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Chromium(II)–Polypyridyl Complexes: Formation, Spectra, and Electron-Transfer Kinetics

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Abstract: Flash photolysis techniques have been employed to obtain kinetic data for electron transfer between the couples $Cr(NN)_3^{2+}$–Fe^{3+} (aq) at ~22 °C in N_2-purged 1 M HCl, aqueous solution for NN = bpy, 4,4′-Ph_2bpy, phen, 5-Me(phen), 5-Cl(phen), 5-Br(phen), 5-Ph(phen), and 4,7-Ph_2phen (under conditions of total quenching of the luminescent ^2E state of $Cr(NN)_3^{3+}$ by Fe^{2+} (aq)). Also for NN = 4,4′-Me_2bpy, 5,6-Me_2phen, and 4,7-Me_2phen, pulse radiolysis techniques were used under pseudo-first-order conditions in Fe^{3+}(aq) in Ar-purged solutions (~25 °C, ionic strength 0.15 M, pH ~1) with the Cr(II) transients formed by selective reduction of the $Cr(NN)_3^{3+}$ complexes by the α-2-propanol radical, $(CH_3)_2\dot{C}OH$. The rates are nearly diffusion-controlled 10^8–10^{10} M^{-1} s^{-1}. Application of the Marcus relationships for electron-transfer processes yields $k_{ex} \approx 10^8$–10^9 M^{-1} s^{-1} for both the self-exchange rate in the $Cr(NN)_3^{3+}$–$Cr(NN)_3^{2+}$ couple and for the couple ($^2E/^2T_1$) $Cr(NN)_3^{3+}$–$Cr(NN)_3^{2+}$. The similar k_{ex} value has been interpreted in terms of identical inner-sphere barriers for electron exchange; $^*\Delta G_{in}^{*} = \Delta G_{in}^{*}$. Near-UV and visible absorption spectra of the polypyridylchromium(II) transients, obtained by both flash photolysis (N_2-purged aqueous solutions) and pulse radiolysis (Ar-purged methanolic solutions), are reported and interpreted in terms of simple ligand field theory.

Introduction

Although $Cr(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) has been used for many years as a reducing agent in inorganic electron-transfer reactions, interest in the properties of polypyridyl complexes of chromium(II), $Cr(NN)_3^{2+}$,[2] has increased dramatically recently due to the observation that $Cr(NN)_3^{2+}$ can be generated photochemically from the reductive quenching of the ^2E excited state of $Cr(NN)_3^{3+}$.[3] In particular, recognizing the potential utility of $Cr(NN)_3^{3+}$ complexes in solar energy conversion and storage schemes,[4,5] $Cr(NN)_3^{2+}$ species could serve as potential charge carriers in photogalvanic cells[6] and as mediators with sufficient potential to reduce H_2O. In fact, it has been reported that $Cr(bpy)_3^{2+}$ reduces H_2O to H_2 in acidic media[7,8] and disproportionates to $Cr(bpy)_3^{+}$ and $Cr(bpy)_3^{3+}$ in alkaline solutions.[9]

We have been engaged in a detailed study of the photochemistry and photophysics of the ^2E excited state of $Cr(NN)_3^{3+}$ complexes which is metal-centered and luminescent.[3,10] As part of this systematic approach toward the understanding of the competitive modes of energy partitioning in excited states, we have focused this study on the formation of $Cr(NN)_3^{2+}$ by the reductive quenching of (^2E) $Cr(NN)_3^{3+}$ with Fe^{2+}(aq) and by the direct reduction of $Cr(NN)_3^{3+}$ with radiation-generated free radicals. We report here the absorption spectra of $Cr(NN)_3^{2+}$ transients and the kinetics of electron back-transfer between $Cr(NN)_3^{2+}$ and Fe^{3+}(aq) studied by use of the techniques of flash photolysis and pulse radiolysis.

Experimental Section

Complexes. The following complexes were available from an earlier study: $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$, $[Cr(4,4'\text{-}Ph_2bpy)_3](ClO_4)_3\cdot 2H_2O$, $[Cr(4,4'\text{-}Me_2bpy)_3](ClO_4)_3\cdot H_2O$, $[Cr(phen)_3](ClO_4)_3\cdot 2H_2O$, $[Cr(5\text{-}Cl(phen))_3](ClO_4)_3\cdot 2H_2O$, $[Cr(4,7\text{-}Me_2phen)_3](ClO_4)_3\cdot 2H_2O$, $[Cr(4,7\text{-}Ph_2phen)_3](ClO_4)_3\cdot 4H_2O$, and $[Cr(3,4,7,8\text{-}Me_4phen)_3](ClO_4)_3\cdot 2.5H_2O$. The following ligands were obtained from G.F. Smith and Co. and used as received: 5-methyl-1,10-phenanthroline (5-Me(phen)), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen), 5-phenyl-1,10-phenanthroline (5-Ph(phen)), and 5-bromo-1,10-phenanthroline (5-Br(phen)).

The preparation of new $Cr(NN)_3^{3+}$ complexes was carried out according to procedures established earlier.[3] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$[Cr(5\text{-}Br(phen))_3](ClO_4)_3\cdot 3.5H_2O$: Absorption spectrum in 0.1 M HCl, λ (log ϵ) 213 nm (4.97), 240 (4.85), 275 (4.75), 367 (sh, 3.55), 436 (sh, 2.88), 470 (sh, 2.58). Anal. Calcd C, 36.31; H, 2.37; N, 7.06; Cl, 8.93; Cr, 4.37; Br, 20.13. Found: C, 36.24; H, 2.24; N, 7.03; Cl, 9.13; Cr, 4.55; Br, 19.98.

$[Cr(5\text{-}Me(phen))_3](ClO_4)_3\cdot 2H_2O$: Absorption spectrum in 1 M HCl, λ (log ϵ) 212 nm (5.06), 225 (sh, 5.01), 275 (4.92), 310 (sh, 4.36), 370 (sh, 3.61). 440 (sh, 2.75), 470 (sh, 2.47). Anal. Calcd: C, 48.34; H, 3.54; N, 8.67; Cl, 10.97; Cr, 5.36. Found: C, 48.68; H, 3.52; N, 8.65; Cl, 10.89; Cr, 5.16.

$[Cr(5\text{-}Ph(phen))_3](ClO_4)_3\cdot 2.5H_2O$: Absorption spectrum in 1 M HCl (with ~5% v/v MeOH), λ (log ϵ) 227 nm (5.02), 243 (4.97), 279 (4.87), 370 (sh, 3.76), 470 (sh, 2.71). Anal. Calcd: C, 55.71; H, 3.55; N, 7.22; Cl, 9.13; Cr, 4.46. Found: C, 55.52; H, 3.55; N, 7.36; Cl, 9.31; Cr, 4.19.

$[Cr(5,6\text{-}Me_2phen)_3](ClO_4)_3\cdot 1.5H_2O$: Absorption spectrum in 1 M HCl, λ (log ϵ) 213 nm (4.94), 243 (4.85), 279 (4.77), 320 (sh, 4.21), 380 (sh, 3.53), 470 (sh, 2.58). Anal. Calcd: C, 50.34; H, 3.92; N, 8.31; Cl, 10.52; Cr, 5.19. Found: C, 50.20; H, 3.56; N, 8.24; Cl, 10.80; Cr, 4.99.

Materials. $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (containing 0.005% Fe^{3+}), $NaClO_4$, THF, anhydrous CH_3OH, 95% C_2H_5OH, HCl (0.1 ppm Fe), $HClO_4$ (60%, 0.2 ppm Fe), H_2SO_4, Ar gas (IGT 99.998%), and $Fe(NH_4)(SO_4)_2$ were of reagent quality. Monodistilled water was used or was further purified by distillation from acidic $Cr_2O_7^{2-}$ and alkaline MnO_4^- and fractionation in an all-silica apparatus. For the pulse radiolysis experiments, CH_3OH (Merck or C. Erba) was purified by the method

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(2) The following ligand abbreviations have been used: bpy = 2,2′-bipyridine; 4,4′-Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; 4,4′-Ph_2bpy = 4,4′-diphenyl-2,2′-bipyridine; phen = 1,10-phenanthroline; 5-Cl(phen) = 5-chloro-1,10-phenanthroline; 5-Br(phen) = 5-bromo-1,10-phenanthroline; 5-Me(phen) = 5-methyl-1,10-phenanthroline; 5-Ph(phen) = 5-phenyl-1,10-phenanthroline; 5,6-Me_2phen = 5,6-dimethyl-1,10-phenanthroline; 4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline; and 4,7-Ph_2phen = 4,7-diphenyl-1,10-phenanthroline.

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of Baxendale and Wardman;[11] 2-propanol (Baker Instra Analyzed) was used as received. Nitrous oxide (IGT 99.98%) was passed through NaOH pellets just prior to use.

Apparatus. Absorption spectra of the Cr(III) 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. Flash photolysis experiments were performed by using an apparatus previously described.[12] Emission lifetimes were determined by using a 1 kW N_2 laser (4-ns pulses at 337 nm); the luminescence decay curves were photographed from a Tektronix 7633 oscilloscope and were exponential in all cases (correlation coefficient >99.9%). Pulse radiolyses with optical absorption detection were performed by using the apparatus at the FRAE-CNR Laboratory in Bologna (Italy).[13] Radiation doses of 0.5–2 krad were used in the determination of transient absorption spectra and 0.1–0.5 krad was employed in the study of electron-transfer kinetics.

