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Spectroscopy and photoredox chemistry of ion-paired cobalt(III) am(m)ine complexes

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Abstract

The cationic cobalt(III) am(m)ine complexes, $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$ (en is ethylenediamine) and $Co(NH_3)_5Br^{2+}$, form ion pairs with the tetraphenylborate anion in methanol and 1:9 methanol/dichloromethane solutions. These ion pairs display a tetraphenylborate-to-metal charge transfer absorption band at ~320 nm that tails into the visible wavelength region. Irradiation into this band causes highly efficient redox decomposition of the ion pair owing to the rapid thermal reactions of the primary photoproducts: the corresponding cobalt(II) complex and the tetraphenylboranyl radical. The photoredox quantum yield depends upon complex concentration, excitation wavelength, solvent polarity and concentration of dissolved oxygen. Incorporation of cobalt(III) am(m)ine tetraphenylborate complexes into thin films of an epoxide-functionalized polymer affords photosensitive materials that undergo crosslinking upon irradiation and subsequent heating.

Keywords: Ion pairs; Photochemistry; Photoredox; Cobalt complexes

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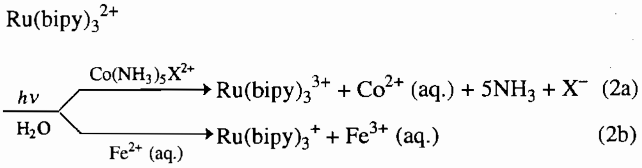
1. Introduction

Photoinduced electron transfer reactions of transition metal complexes have been investigated for over a century [1]. Much of the early interest in this topic centered upon the intramolecular redox chemistry of ligand-to-metal charge transfer (LMCT) excited states. Population of an LMCT state initially produces a reduced metal center and an oxidized ligand, either or both of which can undergo secondary thermal reactions that compete with unproductive back-electron transfer. For the well-studied $Co(NH_3)_5X^{2+}$ family (X is a uninegative ligand such as Cl^-, Br^- or NCS^-) [2–4], photoexcitation to an X-to-Co charge transfer state generates a substitutionally labile cobalt(II) complex. Rapid and irreversible loss of ligands from this species favors net redox decomposition of the parent complex according to Eq. (1).

$$(NH_3)_5Co^{III}X^{2+} \overset{h\nu}{\rightleftarrows} [(NH_3)_5Co^{II},X^{\cdot}]^{2+} \xrightarrow{H_2O} Co^{2+}(aq.) + 5NH_3 + X^{\cdot} \quad (1)$$

Pioneering studies by Gafney and Adamson [5] demonstrated that transition metal complexes also can undergo photoinduced electron transfer via an intermolecular pathway. The archetype of such behavior is $Ru(bipy)_3^{2+}$ (bipy is 2,2′-bipyridine), whose lowest metal-to-ligand charge transfer excited state is susceptible to both oxidative (Eq. (2a)) and reductive (Eq. (2b)) quenching by suitable substrates [6,7]. For the systems described by Eq. (2), the photoexcited ruthenium complex and its redox partner exist in solution as independent ions that must diffuse together prior to electron transfer. An obvious requirement in such cases is that this diffusional encounter must occur within the lifetime of the excited state.



$$Ru(bipy)_3^{2+} \xrightarrow[H_2O]{h\nu} \begin{cases} \xrightarrow{Co(NH_3)_5X^{2+}} Ru(bipy)_3^{3+} + Co^{2+}(aq.) + 5NH_3 + X^- & (2a) \\ \xrightarrow[Fe^{2+}(aq.)]{} Ru(bipy)_3^{+} + Fe^{3+}(aq.) & (2b) \end{cases}$$

Intermolecular redox chemistry also can result from irradiating an ion pair formed between an electron donor and an electron acceptor [8–10]. In Eq. (3), for example, the photoinduced reduction of $Co(en)_3^{3+}$ (en is ethylenediamine) by an anion residing in its second coordination sphere triggers decomposition of the

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$$[\mathrm{Co(en)_3}^{3+},\mathrm{X}^-] \overset{h\nu}{\rightleftharpoons} [\mathrm{Co(en)_3}^{2+},\mathrm{X}^\bullet] \xrightarrow[\mathrm{H_2O}]{} \mathrm{Co}^{2+}(\mathrm{aq.}) + 3\mathrm{en} + \mathrm{X}^\bullet \quad (3)$$

complex. Since the oppositely charged reactants exist as a preassembled unit at the instant of light absorption, diffusional requirements no longer apply and even short-lived excited states can participate in electron transfer. Moreover, ion pairs often exhibit a new absorption band arising from a weak electronic coupling of the donor and acceptor. Irradiation into this ion pair charge transfer (IPCT) band induces direct optical electron transfer between these two components.

