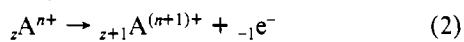


Likewise, in β^- decay, one can write



Rearrangement of electronic charge then yields the product



The results of this study suggest that except for the α or β^- particles that escape the system permanently, such rearrangements generally occur resulting in the neutralization of excess or deficient charge. Thus, within the limits of our ability to observe such effects, the oxidation state of the parent is retained by the progeny.

Another view of the above mechanism has been suggested to explain our results^{2a} in β^- decay;¹⁸ it applies equally well to explain our observations of the effects of α decay. Even though the immediate oxidation state of a thermalized recoil species in a bulk-phase solid might be different from that of the parent cation, there is also a charge balance with anionic species present in that phase that must be considered. This balance promotes the maintenance of oxidation state.

The above hypothesis can explain the bulk-phase solid state system we describe here, i.e., Es $\xrightarrow{\alpha}$ Bk $\xrightarrow{\beta^-}$ Cf. We are not invoking any severe oxidation-state instabilities, with the possible exception of the status of Bk in the decay of solid-state,

divalent Es halides. In another study we have also observed that cation oxidation state is preserved in the α decay of ${}^{244}\text{CmBr}_3 \rightarrow {}^{240}\text{PuBr}_3$. Here again we are invoking no severe chemical instabilities to maintain oxidation state; i.e., both parent and daughter cations exhibit stable trivalent oxidation states.

In sharp contrast to the above results, very severe chemical instabilities could be created if oxidation states in bulk-phase solids are preserved in certain other α or β^- processes, such as Pa $\xrightarrow{\alpha}$ Ac, Th $\xrightarrow{\alpha}$ Ra, and Br $\xrightarrow{\beta^-}$ Kr. Further, if other radioactive decay schemes are considered such as ${}^7\text{Be}^{2+} \xrightarrow{\text{EC}} {}^7\text{Li}^{2+}$, various n,p reactions, etc., maintenance of oxidation state, or structure, does not seem possible. It would be worthwhile to establish the limits of such oxidation-state maintenance.

Expansion of the present work to other compounds and other decay systems is planned to elucidate more completely the chemical consequences of radioactive decay in the bulk-phase solid state. The results of such an expanded study should lead to a better understanding, for example, of the long-term, solid-state storage of nuclear materials.

Registry No. ${}^{253}\text{EsF}_3$, 78891-05-1; ${}^{253}\text{EsCl}_3$, 55484-87-2; ${}^{253}\text{EsBr}_3$, 57137-36-7; ${}^{253}\text{EsI}_3$, 78891-06-2; ${}^{253}\text{EsCl}_2$, 70420-31-4; ${}^{253}\text{EsBr}_2$, 60198-18-7; ${}^{253}\text{EsI}_2$, 70420-32-5; ${}^{249}\text{Bk}$, 14900-25-5; ${}^{249}\text{Cf}$, 15237-97-5; ${}^{253}\text{Es}$, 15840-02-5.

Supplementary Material Available: Spectra of EsBr_2 , EsI_3 , and EsI_2 as a function of time (3 pages). Ordering information is given on any current masthead page.

(18) A. G. Maddock, University Chemical Laboratory, Cambridge, England, private communication, April 18, 1980.

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Photophysics and Photochemistry of Polypyridyl Complexes of Chromium(III)¹

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The quantum yields of photoaquation (Φ_{rx}) and the lifetimes of the ${}^2T_1/{}^2E$ excited states (${}^2\tau$) have been determined in aqueous solution at 22 °C for 12 tris(polypyridyl) complexes of Cr(III), $\text{Cr}(\text{NN})_3^{3+}$ (where NN = bpy, 4,4'-Me₂bpy, 4,4'-Ph₂bpy, phen, 5-Cl(phen), 5-Br(phen), 5-Me(phen), 5-Ph(phen), 5,6-Me₂phen, 4,7-Me₂phen, 4,7-Ph₂phen, or 3,4,7,8-Me₄phen). Φ_{rx} was determined for deaerated solutions containing 1.0 M NaCl and 0.008 M Britton-Robinson buffer at pH 9.5; ${}^2\tau$ was determined under the same conditions of solution medium as well as in 1.0 M HCl (5.0 M HCl for NN = bpy, 4,4'-Me₂bpy, or 4,4'-Ph₂bpy). The values of ${}^2\tau$ for a given complex are dependent on [substrate]; increases in [substrate] result in a decrease in ${}^2\tau$ such that plots of $1/{}^2\tau$ vs. [substrate] are linear. The slopes of such plots yield values of 2k_g , the rate constant for the quenching of ${}^2T_1/{}^2E$ by the ground state (4A_2), that are in the range of 10^6 - 10^8 M⁻¹ s⁻¹. Ground-state quenching of ${}^2T_1/{}^2E$ is seen as a collisional phenomenon between the Cl⁻-associated ground and excited states; large substituents, especially phenyl groups, increase the value of 2k_g . The values of Φ_{rx} are low in acidic solution, rise in the mid-pH region, and reach a plateau at pH 9-10. Coupling the plateau values of Φ_{rx} with ${}^2\tau$, and assuming that the efficiency of ${}^4T_2 \rightarrow {}^2T_1/{}^2E$ intersystem crossing is ~ 1 for all the complexes, we have obtained values of ${}^2k_{\text{rx}}$ ($=\Phi_{\text{rx}}/{}^2\tau$), the rate constant of the reactive decay of ${}^2T_1/{}^2E$. Taking the values of ${}^2k_{\text{rx}}$ as reflecting the ease with which the seven-coordinate intermediate is formed upon interaction of solvent with ${}^2T_1/{}^2E$, we can see that the flexibility of the ligand structure and the degree of hydrophilicity in the vicinity of the interligand pockets are the determining factors. The rate constants of the nonradiative decay of ${}^2T_1/{}^2E$, ${}^2k_{\text{nr}}$, have also been evaluated.

Introduction

2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), and their substituted derivatives comprise an extensive series of tris(polypyridyl) complexes of Cr(III), $\text{Cr}(\text{NN})_3^{3+}$, the photophysics and photochemistry of which can be examined under identical conditions in fluid solution at room temperature.

