As Table V shows, I^- quenches the ^2E states of all the complexes and the values of k_q range over two orders of magnitude. Inasmuch as the lowest excited states in I^- have energies greater than 37.0 × 10^3 cm^{-1},[57] an energy transfer quenching mechanism can be ruled out. In Figure 3, log k_q is plotted against ΔE^f, which demonstrates the electron-transfer nature[13] of the quenching reaction; the strongest oxidant, $(^2E)Cr(5\text{-}Clphen)_3^{3+}$, has the highest value of k_q. It should be noted that the reduction potential for the I/I^- couple in aqueous solution has been estimated as 1.42 V.[58] The rapid (k_q = 1.5 × 10^8 M^{-1} s^{-1}) reaction of I^- with $(^2E)Cr(4,7\text{-}Me_2phen)_3^{3+}$ ($^*E^0$ = 1.25 V) would suggest that the potential for I/I^- may have been overestimated by ~0.1 V.

The reaction of ^2E with I^- can be viewed as occurring via reactions 13-18. In the flash photolysis of $Cr(bpy)_3^{3+}$ in the presence of I^-, the ^2E absorption is rapidly quenched but absorptions due to $Cr(bpy)_3^{2+}$ (λ_{max} 560 nm)[16] or I_2^- (λ_{max} 380 nm)[59] are not detected. Evidently, I atoms never escape the solvent cages and $k_{15} \gg k_{17}$.

$$(^2E)Cr(NN)_3^{3+} + I^- \rightleftarrows (^2E)Cr(NN)_3^{3+}|I^- \qquad (13)$$

$$(^2E)Cr(NN)_3^{3+}|I^- \rightarrow Cr(NN)_3^{2+}|I \qquad (14)$$

$$Cr(NN)_3^{2+}|I \rightarrow Cr(NN)_3^{3+}|I^- \qquad (15)$$

$$Cr(NN)_3^{3+}|I^- \rightarrow Cr(NN)_3^{3+} + I^- \qquad (16)$$

$$Cr(NN)_3^{2+}|I \rightarrow Cr(NN)_3^{2+} + I \qquad (17)$$

$$I + I^- \rightleftarrows I_2^- \qquad (18)$$

In the case of the quenching of $(^2E)Cr(bpy)_3^{3+}$ by Fe_{aq}^{2+}, the observations of the formation of $Cr(bpy)_3^{2+}$ and its second-order decay with Fe_{aq}^{3+} [12] demonstrate the electron-transfer nature of the overall quenching reaction. By analogy with the quenching schemes for the $^*Ru(bpy)_3^{2+}$-Fe_{aq}^{3+} system,[13] the scheme for $(^2E)Cr(NN)_3^{3+}$-Fe_{aq}^{2+} can involve both electron- and energy-transfer modes (reactions 19-24).

$$(^2E)Cr(NN)_3^{3+} + Fe_{aq}^{2+} \rightarrow Cr(NN)_3^{3+} + {}^*Fe_{aq}^{2+} \qquad (19)$$

$$Cr(NN)_3^{3+} + {}^*Fe_{aq}^{2+} \rightleftarrows Cr(NN)_3^{3+}|{}^*Fe^{2+} \qquad (20)$$

$$Cr(NN)_3^{3+}|{}^*Fe^{2+} \rightarrow Cr(NN)_3^{2+}|Fe^{3+} \qquad (21)$$

$$(^2E)Cr(NN)_3^{3+} + Fe_{aq}^{2+} \rightarrow (^2E)Cr(NN)_3^{3+}|Fe^{2+} \qquad (22)$$