We report here a detailed investigation of the spectroscopy and photochemistry of ion pairs formed in solution between cationic cobalt(III) am(m)ine complexes and the tetraphenylborate anion, $\mathrm{BPh_4}^-$. Earlier work by Hennig and co-workers [11,12] demonstrated that this combination of ions undergoes efficient intermolecular photoredox decomposition at wavelengths well into the visible region. Our results expand upon this seminal finding and provide new insights concerning the mechanism of photoinduced electron transfer. Moreover, preliminary experiments suggest that cobalt(III) am(m)ine tetraphenylborate salts may find use as base-releasing photoinitiators for microimaging and curing applications [13].

2. Experimental

2.1. Reagents and equipment

Reagent grade $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ and $[\mathrm{Co(en)_3}]\mathrm{Cl_3}\cdot 3\mathrm{H_2O}$ (Aldrich) were converted to their tetraphenylborate salts by the following metathesis procedure. An aqueous solution of $\mathrm{NaBPh_4}$ (Aldrich) was added slowly with stirring to an aqueous solution of the cobalt complex; a slight stoichiometric excess (3.1 to 1) of $\mathrm{BPh_4}^-$ was used to ensure complete conversion. A yellow solid gradually precipitated, and the resulting mixture was stirred an additional twenty minutes. The solid was filtered, washed with dilute $\mathrm{NaBPh_4}$ solution and distilled water, and then air dried in the dark. *Anal.* Calc. for $[\mathrm{Co(NH_3)_6}](\mathrm{BPh_4})_3\cdot 5\mathrm{H_2O}$: C, 71.57; H, 7.28; N, 6.96. Found: C, 71.44; H, 7.35; N, 6.90%. Calc. for $[\mathrm{Co(en)_3}](\mathrm{BPh_4})_3\cdot 3\mathrm{H_2O}$: C, 74.86; H, 7.20; N, 6.70. Found: C, 74.43; H, 7.29; N, 6.66%. An identical procedure was followed in the conversion of $[\mathrm{Co(NH_3)_5Br}](\mathrm{NO_3})_2$ [14] to the corresponding tetraphenylborate salt. *Anal.* Calc. for $[\mathrm{Co(NH_3)_5Br}](\mathrm{BPh_4})_2\cdot 2\mathrm{H_2O}$: C, 64.20; H, 6.60; N, 7.80. Found: C, 64.48; H, 6.69; N, 7.75%.

A chlorobenzne solution of the copolymer of glycidyl methacrylate and ethyl acrylate (abbreviated COP; Fig. 1) was purchased from Mead Technologies. Methanol (Baker HPLC grade) and dichloromethane (Baker reagent grade) were used without further purification as solvents in the spectral and photochemical experiments. All other chemicals were at least of reagent grade quality and used as received.

Electronic absorption spectra were recorded on a Varian DMS-300 spectrophotometer. Luminescence spectra were obtained with a Perkin Elmer MPF-44B spectrofluorimeter and are uncorrected for photomultiplier response. Luminescence intensities were adjusted for differences in sample absorbance, A, at the excitation wavelength by using Eq. (4), where h is the height of the luminescence band in arbitrary units. The intensities were also adjusted for reabsorption of the emitted light by the sample at the monitoring wavelength.

$$I = h/(1-10^{-A}) \quad (4)$$

Luminescence lifetimes were determined with an estimated accuracy of ±10% by time-correlated single-photon-counting techniques with an Ortec 9200 nanosecond fluorescence spectrometer. Film thickness measurements were taken with an Alpha Step 200 profilometer from Tencor Instruments. Solution photolyses at selected wavelengths above 254 nm were performed with a 200-W high pressure mercury-arc lamp whose output was passed through a high-intensity monochromator. A low-pressure mercury lamp was used for excitation at 254 nm. Incident light intensities were determined by ferrioxalate actinometry [15]. Irradiations of polymer films at 254 nm were conducted with an Optical Associates model 150 illuminator in conjunction with a narrow-bandwidth interference filter. Photon flux was measured with an Optical Associates calibrated power meter.