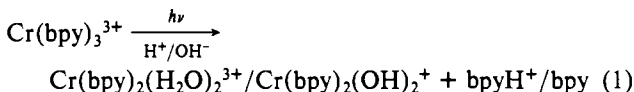
Determination of the lifetime of the thermally equilibrated excited states of lowest energy, ${}^2T_1/{}^2E$, by flash absorption and luminescence decay techniques reveals that ${}^2\tau$ for these metal-centered states is highly dependent on the nature of the ligands.³⁻⁸ Because of the long lifetimes of ${}^2T_1/{}^2E$ in fluid

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(2) (a) Concordia University. (b) Boston University.

- (3) Maestri, M.; Bolletta, F.; Moggi, L.; Balzani, V.; Henry, M. S.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1978**, *100*, 2694.
(4) Serpone, N.; Jamieson, M. A.; Henry, M. S.; Hoffman, M. Z.; Bolletta, F.; Maestri, M. *J. Am. Chem. Soc.* **1979**, *101*, 2907.
(5) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.
(6) Henry, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6138.
(7) Henry, M. S.; Hoffman, M. Z. *Adv. Chem. Ser.* **1978**, No. 168, 91.
(8) Sriram, R.; Hoffman, M. Z.; Jamieson, M. A.; Serpone, N. *J. Am. Chem. Soc.* **1980**, *102*, 1748.

solution at room temperature (tenths of ms) and their strong oxidizing abilities ($E^\circ = 1.2\text{--}1.5\text{ V}$),^{4,5} $\text{Cr}(\text{NN})_3^{3+}$ complexes are viewed as having potential toward solar energy utilization;⁹ recently, it has been reported that $\text{Cr}(\text{NN})_3^{2+}$ reduces H_2O to H_2 in the presence of a Pt catalyst.¹⁰

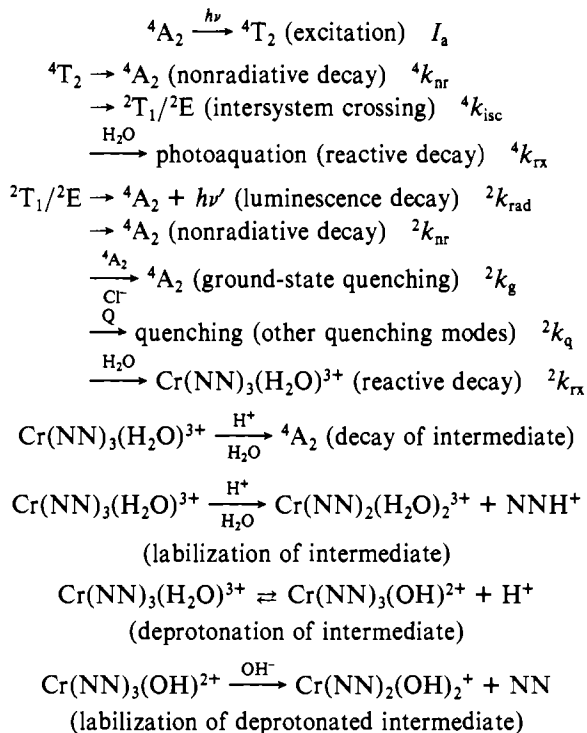
The photochemistry of $\text{Cr}(\text{bpy})_3^{3+}$ has been extensively studied at room temperature in aqueous solution^{3,11,12} revealing that ligand labilization (reaction 1) is the only important



process. The observed photoaquation quantum yield, Φ_{rx} , at 22 °C in the absence of O_2 reaches a lower limit plateau in acidic solution and an upper limit plateau in alkaline solution, describing a "titration curve" centered at pH 5–6 that parallels the dependence of the ground-state thermal aquation rate constant on pH.^{3,12–14} Qualitatively, other Cr(III)–polypyridyl complexes show similar thermal and photochemical stability in acidic media.⁴

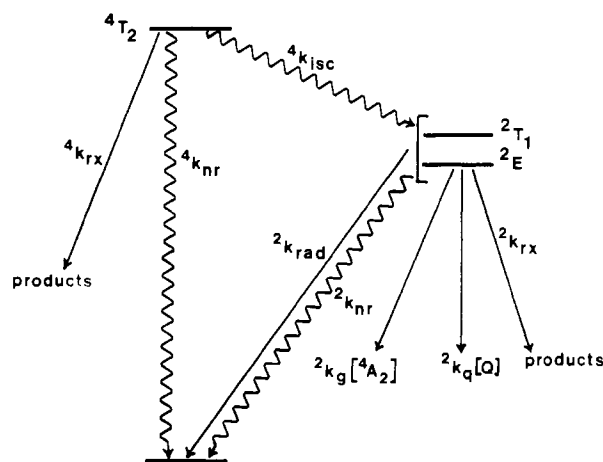
From our previous studies^{3,4,6–8,11,12,15} on the excited-state behavior of $\text{Cr}(\text{NN})_3^{3+}$, the mechanism shown in Scheme I has been formulated; the photophysical aspects are shown in Scheme II.

Scheme I



In the research reported in this paper, values of $^2\tau$ and Φ_{rx} have been determined at specified concentrations of the ground-state complexes in alkaline solutions containing 1.0 M NaCl and 0.008 M Britton–Robinson buffer. The values

Scheme II



are used to evaluate the rate constants of the reactive and nonradiative decays of $^2\text{T}_1/^2\text{E}$ ($^2k_{\text{rx}}$ and $^2k_{\text{nr}}$, respectively) as a function of the structure of the polypyridyl ligands. By determining $^2\tau$ as a function of [substrate], we have been able to evaluate $^2\tau_0$, the lifetime of $^2\text{T}_1/^2\text{E}$ at infinite substrate dilution, and $^2k_{\text{g}}$ for 12 $\text{Cr}(\text{NN})_3^{3+}$ complexes.

Experimental Section

Materials. The $\text{Cr}(\text{NN})_3^{3+}$ complexes, as their ClO_4^- salts, were available from earlier studies;^{4,16} NN represents 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me₂bpy), 4,4'-diphenyl-2,2'-bipyridine (4,4'-Ph₂bpy), 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (5-Cl(phen)), 5-bromo-1,10-phenanthroline (5-Br(phen)), 5-methyl-1,10-phenanthroline (5-Me(phen)), 5-phenyl-1,10-phenanthroline (5-Ph(phen)), 5,6-dimethyl-1,10-phenanthroline (5,6-Me₂phen), 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phen), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph₂phen), or 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-Me₄phen). All other chemicals and solvents were reagent grade or spectrograde.