Procedures. Unless otherwise specified, photochemical experiments were carried out in 1 M HCl aqueous solution at 22–23 °C; radiation chemical experiments were performed at ~25 °C. Solutions were deoxygenated by purging with N_2 or Ar and saturating with N_2O (2.5×10^{-2} M, H_2O, 25 °C, 1 atm)[14] when required. Solutions of limited solubility in water were dissolved in a small amount of CH_3OH (~1%) followed by addition of 1 M HCl or were examined in methanolic solution.

Steady-state luminescence and quenching experiments were carried out with right-angle illumination on 10^{-5}–10^{-6} M solutions of the newly prepared complexes. The excitation wavelength was chosen such that the absorbance of the solution in 1-cm cells was <0.8. In the luminescence quenching experiments with $Fe^{2+}(aq)$ the solutions were air-equilibrated; stock solutions of $Fe^{2+}(aq)$ were prepared immediately prior to use. Where appropriate, the ratio I_0/I was corrected for absorption of light by $Fe^{2+}(aq)$. In the flash photolysis experiments, the xenon flash ($1/e$ decay time = 30 μs) was filtered through acetone ($\lambda > 330$ nm) contained in the outer jacket of a quartz cell (22-cm path length). The analyzing light was filtered through a monochromator (400–700-nm range). The N_2-purged solutions were replaced after every second flash; no changes in the solution absorption spectra were detected as a result of the flash under the experimental conditions used. For the determination of the $Cr(NN)_3^{2+}$ transient spectra, the appropriate solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ for >99% quenching of the (^2E) $Cr(NN)_3^{3+}$ was freshly prepared and added to the $Cr(NN)_3^{3+}$ solution, and the mixture was immediately deoxygenated to prevent any air oxidation of $Fe^{2+}(aq)$.

In the pulse radiolysis experiments, the samples were protected from the photolytic effects of the analyzing light by using an appropriate UV cutoff filter ($\lambda > 400$ nm). In every case, the thermal stability of the $Cr(NN)_3^{3+}$ solution was verified over the period of the experiments. The rates of electron transfer between $Cr(NN)_3^{2+}$ and $Fe^{3+}(aq)$, where NN = 5,6-Me_2phen, 4,7-Me_2phen, and 4,4′-Me_2bpy, were determined under pseudo-first-order conditions with $Fe^{3+}(aq)$ in excess; when $[Cr(NN)_3^{2+}]$ = 1–3 μM (radiation doses of 0.16–0.45 krad), $[Fe^{3+}(aq)]$ = 35–70 μM. The rates were independent of the dose. The disappearance of the absorbance due to $Cr(NN)_3^{2+}$ was monitored at 420 nm with the ionic strength held constant at 0.15 M. The spectra of $Cr(NN)_3^{2+}$ were obtained from the reduction of $Cr(NN)_3^{3+}$ by the α-$(CH_3)_2\dot{C}OH$ radical at pH ~1; $[Cr(NN)_3^{3+}]$ = 40–60 μM containing 0.05 M H_2SO_4 and 0.52 M 2-propanol.

Generation of Reducing Radicals. The radiolysis of aqueous solutions results in the decomposition of the solvent and the generation of the primary radicals according to the following stoichiometry: $H_2O \rightsquigarrow e_{aq}^-$ (2.7), OH (2.7), H (0.55) (where the numbers in parentheses represent the number of species formed per 100 eV of energy absorbed by the solution (G value)). In acidic solution, e_{aq}^- is efficiently scavenged by H^+, yielding H atoms (3.65). In the presence of 2-propanol, H and OH react to form α- and β-$(CH_3)_2\dot{C}OH$ radicals; the α radical is a rather good reducing agent ($E_{1/2}°(NHE) \approx -1.2$ V).[15] The concentration of $(CH_3)_2\dot{C}OH$ generated in the pulse was obtained from the expression $[(CH_3)_2\dot{C}OH] = DfG\rho$ where D = dose in krad, $f = 1.036 \times 10^{-6}$ for H_2O (and methanolic) solutions irradiated by an electron beam, G = G value for the radical (5.5), and ρ = density of the solution. In CH_3OH solutions, G = 2 for e_{solv}^- and ρ = 0.79 g/cm^3.

Table I. Photophysical Data of New $Cr(NN)_3^{3+}$ Complexes in 1 M HCl Solutions

NN	τ_0,^{a} μs	$^2E \times 10^{-3}$ cm^{-1}	$^2T_1 \times 10^{-3}$ cm^{-1}
5-Br(phen)	68	13.74	14.3
5-Ph(phen)	55	13.70	14.3
5-Me(phen)	59	13.70	14.3
5,6-Me_2phen	40	13.66	14.3

^{a} $[Cr(NN)_3^{3+}] \approx 10^{-5}$ M; air-equilibrated solutions; 22 °C.

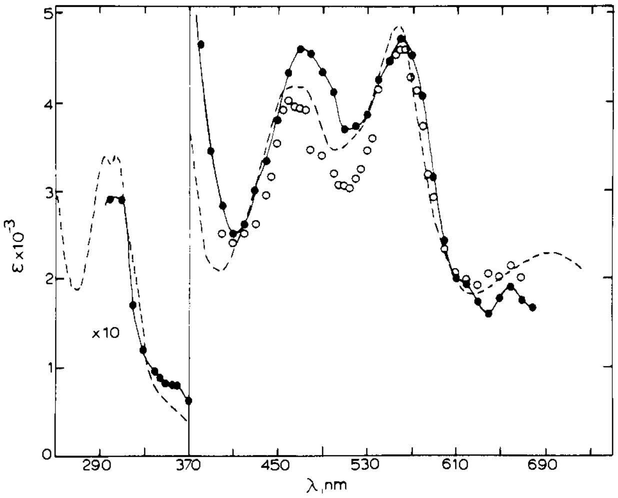

Figure 1. Absorption spectra of $Cr(bpy)_3^{2+}$ (ref 29) (dashed line, ○ (this work)) and of the $Cr(4,4'\text{-}Me_2bpy)_3^{2+}$ (●) transient obtained by reduction of the corresponding Cr(III) complex (53 μM) with $(CH_3)_2\dot{C}OH$ at pH ~1 in Ar-purged aqueous solutions containing 0.26 M 2-propanol and 0.05 M H_2SO_4 (dose/pulse = 1.30 krad; $G(Cr^{II})$ = 5.5).

Results

Table I summarizes the photophysical data for the newly synthesized $Cr(NN)_3^{3+}$: lifetime of ^2E state in air-saturated solution at 22 °C and the energies of the luminescent ^2E and $^2T_1$ states. Comparison of these values with those published for the other complexes shows the close similarity in the behavior and energetics of the lower doublet excited states. The rate constants for the quenching of the ^2E luminescence, k_q, by Fe^{2+} of the new complexes is reported in Table II together with those values for the other complexes.[3] The values of k_q were obtained from linear Stern–Volmer plots of $I_0/I = 1 + k_{SV}[Fe^{2+}(aq)] = 1 + k_q\tau_{air}[Fe^{2+}(aq)]$, where τ_{air} is the lifetime of ^2E in air-saturated 1 M HCl aqueous solution. Also shown in Table II are the kinetics of the reduction of $Cr(NN)_3^{3+}$ by e_{aq}^- and by α-$(CH_3)_2\dot{C}OH$ and the wavelength at which formation of $Cr(NN)_3^{2+}$ was monitored. The 3,4,7,8-Me_4phen complex was too insoluble in aqueous and methanolic solutions to afford the spectrum of the Cr(II) species and the kinetics of its oxidation by $Fe^{3+}(aq)$. In Table II are also summarized the rate constants for the reaction of $Cr(NN)_3^{2+}$ and $Fe^{3+}(aq)$. In the flash photolysis experiments, where $Cr(NN)_3^{2+}$ is generated by the reductive quenching of (^2E) $Cr(NN)_3^{3+}$ by $Fe^{2+}(aq)$, the decay of $Cr(NN)_3^{2+}$ is via second-order kinetics. From knowledge of the absorption spectra of the $Cr(NN)_3^{2+}$ species (see below), the second-order rate constant was obtained. For the cases where NN = 4,4′-Me_2bpy, 5,6-Me_2phen, and 4,7-Me_2phen, the rate constants were also obtained by pulse radiolysis through the selective reduction of Cr(III) in the presence of excess $Fe^{3+}(aq)$ followed by pseudo-first-order decay of $Cr(NN)_3^{2+}$.