$$(^2E)Cr(NN)_3^{3+}|Fe^{2+} \rightarrow Cr(NN)_3^{2+}|Fe^{3+} \qquad (23)$$

$$Cr(NN)_3^{2+}|Fe^{3+} \rightarrow Cr(NN)_3^{2+} + Fe_{aq}^{3+} \qquad (24)$$

The availability of low-lying excited states of Fe_{aq}^{2+} at 10.4 × 10^3 cm^{-1} ($^5T_{2g}$) and at ~14.4 × 10^3 cm^{-1} (probably $^3T_{1g}$)[60] above the $^1A_{1g}$ ground state renders direct energy transfer (reaction 19) energetically feasible. Inasmuch as the reduction potentials of these quintet and triplet excited states of Fe_{aq}^{2+} are ~−0.5 and ~1.0 V, respectively, reaction 21 is thermodynamically allowed. It should be noted that the formation of the quintet state involves the promotion of two electrons into the antibonding levels; formation of the triplet state involves the promotion of one electron. Such transitions are expected to give rise to large Stokes shifts in the $^*Fe_{aq}^{2+}$ species which will decrease the thermodynamic allowedness of electron transfer reaction 21. For the energy-transfer route to be of any consequence in the quenching of $(^2E)Cr(NN)_3^{3+}$ requires $k_{21} > k_{23}$. In this regard, the following considerations suggest that energy transfer is inconsequential: *firstly*, the reorganization energy in the electron-transfer step 21 is expected to be much larger than that of reaction 23 inasmuch as, in reaction 21, electron transfer originates from an antibonding e_g level (in reaction 23, a t_{2g} electron is involved); *secondly*, the orbitals involved in reaction 23 have identical t_{2g} symmetry while in reaction 21 the donor orbital is e_g and the acceptor orbital is t_{2g}.

Figure 3 shows the linear plot of log k_q vs. ΔE^f for the quenching by Fe_{aq}^{2+}; the strongest oxidant, $(^2E)Cr(5\text{-}Clphen)_3^{3+}$, gives the highest rate. The variation in k_q is attributed to direct electron transfer reaction 23.

The quenching data for the ^2E states of closely related $Cr(NN)_3^{3+}$ complexes can now be applied to the Marcus theory of electron-transfer reactions[61] of excited-state species.[13,53] In Figure 4 is plotted log k_q for Fe_{aq}^{2+} quenching vs. log K_{12}, where K_{12} is the equilibrium constant for the cross electron transfer reaction

$$(^2E)Cr(NN)_3^{3+} + Fe_{aq}^{2+} \rightarrow Cr(NN)_3^{2+} + Fe_{aq}^{3+} \quad (25)$$

$E°(Fe^{3+}|Fe^{2+}) = 0.77$ V in 1 M HCl.[62] The linear relationship further supports the formulation of an electron-transfer mechanism for the quenching. The slope of the line is 0.31; the intercept is 4.1.[63] The Marcus relationships for electron transfer[61] are given as

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$
$$\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (26)$$

where k_{11} and k_{22} refer to the Fe_{aq}^{2+}-Fe_{aq}^{3+} and (^2E)-$Cr(NN)_3^{3+}$-$Cr(NN)_3^{2+}$ self-exchange reactions, respectively; k_{12} is the rate constant for cross reaction 25 and Z is the collision number, which is generally taken to be 10^{11} M^{-1} s^{-1}. The self-exchange rate for the reaction

$$(^2E)Cr(NN)_3^{3+} + Cr(NN)_3^{2+} \rightarrow Cr(NN)_3^{2+} + (^2E)Cr(NN)_3^{3+} \quad (27)$$

(k_{22}) can be evaluated from k_{11} (4.0 M^{-1} s^{-1})[64] and from the equations

$$\log k_{12} = 0.50 \log k_{11}k_{22} + 0.50(1 + \alpha) \log K_{12}$$
$$\alpha = (\log K_{12})/4 \log (k_{11}k_{22}/Z^2) \quad (28)$$

The values of α range from -0.14 for $Cr(4,7\text{-}Me_2phen)_3^{3+}$ to -0.23 for $Cr(5\text{-}Clphen)_3^{3+}$. From the intercept of the line in Figure 4, we estimate k_{22} (reaction 27) as 4×10^7 M^{-1} s^{-1}.[65] It is significant to note that, in the reduction of analogous $Ru(NN)_3^{3+}$ complexes by Fe_{aq}^{2+}, the self-exchange rate for the $Ru(NN)_3^{3+}$-$Ru(NN)_3^{2+}$ couple was found to be 2.4×10^3 M^{-1} s^{-1}, six orders of magnitude lower than expected ($\sim 2 \times 10^9$ M^{-1} s^{-1}).[13] The discrepancy was rationalized in terms of the nonadiabaticity of the cross reaction while the self-exchange reactions of Fe_{aq}^{2+} and Ru(III) couples are believed to be adiabatic.[13] A recent estimate[66] of the self-exchange rate for $(^2E)Cr(bpy)_3^{3+}$-$Cr(bpy)_3^{2+}$ is 3×10^5 M^{-1} s^{-1}, nearly two orders of magnitude smaller than the value obtained in this work; by comparison, an exchange rate of 4×10^9 M^{-1} s^{-1} was obtained for $Cr(bpy)_3^{2+}$-$Cr(5,6\text{-}Me_2phen)_3^{3+}$ in methanolic solutions ($\mu = 0.1$ M) at 25 °C.[66] The slower electron transfer exchange rates for the excited-state reactions were explained[67] in terms of the changes in bond lengths and angles that occur upon the excitation of $Cr(bpy)_3^{3+}$. This explanation cannot be correct, however, inasmuch as the Stokes shift between the $^4A_2$ and ^2E states of the $Cr(bpy)_3^{3+}$ complexes is zero, there being coincidence between the $^2E \leftrightarrow {}^4A_2$ emission[7] and absorption[16] bands; Endicott and Ferraudi[67] report a Stokes shift of $\sim 1.5 \times 10^3$ cm^{-1}. However, variations in the adiabaticity[68] of the ground and excited state exchange reactions cannot be ruled out in accounting for such differences in the rates.