Apparatus. Absorption spectra of the complexes were recorded with Aminco-Bowman DW-2 or Cary 118 UV-vis spectrophotometers. Luminescence spectra were taken with a Perkin-Elmer MPF-2A spectrofluorimeter equipped with a red-sensitive R-446 photomultiplier tube and high-intensity accessory. Emission lifetimes in Montreal were determined with use of a 1-kW N_2 laser (4-ns pulses at 337 nm); the luminescence decay curves were photographed from a Tektronix 7633 oscilloscope. The apparatus in Boston consisted of a frequency-doubled pulsed ruby laser yielding ~ 40 -ns pulses at 347 nm. The emission from the complexes centered around 727 nm was collimated and isolated by means of a UV-cutoff filter and a grating monochromator. The detection system consisted of a red-sensitive R-665 photomultiplier and a storage oscilloscope. The samples were contained in 1-cm quartz spectrofluorimeter cells with a Teflon stopcock. Continuous photolyses were carried out at 313 nm with an Oriel 1-kW Hg-Xe lamp and a 0.25-m Bausch & Lomb grating monochromator (22-nm bandwidth). The beam was passed through an 8-cm path of cooled distilled water in order to avoid IR heating of the sample.¹⁷ The intensity of the incident light ($\sim 1 \times 10^{-6}$ einstein min^{-1}) was determined by ferrioxalate actinometry.¹⁸ All measurements of emission spectra, emission lifetimes, and quantum yields were performed at a controlled temperature of 22.0 ± 0.5 °C.

Procedures. For the measurement of emission lifetimes, solutions of $\text{Cr}(\text{NN})_3^{3+}$ were prepared in the appropriate medium and deaerated with prepurified Ar or N_2 for about 30 min at 22 °C. The emission spectra and lifetimes were obtained with use of right-angle or front-surface illumination depending upon the concentration of the substrate.

For the quantum yield and lifetime determinations, neutral and alkaline aqueous solutions (pH 5–10, 0.008 M Britton–Robinson

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(10) Ballardini, R.; Juris, A.; Varani, G.; Balzani, V. *Now. J. Chim.* **1980**, *4*, 563.

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(18) Parker, C. A. "Luminescence of Solutions"; Elsevier: New York, 1968.

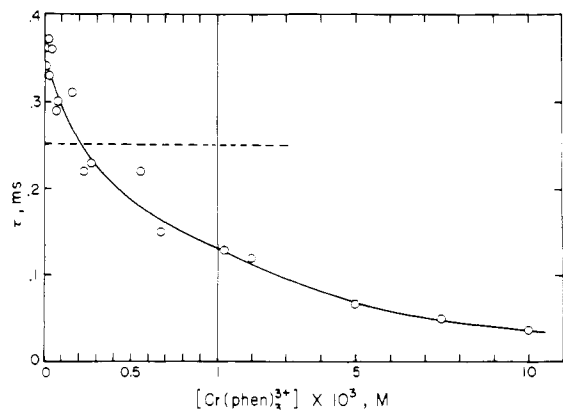


Figure 1. Lifetime of $(^2E)Cr(phen)_3^{3+}$ as a function of [substrate] in deaerated aqueous solutions at 22.0 °C: —, 1.0 M HCl; each point represents the average of 3–10 individual experiments; ---, neat H_2O ; the line represents the average of 10 individual experiments performed at different [substrate]. Solubility restrictions prevent the extension of the range in neat H_2O .

buffer,¹⁹ 1.0 M NaCl) were prepared and handled in dim, red light. The pH values of the buffered solutions were measured with a Metrohm-Herisau pH meter.

For $Cr(phen)_3^{3+}$, the quantum yield for the release of phen into solution was obtained by an extraction procedure very similar to that used previously^{3,11,12} for $Cr(bpy)_3^{3+}$. For the other 10 complexes, the following procedure was employed. Exactly 3.00 mL of a solution of $Cr(bpy)_3^{3+}$ at pH 9.27 (at a concentration such that >99% of the incident radiation at 313 nm is absorbed) in a 1-cm quartz cell fitted with a stopcock was irradiated for successive periods of 5 s each; the absorption spectrum of the solution was recorded after each irradiation up to ~10% change in absorbance at the monitoring wavelength chosen to reflect the loss of substrate. The same procedure was followed for the other complexes except that depending on [substrate], complete absorption of the incident radiation could not be assured. A sample of unirradiated solution was kept in the dark at 22.0 °C and analyzed in the same way; in all cases, the thermal aquation was undetectable.

In order to dissolve the substituted bpy and phen complexes (except 5-Cl(phen) and 5-Me(phen)) in 1.0M HCl or in 1.0 M NaCl and 0.008 M buffer at pH 9.5 sufficient to examine the effect of [substrate], minimum (4% v/v) amounts of CH_3CN were required. In the cases of 4,4'-Ph₂bpy and 4,7-Ph₂phen under photochemical conditions, 40% v/v CH_3OH was required to effect dissolution.

Emission lifetimes were determined either by direct means at the same substrate concentration used in the determination of Φ_{rx} or by interpolation from a plot of $^2\tau$ vs. $[Cr(NN)_3^{3+}]$.

Evaluation of Quantum Yields. The loss of substrate due to successive irradiations was determined by the decrease in absorbance at the monitoring wavelength, and a plot of $[Cr(NN)_3^{3+}]$ vs. irradiation time was made for each complex. Such plots were linear for $\leq 10\%$ reaction. Whenever there were deviations from linearity due to product absorption, the initial slope was taken to determine the rate of loss of substrate, R_{rx} . The quantum yield Φ_{rx} was obtained as the ratio of the slope R_{rx} to the absorbed light intensity, I_a . When >99% of the incident light at 313 nm was absorbed, $I_a = I_0$. Since Φ_{rx} for $Cr(bpy)_3^{3+}$ at 22 °C and pH 9.5 is 0.18, as determined by ferrioxalate actinometry, Φ_{rx} for other complexes under complete light-absorption conditions were conveniently obtained by comparing the rate of loss of the substrate to that of $Cr(bpy)_3^{3+}$: $\Phi_{rx} = (\Phi_{bpy}R_{rx})/R_{bpy}$. In the event that the absorption of light was not complete so that $I_a \neq I_0$, a Beer's law correction was made such that $\Phi_{rx} = (\Phi_{bpy}R_{rx})/(R_{bpy}(1 - 10^{-A}))$ where A is the absorbance of the solution at the irradiation wavelength.