Figures 1 through 10 illustrate the absorption spectra (300–750 nm) of the $Cr(NN)_3^{2+}$ complexes obtained from either the reduction of $Cr(NN)_3^{3+}$ by e_{solv}^- or α-$(CH_3)_2\dot{C}OH$ or the quenching of (^2E) $Cr(NN)_3^{3+}$ by $Fe^{2+}(aq)$. Values of ε were obtained from the pulse radiolysis experiments where the concentration of Cr-

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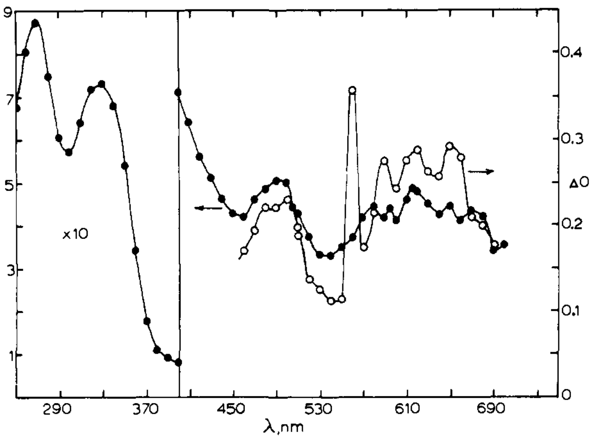

Figure 2. Absorption spectra of the $Cr(4,4'\text{-}Ph_2bpy)_3{}^{2+}$ transient: (○) by flash photolysis methods in N_2-purged 1 M HCl aqueous solutions containing 5% v/v MeOH (see experimental section); (●) by pulse radiolysis methods in which the Cr(III) species (45 μM) were reduced by e_{solv}^- at natural pH in Ar-purged methanolic solutions (dose/pulse = 1.47 krad; $G(Cr^{II})$ = 1.5).

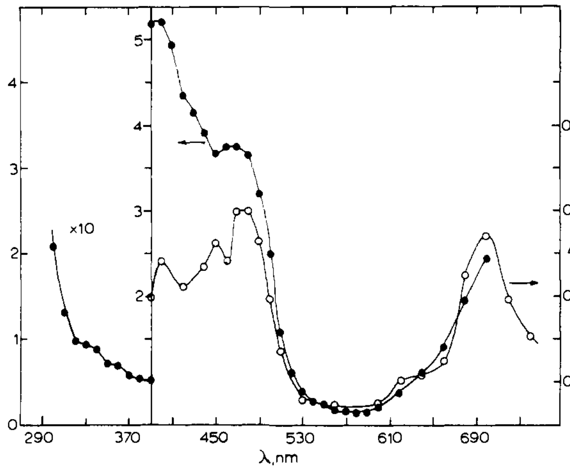

Figure 3. Absorption spectra of $Cr(phen)_3{}^{2+}$: (○) by flash photolysis in N_2-purged 1 M HCl aqueous solutions (see Experimental Section); (●) by pulse radiolysis methods by reduction of the Cr(III) species (52 μM) with $(CH_3)_2\dot{C}OH$ at pH ~2 in Ar-purged aqueous solutions containing 0.26 M 2-propanol and 0.01 M $HClO_4$ (dose/pulse = 1.27 krad; $G(Cr^{II})$ = 4.6).

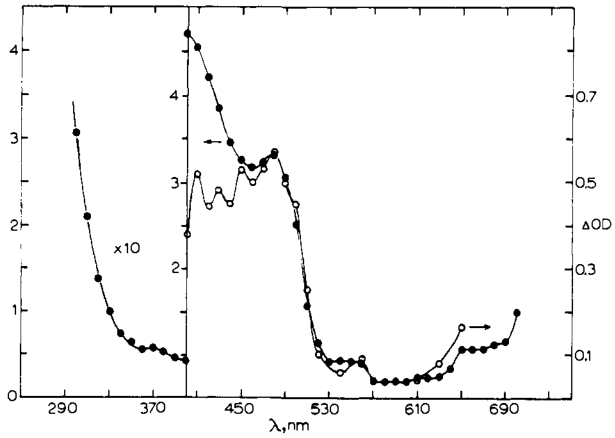

Figure 4. Absorption spectra of the $Cr(5\text{-}Cl(phen)_3{}^{2+}$ ion: (○) by flash photolysis in N_2-purged 1 M HCl aqueous solutions (see Experimental Section); (●) by pulse radiolysis by reduction of Cr(III) species (50 μM) with $(CH_3)_2\dot{C}OH$ at pH ~1 in Ar-purged aqueous solutions containing 0.9 M 2-propanol and 0.1 M $HClO_4$ (dose/pulse = 1.8 krad; $G(Cr^{II})$ = 4.8).

$(NN)_3{}^{2+}$ was established from the quantitative scavenging of the reducing radical. In the case of the 5-Ph(phen) complex, we report

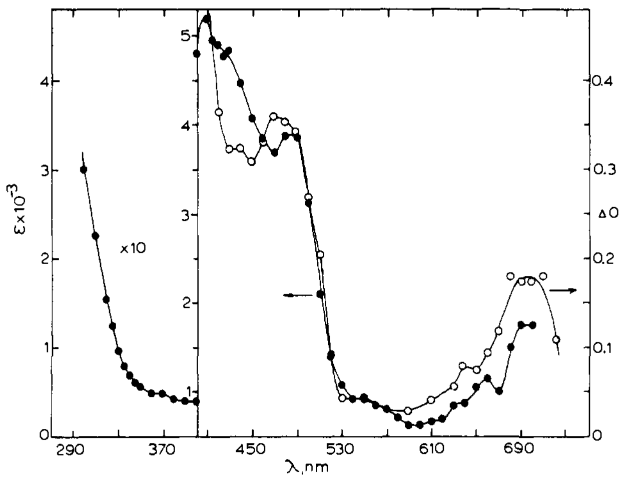

Figure 5. Absorption spectra of $Cr(5\text{-}Br(phen))_3{}^{2+}$ ions: (○) by flash photolysis in N_2-purged aqueous 1 M HCl solutions (see Experimental Section); (●) by pulse radiolysis by reduction of Cr(III) species (39 μM) with $(CH_3)_2\dot{C}OH$ at pH ~1 in Ar-purged aqueous solutions containing 0.52 M 2-propanol and 0.05 M H_2SO_4 (dose/pulse = 0.54 krad; $G(Cr^{II})$ = 5.1).

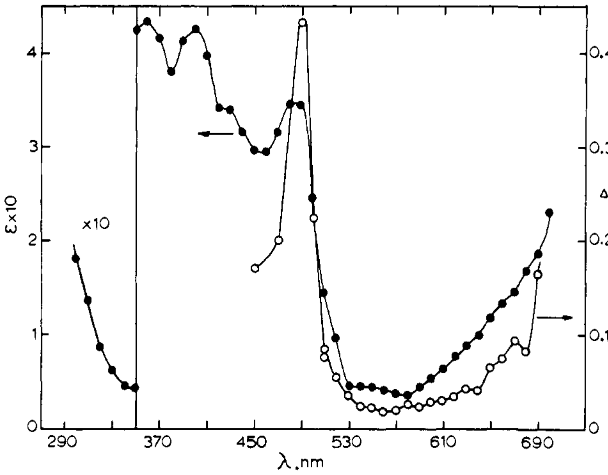

Figure 6. Absorption spectra of $Cr(5\text{-}Me(phen))_3{}^{2+}$: (○) by flash photolysis techniques in N_2-purged aqueous 1 M HCl solutions (see Experimental Section); (●) by pulse radiolysis techniques by reduction of Cr(III) species (52 μM) with $(CH_3)_2\dot{C}OH$ at pH ~1 in Ar-purged aqueous solutions containing 0.26 M 2-propanol and 0.05 M H_2SO_4 (dose/pulse = 0.57 krad; $G(Cr^{II})$ = 5.2).

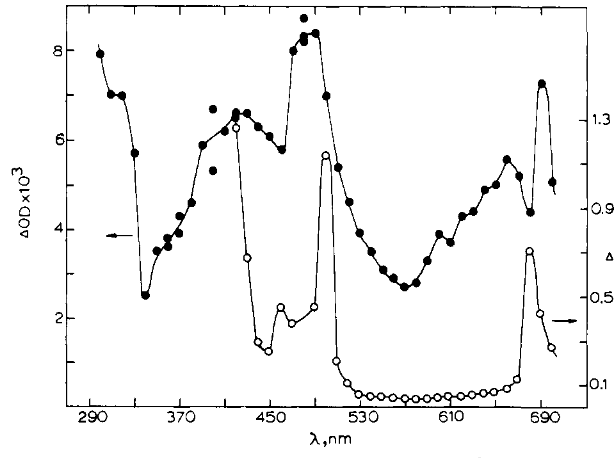

Figure 7. Absorption spectra of the $Cr(5\text{-}Ph(phen))_3{}^{2+}$ species: (○) by flash photolysis in N_2-purged 1 M HCl aqueous solutions containing 1% v/v MeOH (see Experimental Section); (●) by pulse radiolysis methods by reduction of the Cr(III) species (49 μM) with e_{solv}^- in Ar-purged methanolic solutions at natural pH (dose/pulse = 1.20 krad; $G(Cr^{II}) \approx$ 2).