Conclusions

(1) The polypyridyl complexes of Cr(III), $Cr(NN)_3^{3+}$, are relatively stable toward photochemical ligand loss in acidic aqueous media at room temperature.

(2) The ground-state absorption spectra of $Cr(NN)_3^{3+}$ are sensitive to ligand substitution; phenyl substitution increases the absorption in the visible region to a significant extent.

(3) The ^2E metal-centered excited states are two to three orders of magnitude longer lived than are the MLCT excited states of analogous Ru(II) complexes and four to five orders of magnitude longer lived than excited analogous Os(II) complexes.

(4) The lifetimes of the ^2E states can be further prolonged by the presence of high (>1 M) concentrations of anions.

(5) The redox potentials of the ^2E states are strongly dependent on the nature of the ligand substituents; the ^2E states are more powerful oxidants than are the MLCT excited states of analogous Ru(II) and Os(II) complexes.

(6) The properties and behavior of the ^2E states can be "fine tuned" by means of judicious molecular engineering and alteration of the solution medium.

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The Onset of Band-Like Properties in the Ligand-Bridged, Trimeric Cluster $\{[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]\}$

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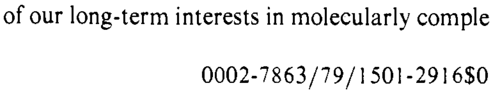
Abstract: The ligand-bridged trimeric cluster $\{[(py)_2Ru_3O(CH_3CO_2)_6(pyr)]_2[Ru_3O(CH_3CO_2)_6(CO)]\}(PF_6)_2$ (py = pyridine, pyr = pyrazine) has been prepared by a reaction between the monomeric clusters $[Ru_3O(CH_3CO_2)_6(py)_2(pyr)]^+$ and $[Ru_3O(CH_3CO_2)_6(CH_3OH)_2(CO)]$. Electrochemical studies show that the trimer has an extraordinary degree of reversible electron-transfer chemistry. Its optical and redox properties are of interest when compared to those of the monomer units which make it up. When its total electron content is low, which is the case, for example, in the 2+ ion mentioned above, its properties are those expected for isolated cluster units where intercluster electronic interactions are weak. However, the results of electrochemical studies suggest that as electron content increases, electronic coupling between the cluster sites is enhanced and the appearance of a series of closely spaced, one-electron waves may signal the appearance of band-like behavior in this discrete chemical system.

Introduction

The tri-μ-oxo-carboxylate-bridged cluster system $[Ru_3O(OAc)_6(py)_3]^{3+/2+/+/0/-}$ (OAc is acetate; py is pyridine) (Figure 1) is remarkable for the extent of its reversible redox chemistry.[1-3] Spectral studies suggest that the observed "electron-sponge"-like behavior is based on the gain or loss of electrons from molecular levels which are delocalized over the Ru_3O core.[2] The molecular complexity of such systems can be extended since we recently devised synthetic procedures for linking cluster units through bridging ligands as in the dimer i. It is now clear that a systematic synthetic chemistry is available for preparing higher oligomers.



i

One of our long-term interests in molecularly complex metal systems is the possibility of observing and controlling transitions in properties from those of discrete molecules in solution to those more normally associated with the infinite systems of the solid state. In the process of building up higher oligomers based on the ruthenium clusters, an important synthetic intermediate has turned out to be the cluster trimer $[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]^{2+}$ (Figure 2). We report here the preparation and properties of the trimer for two reasons. One is that linking together the clusters results in the creation of a chemical system which has truly remarkable, reversible electron-transfer properties. The second is that when electron rich, the properties of the trimer are consistent with the beginnings of a band-like electronic structure which may be realizable in higher oligomers.

Experimental Section

Measurements. Electrochemical measurements made were vs. the

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