Results

One of the earliest observations made during the course of this investigation was that $^2\tau$ for $Cr(NN)_3^{3+}$ is dependent on

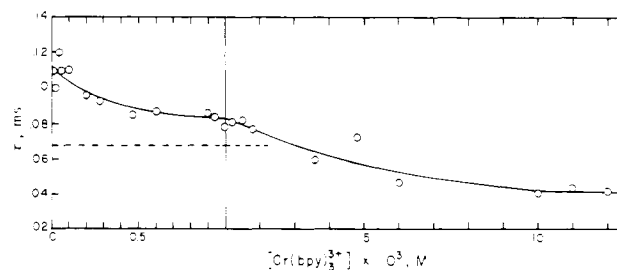


Figure 2. Lifetime of $(^2E)Cr(bpy)_3^{3+}$ as a function of [substrate] in deaerated aqueous solutions at 22.0 °C: —, 5.0 M HCl; each point represents the average of 3–10 individual experiments; ---, neat H_2O ; the line represents the average of 10 individual experiments performed at different [substrate]. Solubility restrictions prevent the extension of the range in neat H_2O .

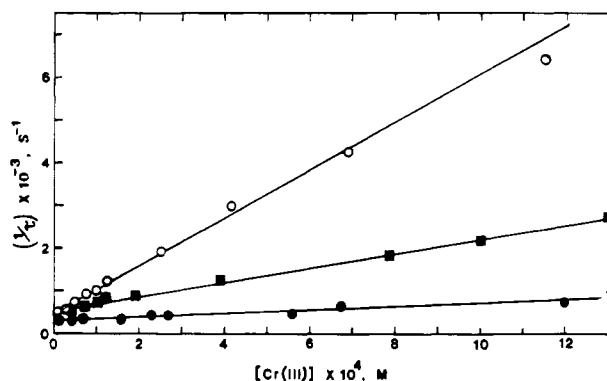


Figure 3. Plot of $1/2\tau$ for $Cr(NN)_3^{3+}$ as a function of [substrate] in deaerated 1.0 M HCl solution at 22.0 °C: (O) 5-Ph(phen) in 4% v/v CH_3CN ; (■) 5-Cl(phen); (●) phen.

[substrate] in the presence of 1 M HCl or NaCl. Accordingly, we examined this functionality in great detail. The dependence of $^2\tau$ for $Cr(phen)_3^{3+}$ in 1.0 M HCl on [substrate] is shown in Figure 1, where each point represents the average of 3–10 individual runs. By comparison, the average of 10 individual experiments yields $^2\tau = 0.25 (\pm 0.03)$ ms over the substrate concentration range 1.2×10^{-5} – 1.2×10^{-3} M in the absence of HCl; solubility restrictions prevent the extension of the range in neat H_2O . In contrast, $^2\tau$ values for $Cr(bpy)_3^{3+}$ in 1.0 M HCl and neat H_2O are virtually indistinguishable: $^2\tau = 0.073 (\pm 0.008)$ ms in 1.0 M HCl and $0.068 (\pm 0.008)$ ms in H_2O over the substrate concentration range 1.4×10^{-5} – 2.5×10^{-3} M. In order to observe the ground-state quenching phenomenon for $Cr(bpy)_3^{3+}$ and $Cr(4,4'-Me_2bpy)_3^{3+}$, 5.0 M HCl was used; $^2\tau$ values for $Cr(bpy)_3^{3+}$ are shown in Figure 2. As we have shown previously,⁸ plots of $1/2\tau$ vs. $[Cr(III)]$ are linear with a slope equal to 2k_g and an intercept equal to $1/2\tau_0$; sample plots are shown in Figure 3. Values of 2k_g and $^2\tau_0$ are given in Table I for solution media containing 1.0 M (or 5.0 M) HCl or 1.0 M NaCl and 0.008 M Britton–Robinson buffer at pH 9.5. It should be noted that $^2\tau$ for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ at 1.2×10^{-4} M are unaffected by changes in pH (5.5–10.5) in the presence or absence of 0.008 M Britton–Robinson buffer in a solution containing 1.0 M NaCl.

It is important to recognize that no changes, within the sensitivities of the instruments used, are observed in either the absorption or emission spectra, outside of intensity, of the complexes due to the change in [substrate]. Absorption spectra showed no shift in the profile nor changes in ϵ values. Emission spectra showed no new bands or shift in the profile.

Because of the ground-state quenching phenomenon, measurements of Φ_{rx} and $^2\tau$ were made in well-defined solution media. Table II shows the following data for 12 $Cr(NN)_3^{3+}$ complexes in deaerated solution at 22 °C: Φ_{rx} as a function

(19) Mongay, C.; Cerda, V. *Ann. Chim. (Paris)* **1974**, *64*, 409. 0.008 M each of H_3BO_3 , H_3PO_4 , and CH_3CO_2H in water.