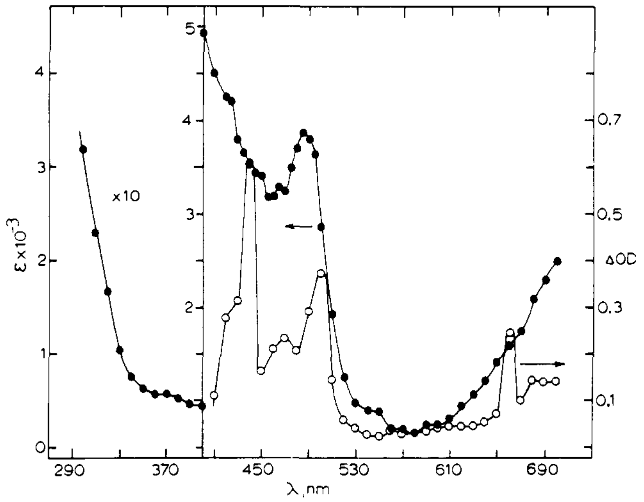

Figure 8. Absorption spectra of the $Cr(5,6\text{-}Me_2phen)_3^{2+}$ ion: (○) by flash photolysis in N_2-purged aqueous 1 M HCl solutions (see Experimental Section); (●) by pulse radiolysis methods by reduction of Cr(III) species (53 μM) with $(CH_3)_2\dot{C}OH$ at pH ~1 in Ar-purged aqueous solutions containing 0.26 M 2-propanol and 0.05 M H_2SO_4 (dose/pulse = 1.37 krad; $G(Cr^{II}) = 4.9$).

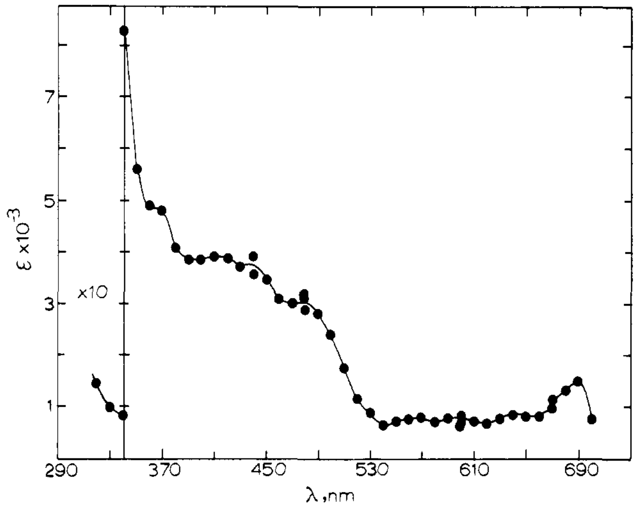

Figure 9. Absorption spectrum of $Cr(4,7\text{-}Me_2phen)_3^{2+}$ species obtained by pulse radiolysis techniques by reduction of the corresponding Cr(III) species (54 μM) with e_{solv}^- in Ar-purged methanolic solutions at natural pH (dose/pulse = 1.67 krad; $G(Cr^{II}) = 1.8$).

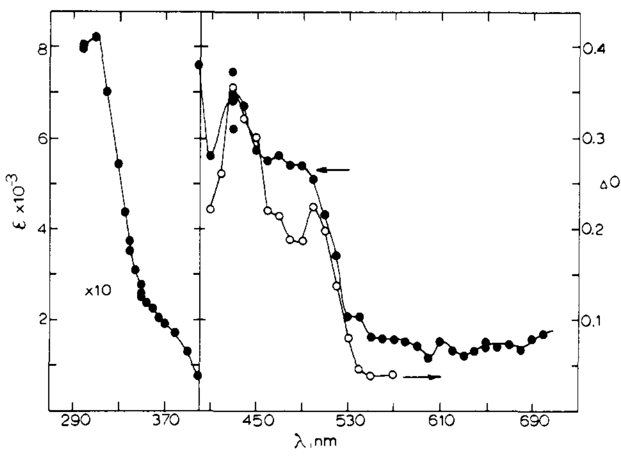

Figure 10. Absorption spectra of the $Cr(4,7\text{-}Ph_2phen)_3^{2+}$ transient: (○) by flash photolysis in N_2-purged 1 M HCl aqueous solutions containing 5% v/v MeOH (see Experimental Section); (●) by pulse radiolysis methods by reduction of the Cr(III) species (48 μM) with e_{solv}^- in Ar-purged methanolic solutions at natural pH (dose/pulse = 1.67 krad; $G(Cr^{II}) = 1.9$).

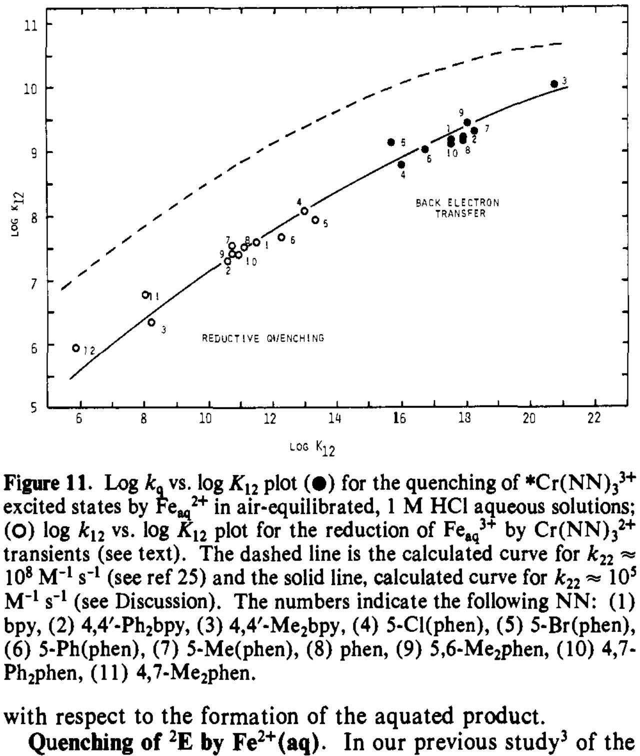

Figure 11. Log k_q vs. log K_{12} plot (●) for the quenching of $^*Cr(NN)_3^{3+}$ excited states by Fe_{aq}^{2+} in air-equilibrated, 1 M HCl aqueous solutions; (○) log k_{12} vs. log K_{12} plot for the reduction of Fe_{aq}^{3+} by $Cr(NN)_3^{2+}$ transients (see text). The dashed line is the calculated curve for $k_{22} \approx 10^8\ M^{-1}\ s^{-1}$ (see ref 25) and the solid line, calculated curve for $k_{22} \approx 10^5\ M^{-1}\ s^{-1}$ (see Discussion). The numbers indicate the following NN: (1) bpy, (2) 4,4'-Ph_2bpy, (3) 4,4'-Me_2bpy, (4) 5-Cl(phen), (5) 5-Br(phen), (6) 5-Ph(phen), (7) 5-Me(phen), (8) phen, (9) 5,6-Me_2phen, (10) 4,7-Ph_2phen, (11) 4,7-Me_2phen.

only ΔOD vs. λ; the spectrum was taken 1 μs after the pulse corresponding to ~90% formation of $Cr(NN)_3^{2+}$. After this time, however, an additional reaction was observed, perhaps involving radical attack on the ligand, which yields products absorbing in the same spectral region. Thus, for the 5-Ph(phen) complex, the calculation of ε values carries some uncertainty. In Table III we have summarized the spectral characteristics of the $Cr(NN)_3^{2+}$ complexes.

Discussion

Excitation of ground-state ($^4A_2$) $Cr(NN)_3^{3+}$ into the spin-allowed quartet manifold forms ($^4T_2$) $Cr(NN)_3^{3+}$ which, upon intersystem crossing, produces (^2E) $Cr(NN)_3^{3+}$. This long-lived, metal-centered, luminescent state can be quenched by Fe^{2+}(aq) in competition with its radiative, nonradiative, reactive, and ground-state quenching modes of decay. At low [substrate] (10^{-5}–10^{-6} M), ground-state quenching is negligible; in 1 M HCl, the complexes are thermally[16,17] and photochemically[18,20] stable with respect to the formation of the aquated product.

Quenching of ^2E by Fe^{2+}(aq). In our previous study[3] of the excited-state behavior of $Cr(NN)_3^{3+}$ complexes, we concluded that the quenching of (^2E) $Cr(NN)_3^{3+}$ by Fe^{2+}(aq) is via electron-transfer reaction 1; excluded were oxidative quenching by Fe^{2+}(aq)

$$(^2E)\ Cr(NN)_3^{3+} + Fe^{2+}(aq) \rightarrow Cr(NN)_3^{2+} + Fe^{3+}(aq) \qquad (1)$$

or electronic energy transfer.[3,21] The observation of the formation of the spectra of $Cr(NN)_3^{2+}$ and the dependence of k_q on the value of $^*E°[(^2E)\ Cr(NN)_3^{3+}/Cr(NN)_3^{2+}1]$ affords evidence for reductive electron transfer.