Table I. Ground-State Quenching Parameters for $\text{Cr}(\text{NN})_3^{3+}$ at 22 °C

NN	solution medium			
	1.0 M HCl		1.0 M NaCl and 0.008 M Britton-Robinson buffer at pH 9.5	
	$^2k_g, \text{M}^{-1} \text{s}^{-1}$	$^2\tau_0, \text{ms}$	$^2k_g, \text{M}^{-1} \text{s}^{-1}$	$^2\tau_0, \text{ms}$
bpy	1.3×10^6 ^a	0.10 ^a		0.071
4,4'-Me ₂ bpy	2.0×10^6 ^{a,b}	0.31 ^{a,b}		0.18 ^b
		0.20		
4,4'-Ph ₂ bpy	1.4×10^8 ^b	0.17 ^b	6.0×10^7 ^c	0.053 ^c
	1.0×10^8 ^{a,b}	0.19 ^{a,b}		
phen	3.0×10^6 ^a	0.32 ^a	6.1×10^6	0.23
	2.3×10^6	0.33		
5-Cl(phen)	1.7×10^7	0.18	3.5×10^7	0.15
5-Br(phen)	5.4×10^7 ^b	0.18 ^b	8.1×10^7 ^b	0.17 ^b
5-Me(phen)	5.0×10^6	0.42	1.4×10^7	0.27
5-Ph(phen)	5.7×10^7 ^b	0.22 ^b	9.3×10^7 ^b	0.18 ^b
5,6-Me ₂ phen	7.5×10^6 ^b	0.42 ^b	1.7×10^7 ^b	0.29 ^b
4,7-Me ₂ phen	1.0×10^7 ^b	0.57 ^b	1.4×10^7 ^b	0.42 ^b
4,7-Ph ₂ phen	7.4×10^7 ^b	0.57 ^b	3×10^8 ^{c,d}	0.089 ^c
3,4,7,8-Me ₄ phen	1.5×10^7 ^b	0.64 ^b	3.9×10^7 ^b	0.62 ^b

^a 5.0 M HCl. ^b Solution contains 4% v/v CH₃CN. ^c Solution contains 40% v/v CH₃OH. ^d From Figure 4.

of pH and $^2\tau$ in solutions containing 1.0 M NaCl and 0.008 M Britton-Robinson buffer at pH 9–10 at specified [substrate].

Discussion

The values of $^2\tau$ for $(^2T_1/{}^2E)\text{Cr}(\text{NN})_3^{3+}$ result from the contribution of all the modes of decay. Thus, $1/{}^2\tau = {}^2k_{\text{rad}} + {}^2k_{\text{nr}} + {}^2k_{\text{rx}} + {}^2k_g[{}^4A_2] + {}^2k_q[Q]$. Inasmuch as the quantum yield of luminescence is $\sim 10^{-3}$,²⁰ the contribution of ${}^2k_{\text{rad}}$ to $^2\tau$ is small and can be neglected. In the absence of deliberately added redox or energy quenchers, [Q] represents the concentration of adventitious impurities in the reagents. As seen in Table I, 2k_g has values in the range of 10^6 – $10^8 \text{ M}^{-1} \text{ s}^{-1}$; the Cl⁻-mediated quenching of ${}^2T_1/{}^2E$ by 4A_2 is quite extensive and proves to be one of the major determinants of the value of $^2\tau$. At infinite substrate dilution in the absence of any adventitious quenchers, the intrinsic lifetime of ${}^2T_1/{}^2E$ in the solution medium, ${}^2\tau_0$, is given by the function $1/({}^2k_{\text{nr}} + {}^2k_{\text{rx}})$.

The population of ${}^2T_1/{}^2E$ available for its various modes of decay including photoaquation depends on the efficiency of intersystem crossing from 4T_2 to ${}^2T_1/{}^2E$ (${}^4\eta_{\text{isc}}$) where ${}^4\eta_{\text{isc}} = {}^4k_{\text{isc}}/({}^4k_{\text{isc}} + {}^4k_{\text{nr}} + {}^4k_{\text{rx}})$. The value of Φ_{rx} for each complex is a result of all the processes that eventually lead to the aquated products. As can be seen in Table II, all the observed values of Φ_{rx} reach a plateau in the vicinity of pH 9–10 and decrease as the solution is made more acidic. If it is true, as it is believed, that all ${}^2T_1/{}^2E$ species that pass to seven-coordinate $\text{Cr}(\text{NN})_3(\text{OH})^{2+}$ in alkaline solution lead rapidly, irreversibly, and quantitatively to $\text{Cr}(\text{NN})_2(\text{OH})_2^+$, then $\Phi_{\text{rx}} = ({}^4\eta_{\text{isc}}{}^2\eta_{\text{rx}}) + {}^4\eta_{\text{rx}}$ where ${}^2\eta_{\text{rx}}$ is the efficiency of reaction out of ${}^2T_1/{}^2E$ ($= {}^2k_{\text{rx}}/{}^2\tau$) and ${}^4\eta_{\text{rx}}$ is the efficiency of reaction out of 4T_2 . Inasmuch as the portion of the observed value of Φ_{rx} that cannot be quenched by I⁻ (which efficiently quenches the photoreaction of ${}^2T_1/{}^2E$)³ is less than 10% of Φ_{rx} ,²¹ ${}^4\eta_{\text{rx}}$ may be neglected. Therefore, $\Phi_{\text{rx}} = {}^4\eta_{\text{isc}}{}^2k_{\text{rx}}{}^2\tau$.

Now, Balzani and co-workers²² have evaluated ${}^4\eta_{\text{isc}}$ for $\text{Cr}(\text{bpy})_3^{3+}$ and $\text{Cr}(\text{phen})_3^{3+}$ to be ~ 1 and ~ 0.2 , respectively. However, a recent reexamination of these systems²³ has re-

Table II. Photoaquation Quantum Yields and 2E Lifetimes for $\text{Cr}(\text{NN})_3^{3+}$ Complexes at 22 °C in Deaerated Solution^a