The Marcus relationships for electron transfer[22] are usually formulated[23] as $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$ and $\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2)$ where k_{11} and k_{22} refer to the rate constants of

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Table II. Kinetics of Electron-Transfer Processes in Chromium–Polypyridyl Complexes in 1 M HCl Aqueous Solutions (~22–24 °C)

complexes	$10^{-7}k_q$,[a] $M^{-1}\ s^{-1}$ ${}^2E + Fe^{2+}(aq)$	$^*E°$, V (${}^2E$) Cr(III)/Cr(II)	$10^{-9}k$, $M^{-1}\ s^{-1}$ reducing agent + Cr(III)	$10^{-9}k$, $M^{-1}\ s^{-1}$ Cr(II) + Fe^{3+}	$E°$, V Cr(III)/Cr(II)
$Cr(bpy)_3{}^{3+}$	3.7^b $(1.6)^c$	1.44^b		1.44 ± 0.04	-0.26^b
$Cr(4,4'\text{-}Ph_2bpy)_3{}^{3+}$	2.0^b	$(1.39)^e$	e_{solv}^-; 100 (600 nm)^f	1.6 ± 0.2	$(-0.28)^e$
$Cr(4,4'\text{-}Me_2bpy)_3{}^{3+}$	0.22^b $(0.082)^c$	1.25^b	$(CH_3)_2\dot{C}OH$; 2 (480 nm)	10.6 ± 0.6	-0.45^b
				0.70 ± 0.02^i	
$Cr(5\text{-}Cl(phen))_3{}^{3+}$	12^b $(4.8)^c$	1.53^b	$(CH_3)_2\dot{C}OH$; 2.8 (400 nm)	0.61 ± 0.08	-0.17^b
$Cr(5\text{-}Br(phen))_3{}^{3+}$	8.4	1.55	$(CH_3)_2\dot{C}OH$; 3.8 (420 nm)	1.4 ± 0.4	-0.15^g
$Cr(5\text{-}Ph(phen))_3{}^{3+}$	4.5	1.49	e_{solv}^-; 50–80	$(1.9 \pm 0.6)^j$	-0.21^k
$Cr(5\text{-}Me(phen))_3{}^{3+}$	3.4^d $(1.0)^c$	1.40	$(CH_3)_2\dot{C}OH$; 3.1 (400 nm)	2.0 ± 0.7	-0.30^g
$Cr(phen)_3{}^{3+}$	3.2^b $(1.5)^c$	1.42^b	$(CH_3)_2\dot{C}OH$; 4.1 (480 nm)	1.3 ± 0.3	-0.28^b
$Cr(5,6\text{-}Me_2phen)_3{}^{3+}$	2.6	1.40	$(CH_3)_2\dot{C}OH$; 3.6 (420 nm)	2.7 ± 1.0	-0.29^k
				0.48 ± 0.03^i	
$Cr(4,7\text{-}Ph_2phen)_3{}^{3+}$	2.5^b	(1.41)	e_{solv}^-; 82 (575 nm)	1.4 ± 0.4	$(-0.26)^e$
$Cr(4,7\text{-}Me_2phen)_3{}^{3+}$	0.60^b $(0.089)^c$	1.24^b	e_{solv}^-; 81 (575 nm)	$(7)^l$	-0.45^b
				0.71 ± 0.09^i	
$Cr(3,4,7,8\text{-}Me_4phen)_3{}^{3+}$	0.092^b	$(1.11)^e$	h	$(18)^{l,m}$	$(-0.57)^e$

[a] Phosphorescence quenching; air-saturated solutions; $[Cr(NN)_3{}^{3+}] \approx 10^{-5}$ M. [b] Reference 3. [c] In 1 M H_2SO_4.[21] [d] In 1 M H_2SO_4, $k_q = 1 \times 10^7\ M^{-1}\ s^{-1}$.[21] [e] Calculated by interpolation from log k_{12} obtained from the log k_q vs. log K_{12} plot of Figure 11. See also footnote 63 in ref 3. [f] Wavelength at which kinetics were monitored. [g] Reference 21. [h] This complex was too insoluble in solvents used for pulse radiolysis. [i] pH ~1; ionic strength 0.15; in Ar-purged solutions containing 0.05 M H_2SO_4 and 0.52 M 2-propanol. [j] This value may be uncertain due to uncertainties in the ϵ values of $Cr(5\text{-}Ph(phen))_3{}^{2+}$ (see text). [k] Vs. NHE; calculated taking $E°$ of $Cr(phen)_3{}^{3+}/Cr(phen)_3{}^{2+}$ as −0.28 (ref 21) and using ΔE^f values for the appropriate Cr(III)/Cr(II) couples (see Table IV of M. C. Hughes and D. J. Macero, *Inorg. Chem.*, **13**, 2739 (1974)). [l] Calculated by interpolation from the plot of log k vs. log K_{12} and included the complexes for which $E°$'s were calculated as noted in footnote *e*. [m] The concentration of Fe^{3+} in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was too high to permit the observation of the Cr(II) transient and therefore to measure the rate of the electron-transfer process (see text).

the $Fe^{2+}(aq)$–$Fe^{3+}(aq)$ and (${}^2E$) $Cr(NN)_3{}^{3+}$–$Cr(NN)_3{}^{2+}$ self-exchange reactions, respectively, k_{12} is the rate constant for the cross-reaction (k_q of reaction 1), and Z is the collision number (generally taken as $10^{11}\ M^{-1}\ s^{-1}$). The value of the rate constant (k_{22}) of reaction 2 can be evaluated from k_{11} ($4.0\ M^{-1}\ s^{-1}$)[24] and

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

the plot in Figure 11 (open circles). Using the relationship log $k_{12} = 0.50 \log k_{11}k_{22} + 0.50(1 + \alpha)\log K_{12}$, where $\alpha = (\log K_{12})/4 \log (k_{11}k_{22}/Z^2)$, we obtain an apparent $k_{22} \approx 10^5\ M^{-1}\ s^{-1}$.[25] Recently, Sutin and Creutz[26] have demonstrated that although reactions of poly(pyridine)metal complexes with $Fe^{2+}(aq)$ give a free-energy plot having the proper slope, the intercept at $K_{12} = 1$ is less than expected by several orders of magnitude. Endicott and Ferraudi[27] have also estimated k_{22} to be $3 \times 10^5\ M^{-1}\ s^{-1}$. In a related study, Brunschwig and Sutin[21] estimated k_{22} as $\sim 1 \times 10^8\ M^{-1}\ s^{-1}$ in 1 M H_2SO_4 at 25 °C. Experimentally, however, the intercept of the line from which the exchange rate was evaluated was 1.7 from which $k_{ex} \approx 600\ M^{-1}\ s^{-1}$ is calculated. The 6 orders of magnitude discrepancy between the experimental and theoretically estimated values was explained in terms of the nonadiabaticity of the cross-reaction (1) while the self-exchange reactions are probably adiabatic. The Marcus relationship was modified[21] to include a term for the probability of electron transfer in the activated complex;[28] $k_{12} = p_{12}(k_{11}k_{22}K_{12}f_{12}/p_{11}p_{22})^{1/2}$, where p are the respective probabilities of electron transfer in the activated complexes. Clearly, this expression reduces to the usual Marcus equation when $p_{12} = p_{11} = p_{22} = 1$, that is, when the self-exchange reactions and the cross-reaction are adiabatic. From above, $p_{11} = p_{22} = 1$ but $p_{12} \ll 1$ such that a plot of log k_{12} vs. log K_{12} yields an intercept from which $k_{22}p_{12}{}^2$ rather than k_{22} is evaluated. Inasmuch as $p_{12} \ll 1$, the actual self-exchange rate k_{22} for reaction 2 is $>10^5\ M^{-1}\ s^{-1}$, probably $\sim 10^8$–$10^9\ M^{-1}\ s^{-1}$.[21]

Chromium(II) Spectra. The reaction of e_{solv}^- and $(CH_3)_2\dot{C}OH$ with $Cr(NN)_3{}^{3+}$ yields $Cr(NN)_3{}^{2+}$ rapidly according to reaction 3 and 4; the values of the rate constants are given in Table II.

$$Cr(NN)_3{}^{3+} + e_{solv}^- \rightarrow Cr(NN)_3{}^{2+} \qquad (3)$$

$$Cr(NN)_3{}^{3+} + (CH_3)_2\dot{C}OH \rightarrow Cr(NN)_3{}^{2+} + (CH_3)_2CO + H^+ \qquad (4)$$

From the fact that e_{solv}^- and $(CH_3)_2\dot{C}OH$ are scavenged quantitatively and rapidly, the ϵ values of the absorption bands of $Cr(NN)_3{}^{2+}$ are obtained as a function of λ. In the flash photolysis experiments, spectra are recorded approximately 50 μs after the flash upon complete quenching of (${}^2E$) $Cr(NN)_3{}^{3+}$ by $Fe^{2+}(aq)$. Comparison of the spectra in Figures 1 through 10 obtained by the two methods shows reasonable coincidence. Absorption band maxima and ϵ values are summarized in Table III.