NN	$[\text{Cr}(\text{NN})_3^{3+}]$, mM	Φ_{rx} (pH)	$^2\tau$, ms
bpy	1.0	0.13 (9.8)	0.071
4,4-Me ₂ bpy ^b	0.12	0.002 ± 0.001 (5.1) 0.064 ± 0.013 (9.3) 0.061 ± 0.001 (10.4)	0.18
4,4'-Ph ₂ bpy ^c	0.048	0.011 ± 0.002 (5.1) 0.024 ± 0.005 (9.3) 0.018 ± 0.001 (10.4)	0.050
phen	1.5	~ 0.0005 (5.1) 0.005 ± 0.002 (9.2) 0.006 ± 0.001 (10.4)	0.074
5-Cl(phen)	0.14	0.0020 ± 0.0001 (5.1) 0.010 ± 0.001 (9.2) 0.013 ± 0.003 (10.4)	0.086
5-Br(phen) ^b	0.12	0.0062 ± 0.0002 (5.2) 0.009 ± 0.001 (9.2) 0.007 ± 0.001 (10.4)	0.063
5-Me(phen)	0.12	0.0044 ± 0.0004 (5.2) 0.012 ± 0.001 (9.2) 0.012 ± 0.001 (10.4)	0.18
5-Ph(phen) ^b	0.072	0.0033 ± 0.0005 (5.2) 0.006 ± 0.001 (9.2) 0.006 ± 0.001 (10.4)	0.081
5,6-Me ₂ phen ^b	0.11	0.0047 ± 0.0002 (5.2) 0.006 ± 0.001 (9.3) 0.007 ± 0.001 (10.4)	0.19
4,7-Me ₂ phen ^b	0.11	~ 0.0003 (5.1) 0.004 ± 0.001 (9.3) 0.003 ± 0.001 (10.4)	0.25
4,7-Ph ₂ phen ^c	0.034	0.0012 ± 0.0003 (5.1) 0.0015 ± 0.0001 (9.3) 0.0013 ± 0.0001 (10.4)	0.074
3,4,7,8-Me ₄ phen ^b	0.084	~ 0.0002 (5.1) 0.0014 ± 0.0002 (9.3) 0.0018 ± 0.0002 (10.4)	0.21

^a $\lambda_{\text{excit}} = 313 \text{ nm}$; solution contains 1.0 M NaCl in 0.008 M Britton-Robinson buffer at $[\text{Cr}(\text{NN})_3^{3+}]$ shown; pH 9–10. Φ_{rx} is reported as the mean value of 2–6 determinations with the error as the deviation from the mean. ^b Solution contains 4% v/v CH₃CN. ^c Solution contains 40% v/v CH₃OH.

vealed that in aqueous solution, these values are equal and ~ 1 . This result requires that ${}^4k_{\text{isc}} \gg {}^4k_{\text{nr}}$ for both complexes. In the absence of any direct information about ${}^4\eta_{\text{isc}}$ for the other complexes, we assume that ${}^4\eta_{\text{isc}} \sim 1$. It must be noted, however, that we have observed previously⁷ that ${}^4\eta_{\text{isc}}$ for $\text{Cr}(\text{bpy})_3^{3+}$ is diminished as the mole fraction of the organic component of mixed aqueous–nonaqueous solvents is increased. However, the effect of 4% v/v CH₃CN, which corresponds to a mole fraction of CH₃CN of < 0.02 , is of no consequence⁷ in the case of $\text{Cr}(\text{bpy})_3^{3+}$ and can be ignored in the case of those complexes for which CH₃CN was required to effect dissolution. On the other hand, 40% v/v CH₃OH corresponds to a mole fraction of CH₃OH of ~ 0.25 , which, in the case of $\text{Cr}(\text{bpy})_3^{3+}$, shows reduction of ${}^4\eta_{\text{isc}}$ to a value $\sim 50\%$ of the value in neat water. Thus, in the cases of the 4,7-Ph₂phen and 4,4'-Ph₂bpy complexes, ${}^4\eta_{\text{isc}}$ may be < 1 , causing the observed values of Φ_{rx} to be lower than those observed for the systems in water.

So, $\Phi_{\text{rx}} = {}^2k_{\text{rx}}{}^2\tau$ by assuming that ${}^4\eta_{\text{isc}} \sim 1$, recognizing the problem with regard to the 4,7-Ph₂phen and 4,4'-Ph₂bpy complexes, and evaluating Φ_{rx} and $^2\tau$ in identical solution media. Calculated values of ${}^2k_{\text{rx}}$ are recorded in Table III.

According to our model, ${}^2k_{\text{rx}}$ reflects the ease with which the seven-coordinate intermediate forms upon interaction of the solvent with $(^2T_1/{}^2E)\text{Cr}(\text{NN})_3^{3+}$. It is possible to visualize the distortion and loosening of the ligand structure in order to accommodate the incoming H₂O molecule and the ultimate formation of some capped octahedron or pentagonal-bipyramidal structure.²⁴ Thus, the flexibility of the ligand structure

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Table III. Photophysical and Photochemical Parameters for $\text{Cr}(\text{NN})_3^{3+}$ at 22 °C in 1.0 M NaCl and 0.008 M Britton-Robinson Buffer at pH 9.5

NN	${}^2k_{\text{rx}}, \text{s}^{-1}$	${}^2k_{\text{nr}}, \text{s}^{-1}$
bpy	1.6×10^3	1.3×10^4
4,4'-Me ₂ bpy ^a	3.5×10^2	5.2×10^3
4,4'-Ph ₂ bpy ^b	4.2×10^2	1.8×10^4
phen	7.5×10	4.3×10^3
5-Cl(phen)	1.3×10^2	6.5×10^3
5-Br(phen) ^a	1.3×10^2	5.7×10^3
5-Me(phen)	6.7×10	3.6×10^3
5-Ph(phen) ^a	7.4×10	5.5×10^3
5,6-Me ₂ phen ^a	3.4×10	3.4×10^3
4,7-Me ₂ phen ^a	1.4×10	2.4×10^3
4,7-Ph ₂ phen ^b	1.9×10	1.1×10^4
3,4,7,8-Me ₄ phen ^a	7.6	1.6×10^3

^a In 4% v/v CH₃CN. ^b In 40% v/v CH₃OH.

and the extent of hydrophilicity in the vicinity of the interligand pockets will dictate the value of ${}^2k_{\text{rx}}$. Examination of the data in Table III shows that the more flexible bpy framework is more amenable to distortion than is the more rigid phen framework; in all cases ${}^2k_{\text{rx}}$ for bpy complexes is larger than for phen. The highly electronegative chlorine and bromine atoms in the 5 position of phen clearly facilitate water entry (compared to unsubstituted phen) into the pockets by providing an increased hydrophilic environment. Methyl and phenyl derivatives, especially multiply substituted, exhibit lower values of ${}^2k_{\text{rx}}$ due to the increased hydrophobic environment. The values of ${}^2k_{\text{rx}}$ reflect the competition between the hydrophilic quality of the interligand pockets and the flexibility of the ligands in order to accommodate distortion.