(a) bpy Complexes. The absorption spectrum of $Cr(bpy)_3{}^{2+}$ has been reported by König and Herzog[29] as part of their extensive study of the spectra of $Cr(bpy)_3{}^z$ complexes (z = 3+, 2+, 1+, 0); their spectrum of $Cr(bpy)_3{}^{2+}$ is reproduced in Figure 1 and is compared with that obtained in this study. At $\lambda > 310$ nm, the bands are assigned as arising from ligand-to-metal charge-transfer transitions on the basis of intensity, while at $\lambda < 310$ nm the spectrum arises from intraligand transitions.[29] Interestingly, despite the band intensities (log $\epsilon \approx 3$–4), the band maxima at 310–830 nm could be reasonably accounted for in terms of simple ligand field theory by using octahedral microsymmetry yielding $\Delta = 17\,370\ cm^{-1}$ and B (Racah parameter) $= 604\ cm^{-1}$. Alternatively, the spectrum has also been described in terms of absorption to excited states possessing a configuration admixture of metal-to-ligand charge-transfer character, coupled with π–π^* excited states of the three bidentate NN ligands.[30]

The spectrum of the 4,4′-Me_2bpy complex is nearly identical with that of the bpy complex with the prominent band at 470 nm slightly red-shifted by ~10 nm upon methyl substitution; the intraligand π–π^* transition in the 4,4′-Me_2bpy complex occurs at 300 nm. Complexation of the 4,4′-Ph_2bpy ligand with Cr(II) red-shifts the internal ligand transitions by ~15-20 nm, nearly the same as the shift observed in the spectrum of $Cr(4,4'\text{-}Ph_2bpy)_3{}^{3+}$.[3] The visible spectrum of the diphenyl-substituted

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(25) We had earlier[3] reported $k_{22} \approx 10^7\ M^{-1}\ s^{-1}$ obtained by a linear extrapolation to $K_{12} = 1$ from a log k_{12} vs. log K_{12} plot (cf. Figure 11). However, this procedure cannot be correct since the relationship contains the variable α and since the extrapolation may involve a nonlinear region of the Marcus plot. For example, a linear extrapolation of the data of Figure 11 to $K_{12} = 1$ yields $k_{22} \approx 10^8\ M^{-1}\ s^{-1}$. Substitution of this k_{22} value into the log k_{12} vs. log K_{12} relationship gives the curved plot in Figure 11 (dashed line). Clearly $10^8\ M^{-1}\ s^{-1}$ gives a very poor fit of the experimental data, which can be fitted using $k_{22} \approx 10^5\ M^{-1}\ s^{-1}$ (see discussion).

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Table III. Absorption Spectra of $Cr(NN)_3^{2+}$ Transients

complex ion	λ, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	tentative assignts[b]
$Cr(bpy)_3^{2+}$ [a]	287	25.0	NN → NN*
	308	30.5	NN → NN*
	326	7.2	$t_2^4 \rightarrow t_2^2e^2$ (?)
	339	5.2	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	360	4.7	$\rightarrow {}^3T_1$(b) + CT
	463	4.2	$\rightarrow {}^3E$(b) + CT
	(465)[c]	(3.9)[c]	
	(490)[c]	(3.4)[c]	$\rightarrow {}^3A_1$ + CT
	562	4.9	$\rightarrow {}^3A_2$ + CT
		(4.6)[c]	
	690	2.3	$\rightarrow {}^3T_1$(a) + $^3T_2$(a) + CT
	830	1.7	$\rightarrow {}^3E$(a) + CT
$Cr(4,4'\text{-}Me_2bpy)_3^{2+}$ [d]	305	29.0	NN → NN*
	360	8.0	$^3T_1 \rightarrow {}^3T_1$(b) + $^3T_2$(b) + CT
	470	4.6	$\rightarrow {}^3E$(b) + CT
	495	4.2	$\rightarrow {}^3A_1$ + CT
	560	4.5	$\rightarrow {}^3A_2$ + CT
	620	2.0	$\rightarrow {}^3T_2$(a) + CT
	660	1.8	$\rightarrow {}^3T_1$(a) + CT
$Cr(4,4'\text{-}Ph_2bpy)_3^{2+}$ [e]	270	87.5	NN → NN*
	330	73.1	NN → NN*
	410	6.4	$^3T_1 \rightarrow {}^3T_1$(b) + $^3T_2$(b) + CT (?)
	470	4.6	
	485	4.9	$\rightarrow {}^3E$(b) + CT
	515	4.0	$\rightarrow {}^3A_1$ + CT
	575	4.4	$\rightarrow {}^3A_2$ + CT
	595	4.4	
	620	4.8	
	650	4.5	$\rightarrow {}^3T_2$(a) + CT
	670	4.4	$\rightarrow {}^3T_1$(a) + CT
$Cr(phen)_3^{2+}$ [f]	335	8.9	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	(330)[g]		
	360	6.7	$\rightarrow {}^3T_1$(b) + CT
	400	4.6	
	(415)[g]		
	430	3.6	
	470	3.2	$\rightarrow {}^3E$(b) + CT
	(475)[g]		
	550	0.73	$\rightarrow {}^3A_1$
	(550)[g]		
	620	0.88	$\rightarrow {}^3A_2$
	700	2.5	$\rightarrow {}^3T_1$(a) + $^3T_2$(a) + CT
$Cr(5\text{-}Cl(phen))_3^{2+}$ [h]	370	5.8	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	410	4.5	$\rightarrow {}^3T_1$(b) + CT
	480	3.3	$\rightarrow {}^3E$(b) + CT
	550	0.95	
	610	0.74	$\rightarrow {}^3A_1$
	650	1.1	$\rightarrow {}^3A_2$ + CT
	680	1.1	$\rightarrow {}^3T_2$(a) + CT
$Cr(5\text{-}Br(phen))_3^{2+}$ [i]	370	4.9	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	410	5.2	$\rightarrow {}^3T_1$(b) + CT
	430	4.8	
	485	3.9	$\rightarrow {}^3E$(b) + CT
	560	0.85	
	610	0.66	$\rightarrow {}^3A_1$
	630	0.83	
	660	1.1	$\rightarrow {}^3A_2$ + CT
	695	1.7	$\rightarrow {}^3T_2$(a) + CT
$Cr(5\text{-}Me(phen))_3^{2+}$ [j]	360	4.3	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	400	4.2	$\rightarrow {}^3T_1$(b) + CT
	430	3.4	
	485	3.5	$\rightarrow {}^3E$(b) + CT
	550	0.45	
	630	0.89	$\rightarrow {}^3A_1$
	660	1.3	$\rightarrow {}^3A_2$ + CT
	680	1.8	$\rightarrow {}^3T_2$(a) + CT
$Cr(5\text{-}Ph(phen))_3^{2+}$ [e]	~360	(6.4)[k]	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	~390	(4.4)	$\rightarrow {}^3T_1$(b) + CT
	~430	(2.7)	
	~480	(2.6)	$\rightarrow {}^3E$(b) + CT
	~600	(0.99)	
	~620	(1.1)	$\rightarrow {}^3A_1$ + CT
	~640	(1.2)	
	~660	(1.4)	$\rightarrow {}^3A_2$ + CT
	~690	(1.8)	$\rightarrow {}^3T_2$(a) + CT
$Cr(5,6\text{-}Me_2phen)_3^{2+}$ [j]	370	5.9	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	420	4.3	$\rightarrow {}^3T_1$(b) + CT
	445	3.4	
	470	3.2	
	485	3.9	$\rightarrow {}^3E$(b) + CT
	545	0.88	
	570	0.70	
	590	0.74	$\rightarrow {}^3A_1$
	660	1.6	$\rightarrow {}^3A_2$ + CT
$Cr(4,7\text{-}Me_2phen)_3^{2+}$ [e]	370	4.8	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	410	3.9	$\rightarrow {}^3T_1$(b) + CT
	440	3.7	
	480	3.0	$\rightarrow {}^3E$(b) + CT
	565	0.75	$\rightarrow {}^3A_1$
	600	0.68	$\rightarrow {}^3A_2$
	640	0.83	$\rightarrow {}^3T_2$(a)
	690	1.5	$\rightarrow {}^3T_1$(a) + CT
$Cr(4,7\text{-}Ph_2phen)_3^{2+}$ [e]	310	81.9	NN → NN*
	380	17.0	$^3T_1 \rightarrow {}^3T_2$(b) + CT
	430	6.8	$\rightarrow {}^3T_1$(b) + CT
	470	5.6	
	490	5.4	$\rightarrow {}^3E$(b) + CT
	540	2.1	
	570	1.6	
	610	1.5	$\rightarrow {}^3A_1$ + CT
	660	1.4	$\rightarrow {}^3A_2$ + CT

[a] From ref 3. [b] See text and ref 32. [c] This work. [d] In 0.05 M H_2SO_4, 1 M 2-propanol, Ar-purged solutions; 70 μs after the pulse. [e] In methanol, natural pH, Ar-purged solutions; 1 μs after the pulse. [f] In 0.01 M $HClO_4$, 0.26 M 2-propanol, Ar-purged solutions; 20 μs after the pulse. [g] Reference 30. [h] In 0.01 M $HClO_4$, 0.9 M 2-propanol, Ar-purged solutions; 40 μs after the pulse. [i] In 0.05 M $HClO_4$, 0.52 M 2-propanol, Ar-purged solutions; 25 μs after the pulse.

complex is unlike that of the bpy analogue in that several narrow bands are evident at λ > 450 nm.

To the extent that $Cr(NN)_3^{2+}$ are low-spin d^4 complexes ($^3T_1$ ground state in O_h microsymmetry),[31] the spin-allowed band maxima may be estimated by second-order perturbation theory using the equations[32] given by König and Herzog.[29] In the case of the analogous $Cr(NN)_3^{3+}$ complexes, we previously indicated that the value for the ligand field parameter Δ is nearly the same for the three bpy complexes (~23.6 × 10^3 cm^{-1}).[3] Using the empirical relationship[33] $\Delta = f_{\text{ligand}}\, g_{\text{ion}}$ where g_{ion} = 17.4 × 10^3 cm^{-1}, we obtain f_{bpy} = 1.36, in good agreement with the value of 1.33 given by Jørgensen.[33] The g value for low-spin Cr(II) is 12.4 × 10^3 cm^{-1} [34] which, with the f ligand factor, predicts Δ ≈ 16.9 × 10^3 cm^{-1} for the three Cr^{II}–bpy complexes.