Inasmuch as $1/{}^2\tau_0 = {}^2k_0 = {}^2k_{\text{nr}} + {}^2k_{\text{rx}}$, it is possible to evaluate ${}^2k_{\text{nr}}$, the major contributor to the intrinsic decay of ${}^2\text{T}_1/{}^2\text{E}$; the values are given in Table III. It must be pointed out that the values of ${}^2k_{\text{nr}}$ are for aqueous solutions containing 1.0 M NaCl. As seen from Figures 1 and 2, ${}^2k_{\text{nr}}$ is 20–40% lower in neat water than in the ionic medium, a phenomenon evidently due to the effect of ionic association on the nonradiative process.

The values of ${}^2k_{\text{nr}}$ range over almost an order of magnitude between unsubstituted bpy and highly substituted phen. In the past,^{6,7} we have described the nonradiative decay of the ${}^2\text{E}$ state in terms of certain critical vibrational modes of the ligands that provide the perturbing dipole to effect the transfer of the electronic excitation energy from metal-centered orbitals to the ligand vibrations. Unquestionably, all the phen complexes are more rigid than the bpy complexes, which restricts the nonradiative decay of ${}^2\text{E}$. It is clear, however, that the model is more complex, requiring consideration of the coupling of the vibrations of the substituents with the critical ligand modes. In addition, the dipole moments created by electronegative halogen atoms affect ${}^2k_{\text{nr}}$. Further work directed toward an understanding of the nonradiative decay of (${}^2\text{T}_1/{}^2\text{E}$) $\text{Cr}(\text{NN})_3^{3+}$ is currently underway.

Comparison of the values of ${}^2\tau_0$ in 1.0 M HCl and 1.0 M NaCl at pH 9.5 in the presence of buffer (Table I) illustrates the problem that exists in defining the photophysics of the long-lived ${}^2\text{T}_1/{}^2\text{E}$ excited states. Because ${}^2\tau$ values for $\text{Cr}(\text{bpy})_3^{3+}$ and $\text{Cr}(\text{phen})_3^{3+}$ are pH independent in the presence or absence of the buffer, we assume that the intrinsic decay of ${}^2\text{T}_1/{}^2\text{E}$ for the other complexes is independent of pH. Furthermore, the evidence rules out the presence of impurities in the buffer that could quench ${}^2\text{T}_1/{}^2\text{E}$. Apparently, the difference between ${}^2\tau_0$ in 1.0 M HCl and in 1.0 M NaCl at pH 9.5, which mainly reflects differences in ${}^2k_{\text{nr}}$, arises from

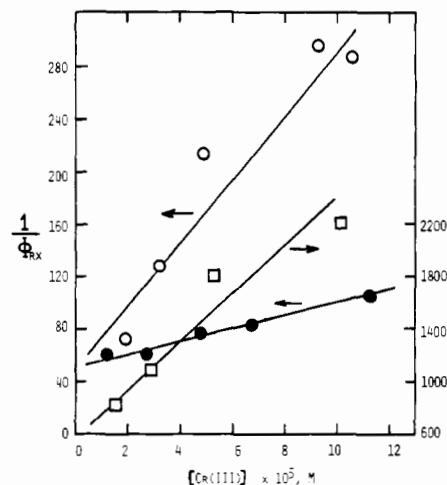


Figure 4. Plot of $1/\Phi_{\text{rx}}$ as a function of [substrate] for $\text{Cr}(\text{NN})_3^{3+}$ in deaerated 1.0 M NaCl solution containing 0.008 M Britton-Robinson buffer at pH 9.5 and 22.0 °C: (O) 5-Ph(phen) in 4% v/v CH₃CN; (●) 5-Br(phen) in 4% v/v CH₃CN; (□) 4,7-Ph₂phen in 40% v/v CH₃OH.

the differences in the nature of the two media. Previously, we accounted for the prolongation of the lifetime of ${}^2\text{T}_1/{}^2\text{E}$ in a highly ionic medium in terms of the interference by the associated anions with the critical vibrations in the ligand that promote the nonradiative process.⁷ However, interaction between Cl⁻ and the complex ion (in both ground and excited states) must be affected by the nature of the cation; it is well-known that the activity coefficient of 1.0 M HCl is larger than that of 1.0 M NaCl. The value of ${}^2k_{\text{nr}}$ seems to reflect the microstructure of the medium around ${}^2\text{T}_1/{}^2\text{E}$. Although one is tempted to ascribe the differences in ${}^2\tau_0$ to differences in the concentrations of quenching impurities present in the two media, it should be noted that the variations in ${}^2\tau_0$ do not fit that pattern in a quantitative manner. Less certain is the case of the two complexes for which the use of 40% v/v CH₃OH is necessary under the photochemical conditions at pH 9.5. There, ${}^2\tau_0$ is substantially lower than in 4% v/v CH₃CN and 1.0 M HCl. Although it has been reported that neither CH₃CN nor CH₃OH quenches ${}^2\text{T}_1/{}^2\text{E}$,^{7,25} it is possible that the presence of redox impurities in the CH₃OH has introduced a ${}^2k_{\text{q}}[\text{Q}]$ term into the expression for 2k_0 . Alternatively, the extreme variation of solution medium in this case alters the microstructure around the ion so that ${}^2k_{\text{nr}}$ is changed. It is clear that further work is necessary on these points.

Table I also shows that, in general, ${}^2k_{\text{g}}$ is greater in 1.0 M NaCl than in 1.0 M HCl. Earlier,⁸ we described ${}^2k_{\text{g}}$ as representing the bimolecular reaction of Cl⁻-associated ground-state ions with Cl⁻-associated ${}^2\text{T}_1/{}^2\text{E}$ excited-state ions. Ionic association results in the reduction of the overall positive charges of the ground- and excited-state complexes and concomitant reduction of the mutual electrostatic repulsion between ${}^2\text{T}_1/{}^2\text{E}$ and ${}^4\text{A}_2$. Due to the differences in the nature of the ionic media related to ionic strength and extent of association, the differences in ${}^2k_{\text{g}}$ of up to a factor of 2 do not seem unreasonable.