Tentative assignments for these bpy complexes are presented in Table III and are based on a comparison between experimental band maxima and calculated energies by using the above rela-

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(31) P. M. Lutz, G. J. Long, and W. A. Baker, Jr., *Inorg. Chem.*, **8**, 2529 (1969).

(32) With the assumption that $C \approx 4B$, the energy maxima for the transitions are as follows: $^3T_1 \rightarrow {}^3E_a$(a), $\Delta - 2B + 64B^2/\Delta - 5.33B$; $^3T_1 \rightarrow {}^3T_1$(a), $\Delta + 52B^2/\Delta - 4.70B$; $^3T_1 \rightarrow {}^3T_2$(a), $\Delta + 2B + 52B^2/\Delta - 6.25B$; $^3T_1 \rightarrow {}^3A_1$, $\Delta - B + 64B^2/\Delta$; $^3T_1 \rightarrow {}^3A_2$, $\Delta + 3B - 80B^2/\Delta$; $^3T_1 \rightarrow {}^3T_2$(b), $\Delta + 14B - 12B^2/\Delta + 6.25B$; $^3T_1 \rightarrow {}^3E$(b), $\Delta + B + 46B^2/\Delta + 5.33B$; $^3T_1 \rightarrow {}^3T_1$(b), $\Delta + 16B - 36B^2/\Delta + 4.70B$.

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tionships[32] with the assumption that the Racah parameter B is constant in this series. The assignments for $Cr(bpy)_3^{2+}$ are based on those given by König and Herzog except that we assign the $^3T_1 \rightarrow {}^3T_1(b)$ and $^3T_1 \rightarrow {}^3T_2(b)$ transitions to the bands at 360 and 339 nm, respectively. In the $Cr(4,4'\text{-}Me_2bpy)_3^{2+}$ spectrum, these two transitions occur at ~360 nm and are not resolved due to the very intense intraligand transition at 305 nm. It is interesting, however, that the transitions $^3T_1 \rightarrow {}^3T_1(a)$ and $\rightarrow {}^3T_2(a)$ are resolved in this spectrum but are not in the bpy analogue. In the $Cr(4,4'\text{-}Ph_2bpy)_3^{2+}$ spectrum, the very intense bands at 270 and 330 nm are ascribed to intraligand $\pi-\pi^*$ transitions on the basis of intensity and by comparison with the spectrum of the protonated form of the free ligand which has bands at 260 and 312 nm.[35] The much richer spectrum of the diphenyl complex is probably due to either vibrational components[3] or to transitions predominantly charge transfer in nature. The low-energy transition $^3T_1 \rightarrow {}^3E(a)$ is expected to occur at $\lambda > 700$ nm in the Me_2- and Ph_2bpyCr^{II} spectra.

(b) phen Spectra. Unlike the spectra of the bpy complexes, those of the Cr^{II}phen complexes reveal relatively weak, barely discernible bands at ~520–650 nm. It is likely that transitions in this region have little or no charge-transfer character. At $\lambda < 520$ nm and > 650 nm, intense bands are observed and, therefore, must be, to a large extent, charge transfer in nature.

Earlier we reported $\Delta \approx 23.4 \times 10^3$ cm^{-1} for the 4,7-Me_2phen, 3,4,7,8-Me_4phen, and phen complexes of Cr(III), 22.2×10^3 cm^{-1} for the 5-Cl(phen) complex and 21.6×10^3 cm^{-1} for the 4,7-Ph_2phen complex.[3] From the absorption spectra of the new Cr(III) complexes reported here, $\Delta \approx 22 \times 10^3$ cm^{-1} for the 5-Br(phen)- and 5-Me(phen)Cr^{III} complexes and ~21.3×10^3 cm^{-1} for the 5-Ph(phen) and 5,6-Me_2phen analogues. Taking g(Cr(III)) as 17.4×10^3 cm^{-1} [33] and the above Δ values, $f_{\text{ligand}} = 1.34$ for 4,7-Me_2phen, 3,4,7,8-Me_4phen, and phen, in excellent agreement with the value of 1.34 reported for phen by Jørgensen,[33] 1.27 for the 5-Cl-, 5-Br-, and 5-Me-substituted phen, and 1.23 for 4,7-Ph_2phen, 5-Ph(phen), and 5,6-Me_2phen. With the value of g for Cr(II),[34] the values of Δ for the $Cr(NN)_3^{2+}$ species are 16.6×10^3 cm^{-1} for NN = 4,7-Me_2phen, 3,4,7,8-Me_4phen, and phen, 15.7×10^3 cm^{-1} for NN = 5-Cl(phen), 5-Br(phen), and 5-Me(phen), and 15.3×10^3 cm^{-1} for NN = 4.7-Ph_2phen, 5-Ph(phen), and 5,6-Me_2phen. To estimate the energy maxima on the basis of ligand field considerations,[32] we have made the assumption that the value of the Racah parameter B (~600 cm^{-1}) for these phen complexes is nearly the same as that of the bpy complexes. This is not unreasonable since the B values for $Ni(bpy)_3^{2+}$ and $Ni(phen)_3^{2+}$ are nearly identical (898 and 908 cm^{-1}, respectively).[36] The tentative assignments in Table III have been based on such estimates.

The analysis indicates that the $^3T_1 \rightarrow {}^3T_1(b)$ and $\rightarrow {}^3T_2(b)$ transitions should be degenerate in all of the spectra of the phen complexes. This is not generally observed (cf. Table III). We note that transitions to the $^3E(a)$ excited states are not seen in the spectrum of the phen complex, which we attribute to the band maxima lying at $\lambda > 700$ nm. The $^3T_1 \rightarrow {}^3T_1(a)$ and $\rightarrow {}^3E(a)$ transitions are expected at $\lambda > 700$ nm in the spectrum of the 5-substituted phen complexes; the extra bands at ~400–560 nm have not been assigned. In general, substituents at the 5-phen position red-shift the corresponding transitions in the parent phen complex by ~20–40 nm; the 5-Br and 5-Ph substituents effect a larger red shift.

Methyl and phenyl substituents at the 5,6- and 4,7-positions on the phen ring system also red-shift the transitions of $Cr(phen)_3^{2+}$. Phenyl substituents at the 4,7-position and 5,6-dimethyl substituents are particularly effective, to the extent that $^3T_1 \rightarrow {}^3T_2(a)$, $^3T_1(a)$, and $^3E(a)$ occur at $\lambda > 700$ nm. Additional unassigned bands are also evident in the spectra of these disubstituted phen complexes. It is likely that these bands also possess d–d character and the rich spectra probably originate from transitions between states of the trigonal symmetry, D_3, of the complexes.

Reaction of $Cr(NN)_3^{2+}$ with $Fe^{3+}(aq)$. Reaction 5 represents

$$Cr(NN)_3^{2+} + Fe^{3+}(aq) \rightarrow Cr(NN)_3^{3+} + Fe^{2+}(aq) \quad (5)$$

the electron back-transfer process between the products of the excited-state quenching reaction (1). Insofar as reaction 1 or its analogue involving other reductive quenchers is of potential importance in solar energy schemes,[8] knowledge of the rate constants of reaction 5, k_{bet}, as a function of ligand structure and kinetic parameters is necessary. As seen in Table II, the values of k_{bet} span the range 10^8–10^{10} M^{-1} s^{-1} with the slowest rate shown by the 5-Cl(phen) complex and the fastest by the 3,4,7,8-Me_4phen complex; the latter rate was estimated from the plot in Figure 11. Most of the rate constants were obtained by the flash photolysis technique from the second-order decay of $Cr(NN)_3^{2+}$ according to reaction 5; $Cr(NN)_3^{2+}$ and $Fe^{3+}(aq)$ are generated in equimolar amounts in reaction 1. For the 4,7-Me_2phen and 3,4,7,8-Me_4phen complexes, the low values (~10^6 M^{-1} s^{-1}) of the rate constant of reaction 1 (k_q) require rather large concentrations of $Fe^{2+}(aq)$ in order to quench completely (>99%) (^2E) $Cr(NN)_3^{3+}$. Unfortunately, the concentration of $Fe^{3+}(aq)$ impurity in the $Fe(NH_4)_2(SO_4)_2$ used is sufficiently high such that reaction 5 shows pseudo-first-order kinetics, too rapid to be followed within the time resolution of the flash photolysis apparatus (~30 μs). Instead, the pulse radiolytic technique was employed with reactions 2 and 3 forming $Cr(NN)_3^{2+}$ in the presence of an excess of $Fe^{3+}(aq)$ relative to $Cr(NN)_3^{2+}$; the kinetic concentration of $Fe^{3+}(aq)$ was always less than that of $Cr(NN)_3^{3+}$. The values of k_{bet} for the 4,4'-Me_2bpy, 4,7-Me_2phen, and 5,6-Me_2phen complexes were obtained at pH 1 and an ionic strength of 0.15 M. The plot of Figure 11, based on the data of k_{bet} at 1 M ionic strength and the values of $E°(Cr(NN)_3^{3+}/Cr(NN)_3^{2+})$ from Table II, provides the estimates of k_{bet} for the 4,7-Me_2phen and 3,4,7,8-Me_4phen complexes in 1 M HCl. Comparison of these data and those taken at 1 M ionic strength for the same complexes reveals an order of magnitude difference which we attribute to the differences in solution medium.