Examination of the values of ${}^2k_{\text{g}}$ for the complexes in a fixed solution medium reveals a pattern that is consistent with the view that ground-state quenching is a collisional phenomenon between the Cl⁻-associated ground and excited states. The lowest values of ${}^2k_{\text{g}}$ are exhibited by the unsubstituted ligands; increasing substitution, especially of phenyl groups, increases the value of ${}^2k_{\text{g}}$ by up to almost two orders of magnitude. It appears that substituents increase the size of the reacting

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species, which enhances collisional interaction. The large effect seen for phenyl substitution may be due to favorable orbital overlap in the formation of the Cl⁻-associated transition state.

Ground-state quenching of ${}^2T_1/{}^2E$ results in a diminution in the population of the states and must result in a diminution of the quantum yields of the various processes that arise from ${}^2T_1/{}^2E$. Φ_{rx} , for example, would be expected to decrease with increasing [Cr(III)] in 1.0 M NaCl inasmuch as $\Phi_{rx} = {}^2k_{rx}{}^2\tau$ and ${}^2\tau = 1/({}^2k_0 + {}^2k_g[\text{Cr(III)}])$. It is easily seen that a plot of $1/\Phi_{rx}$ vs. [Cr(III)] is predicted to be linear with a slope of ${}^2k_g/{}^2k_{rx}$ and an intercept of ${}^2k_0/{}^2k_{rx}$; the slope/intercept ratio represents ${}^2k_g/{}^2k_0$. It is also clear that the maximum effect will be seen for those complexes with a combination of large values of 2k_g and low values of ${}^2k_{rx}$. Unfortunately, a low value of ${}^2k_{rx}$ implies a low value of Φ_{rx} rendered even lower by ground-state quenching. The low value of Φ_{rx} becomes more uncertain; the large value of $1/\Phi_{rx}$ has very large error limits.

As a result, although we have determined Φ_{rx} as a function of [Cr(III)] for 11 complexes over a concentration range of greater than an order of magnitude, only three complexes show the effect outside of experimental error. Figure 4 illustrates the data for the 5-Br(phen), 5-Ph(phen), and 4,7-Ph₂phen complexes, which have the largest values of 2k_g . Comparison of the slope/intercept ratios from Figure 4 with the values of 2k_g and ${}^2\tau_0$ from Table I shows agreement of the values within a factor of 3. Considering the errors involved in the data and the extrapolations, such agreement must be considered to be quite good.

Registry No. Cr(bpy)₃³⁺, 15276-15-0; Cr(4,4'-Me₂bpy)₃³⁺, 58220-56-7; Cr(4,4'-Ph₂bpy)₃³⁺, 58220-56-7; Cr(phen)₃³⁺, 15276-16-1; Cr(5-Cl(phen))₃³⁺, 51194-62-8; Cr(5-Br(phen))₃³⁺, 51194-64-0; Cr(5-Me(phen))₃³⁺, 51194-70-8; Cr(5-Ph(phen))₃³⁺, 51194-60-6; Cr(5,6-Me₂phen)₃³⁺, 51261-67-7; Cr(4,7-Me₂phen)₃³⁺, 51194-72-0; Cr(4,7-Ph₂phen)₃³⁺, 69178-81-0; Cr(3,4,7,8-Me₄phen)₃³⁺, 51194-74-2.

Contribution from the Departments of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel, the Nuclear Research Center Negev, Beer-Sheva, Israel, and the University of Rhode Island, Kingston, Rhode Island

Difference in the Stabilities of the Diastereoisomers of the Tervalent Nickel Complex with 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane in Sulfate- and Perchlorate-Containing Aqueous Solutions. An Electrochemical and Pulse Radiolysis Study

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The electrochemical oxidation of two isomers of the complex of divalent nickel with *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in aqueous solutions containing perchlorate and sulfate was studied. These oxidations are less reversible than that of the analogous meso complex. Furthermore the kinetic stabilization of the trivalent meso complex by sulfate, through the formation of NiL(SO₄)₂⁻, is ca. 5000 times larger than that of the racemic complexes. The oxidation of a racemic complex by hydroxyl radicals was studied. The p*K*_H of the axial water bound to the trivalent nickel complex thus formed is 3.7. The stability constant for complexation by the first sulfate is 2200 M⁻¹, i.e., ca. one order of magnitude less than that observed for the corresponding meso complex. The rate-determining step in the anation by sulfate of the trivalent racemic complex is an isomerization of the latter, the rate of which is independent of sulfate concentration. The reasons for the large differences in properties of these diastereoisomers are discussed. The decomposition of several trivalent nickel complexes in alkaline media is first-order in hydroxide ion concentration. Kinetic salt effects on this reaction indicate that at pH 10.0 the trivalent complexes have the formula NiLOH²⁺ for L = the racemic and meso isomers as well as for the corresponding hexamethyl[14]diene ligand and NiL(OH)₂⁺ for L = cyclam. This means that in the latter complex the trivalent nickel is in an octahedral environment whereas in the former ones it is pentacoordinated.

We have recently reported that axial ligation of sulfate and other anions to several trivalent nickel complexes with tetraaza macrocyclic ligands lengthens considerably the lifetime of the trivalent nickel complexes in slightly acidic aqueous solutions.^{2,3} A detailed study indicated that in concentrated sulfate solutions the stabilization is due to the equilibrium reaction



where $k_1 \sim 10^5 \text{ M}^{-2}$ and $5 \times 10^6 \text{ M}^{-2}$ for L = L₁ = 1,4,8,11-tetraazacyclotetradecane and L = L₂ = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively.^{4,5} However, whereas the addition of 0.5 M Na₂SO₄ to NiL₂³⁺ at pH 1.6 lengthens the half-life of the trivalent nickel from ~1.2 min to ≥1 year, the addition of the same sulfate concentration to NiL₁³⁺ increases its lifetime only from ~10 h to ~5 days.⁶ These results indicate that

NiL₂(SO₄)₂⁻ decomposes only via NiL₂(H₂O)₂³⁺ whereas NiL₁(SO₄)₂⁻ decomposes by oxidation of the ligand L₁, without loss of the axial sulfates.^{4,7}

These very different effects of sulfate on the properties of otherwise very similar complexes seemed to indicate that steric factors considerably affect the chemical properties of these trivalent nickel complexes. We decided therefore to study the

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- (7) A small contribution of NiL₂(SO₄)(H₂O)⁺ to the decomposition reaction cannot be ruled out.

[†]Dr. Gregory Ginzburg passed away August 5, 1981.