The data for k_{bet} can also be treated by the Marcus relationships. The plot of log k_{bet} vs. log K_{12} (closed circles, Figure 11) also yields an apparent self-exchange rate constant for reaction 6 of of ~10^5 M^{-1} s^{-1} with the actual value ~10^8–10^9 M^{-1} s^{-1} (see

$$(^4A_2)\ Cr(NN)_3^{3+} + Cr(NN)_3^{2+} \rightarrow Cr(NN)_3^{2+} + (^4A_2)\ Cr(NN)_3^{3+} \quad (6)$$

above discussion). Ferraudi and Endicott[37] have reported k_6 to be ~4×10^9 M^{-1} s^{-1} (for NN = bpy) in 90% CH_3OH at 25 °C and at an ionic strength of 0.1 M. Irrespective of this difference, which may reflect the different solution medium and the errors intrinsic in the technique, it must be noted that, for very similar conditions of solution medium, temperature, and ionic strength, the rate of the excited-state self-exchange reaction (2) is identical with the corresponding rate of the ground-state self-exchange reaction (6).

To a first approximation, the work terms and solvent reorganization barriers for reactions 2 and 6 are expected to be the same for the following reasons: (1) the complexes involved in both reactions have the same charges; (2) (^2E) $Cr(NN)_3^{3+}$ and ($^4A_2$) $Cr(NN)_3^{3+}$ are isogeometric inasmuch as the Stokes shift between the $^2E \leftrightarrow {}^4A_2$ emission[38] and absorption[29] bands is zero and their orbital population is identical (t_{2g}^3), although different in spin $[(\alpha)(\alpha)(\beta)$ vs. $(\alpha)(\alpha)(\alpha)]$.[39] Consequently, if both the ground-state and excited-state reactions are adiabatic, they can only differ in their inner-sphere barriers.[21] Differences in these barriers for the ground-state (ΔG_{in}^*) and excited-state ($^*\Delta G_{\text{in}}^*$) exchange reactions have been approximated[21] by eq 7 for metal-centered excited states, where f is a breathing force constant, a is the Cr–N

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[36] J. Josephsen and C. E. Schäffer, *Acta Chem. Scand., Ser.* A, **A31** 813 (1977).

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[39] α and β represent electron spins in the three t_{2g} orbitals.

$$\begin{aligned}\Delta(\Delta G_{\text{in}}{}^{\ddagger}) &= {}^{*}\Delta G_{\text{in}}{}^{\ddagger} - \Delta G_{\text{in}}{}^{\ddagger} \\ &= \frac{3f_2}{f_2 + f_3}\left[(f_3{}^{*} - f_3)a_2{}^2 + \frac{E_s}{6}\left(\frac{a_3{}^{*} + \mathrm{a}_3 - 2a_2}{a_3{}^{*} - \mathrm{a}_3}\right)\right]\end{aligned} \tag{7}$$

bond distance, and the subscripts 2 and 3 denote the charges on the complexes. Inasmuch as both ^{2}E and $^4A_2$ states have the same $t_{2g}{}^3$ configuration, the first term in eq 7 is expected to be small.[42] Five possible cases have been described[21] for the second term of equation 7. (i) $E_s = 0$ (i.e., $a_3{}^{*} - a_3 = 0$), so that $\Delta(\Delta G_{\text{in}}{}^{\ddagger})$ also equals 0 and the inner-sphere barriers for the ground-state and excited-state reactions are the same. This suggests that the exchange rate for these two reactions should be nearly identical, as is observed. Also, (ii) If $a_3{}^{*} > a_3$ and $a_2 > {}^1/_2(a_3{}^{*} + a_3)$, then ${}^{*}\Delta G_{\text{in}}{}^{\ddagger} < \Delta G_{\text{in}}{}^{\ddagger}$. (iii) If $a_3{}^{*} > a_3$ but $a_2 < {}^1/_2(a_3{}^{*} + a_3)$, then ${}^{*}\Delta G_{\text{in}}{}^{\ddagger} > \Delta G_{\text{in}}{}^{\ddagger}$. (iv) If $a_3{}^{*} < a_3$ but $a_2 > {}^1/_2(a_3{}^{*} + a_3)$, then ${}^{*}\Delta G_{\text{in}}{}^{\ddagger} > \Delta G_{\text{in}}{}^{\ddagger}$. (v) If $a_3{}^{*} < a_3$ but $a_2 < {}^1/_2(a_3{}^{*} + a_3)$, then ${}^{*}\Delta G_{\text{in}}{}^{\ddagger} < \Delta G_{\text{in}}{}^{\ddagger}$. The cases ii–v, which are dependent on whether the excited state has Cr–N bond lengths longer than or shorter than those in the ground-state species, are inconsequential in the present system. However, it is clear that if electron exchange involved addition of electrons to antibonding $e_g{}^{*}$ orbitals, significant changes in the bond lengths and breathing force constants would take place.[40,41] Interestingly, ^{2}E does not appear to be the state involved in the reductive quenching reaction (8); a higher energy state has been suggested but not identified.[37]

$$^{*}\mathrm{Cr(bpy)_3{}^{3+}} + \mathrm{ROH} \rightarrow \mathrm{Cr(bpy)_3{}^{2+}} + \mathrm{ROH^+} \tag{8}$$

Involvement by the $^4T_2$ state in excited-state self-exchange reactions can be ruled out due to its very short lifetime (<1 ns, probably $\sim 10^{-10}$ s);[42] the excited-state self-exchange reaction could not compete with $^4T_2$ decay. Consideration should also be given to the possible involvement of the $^2T_1$ excited state which has always been taken to be in thermal equilibrium with ^{2}E. Separated in energy by $\sim$600 cm^{-1}, $^2T_1$ constitutes $\sim$5% of the population of the $^2T_1/^2$E pair at room temperature. Although $^2T_1$ and ^{2}E have the same overall $t_{2g}{}^3$ orbital population, $^2T_1$ differs in that the spin density in one of the t_{2g} orbitals is drastically reduced, approximating $(\alpha)(\alpha\beta)(\square)$. In previous studies[43] of the ligand labilization of (^{2}E) Cr(bpy)$_3{}^{3+}$, we concluded that the $^2T_1$ state was the reactive entity due to the vacant t_{2g} orbital situated in the vicinity of the interligand pockets.[44] If $^2T_1$ were the sole contributor to reaction 2 and to the extent that the overall rate constant for this reaction is $\sim 10^8$–10^9 M^{-1} s^{-1}, taking into account the population of $^2T_1$, k_{ex} is expected to be $\sim 10^9$–10^{10} M^{-1} s^{-1}. Unfortunately, the presently available data and the uncertainties inherent in the Marcus relationships preclude a delineation as to the reactive state in the self-exchange reactions involving the $^2T_1/^2$E pair.

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Preparation of Aluminoborane Analogues of the Lower Boron Hydrides[1]

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Abstract: The reactions of Al(BH$_4$)$_3$ with volatile boron hydrides have been found to result in the formation of an unprecedented series of aluminoborane compounds of exceptionally high thermal stability. Reaction of Al(BH$_4$)$_3$ with B$_2$H$_6$ in benzene solution at 100 °C for 18 h produced a nonvolatile, amorphous, pyrophoric solid of empirical formula AlB$_4$H$_{11}$. This compound can also be prepared from the reaction of (CH$_3$)$_3$Al with B$_2$H$_6$ under similar conditions. On the basis of the physical and chemical properties of this compound, a polymeric structural arrangement such as that found in (AlH$_3$)$_x$ is proposed, with a borane framework similar to that of B$_5$H$_{11}$. Aluminum occupies the apex (1) BH$_2$ position in the borane cage and, as such, can polymerize through adoption of a six-coordinate, hydrogen-bridging configuration. Reaction of Al(BH$_4$)$_3$ with B$_5$H$_9$ under similar conditions gave another aluminoborane species, AlB$_5$H$_{12}$, with a similar arrangement of bridging hydrogens between aluminum atoms as proposed for AlB$_4$H$_{11}$. The reactions of AlB$_5$H$_{12}$ with H$_2$O and gaseous HCl are unusual in that the dihydroboron cation, BH$_2{}^+$, is apparently formed in each case. Thermal decomposition of (BH$_4$)Al(B$_3$H$_8$)$_2$, prepared from the reaction of Al(BH$_4$)$_3$ with B$_4$H$_{10}$, resulted in the formation of a third aluminoborane, AlB$_6$H$_{13}$. Reactions of AlB$_4$H$_{11}$ and AlB$_5$H$_{12}$ with BH$_4{}^-$ in diglyme produced the anions AlB$_5$H$_{11}{}^-$ and AlB$_6$H$_{12}{}^-$, respectively, demonstrating a strong structural similarity between members of the aluminoborane series.

Introduction

Within the last 10 years, the field of metalloborane chemistry has evolved from a study of metal BH$_4{}^-$ and B$_3$H$_8{}^-$ derivatives to an area nearing the chemical complexity and structural diversity of organometallic chemistry. Metalloboranes may be roughly classed into three major categories: (1) those involving metal–hydrogen–boron bridging, such as the aforementioned metal tetrahydroborates and octahydrotriborates; (2) those involving simple coordination to a boron–boron bond, such as (OC)$_4$Fe-B$_6$H$_{10}$[2] and *trans*-Cl$_2$Pt(B$_6$H$_{10}$)$_2$;[2,3] and (3) metalloboranes in

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