2.2. Photochemical studies

In a typical solution photolysis experiment, a 3 ml aliquot of the sample was placed in a 1 cm rectangular quartz cell and a small magnetic stirring bar added to provide continuous agitation during irradiation. The cell was capped, placed in a thermostatted cell holder, and its contents allowed to equilibrate at 20 °C for 15 min. In some runs, the sample solution was bubbled

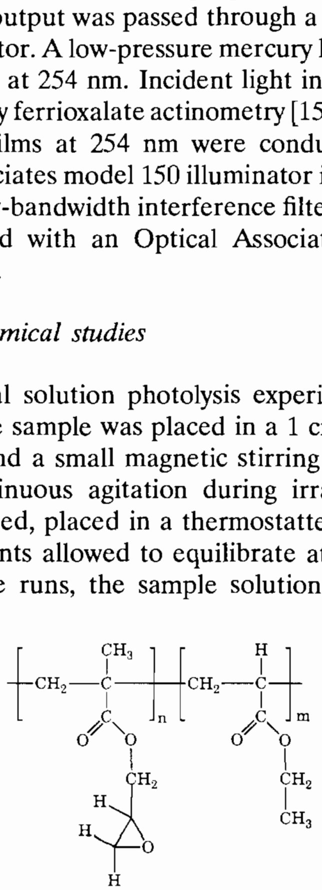


Fig. 1. Structure of the copolymer of glycidyl methacrylate and ethyl acrylate, COP ($n/m = 0.75$).

with nitrogen or oxygen gas during this equilibration period.

Photolyzed solutions were analyzed for Co^{2+} by a modification of the procedure reported by Kitson [16]. In brief, 2.5 ml of freshly prepared aqueous ammonium thiocyanate (50 g of NH_4NCS dissolved in 100 ml of distilled water), 5 ml of chlorostannous acid reagent (20 g of $SnCl_2$ dissolved in 40 ml of concentrated hydrochloric acid, followed by dilution to 100 ml with distilled water; metallic tin was added as a stabilizer), and 25 ml of acetone were mixed together in a 50 ml volumetric flask. Then 3 ml of the photolyte were added and the flask was filled to the mark with distilled water. The absorbance of the resulting solution was measured at 625 nm. A similar procedure performed on an unirradiated sample provided a blank value. A previously constructed calibration curve was used to convert absorbance readings to Co^{2+} concentrations. Biphenyl was detected in photolyzed solutions by high performance liquid chromatography.

Photochemical experiments on thin films of COP containing a cobalt(III) am(m)ine tetraphenylborate salt were conducted as follows. A weighed amount (typically 100 mg) of the salt was dissolved with stirring in 2 ml of acetone. This solution was stirred for 10 min with 3 ml of the commercial COP material and the resulting solution filtered through a 0.22 μm disk filter. Several one inch diameter quartz wafers were spin coated with the filtrate at 1800 rpm for 30 s and then baked on a hotplate at 50 °C for 3 min to remove solvent. Following exposure to 254 nm radiation, each coated wafer was placed in a small vial containing 5 ml of acetone and a magnetic stirring bar. The contents of the vial were stirred for 10 min to dissolve the film, and the resulting solution was analyzed for Co^{2+} by the procedure described earlier.

The quantum yield of photoredox decomposition; $\phi_{Co^{2+}}$, was calculated from the relation (mol of Co^{2+} produced)/(mol of light absorbed). The fraction of incident light absorbed by a sample during the course of photolysis was calculated from the expression, $1-10^{-A}$, where A is the average of the initial and final absorbance values at the excitation wavelength.

3. Results and discussion

3.1. Electronic absorption spectra

Fig. 2 displays the electronic absorption spectra of $[Co(NH_3)_6](BPh_4)_3$ over a tenfold concentration range in methanol at 20 °C. The weak bands at 476 and 340 nm (spectrum a) correspond to the ligand field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, of the low-spin, d^6 $Co(NH_3)_6{}^{3+}$ ion (group theoretical labels refer to O_h microsymmetry) [17]. The sharply rising absorbance in the UV region is composed of two overlapping components: a spin-allowed N → Co charge transfer transition of $Co(NH_3)_6{}^{3+}$ [17] and a spin-allowed π–π^* transition localized on a phenyl ring of $BPh_4{}^-$ [18]. Increasing the concentration of $[Co(NH_3)_6](BPh_4)_3$ causes the growth of a new band at ~320 nm (spectrum b and inset). We assign this band as a $BPh_4 \rightarrow Co$ IPCT transition of a $[Co(NH_3)_6{}^{3+},BPh_4{}^-]$ ion pair that exists in equilibrium with the free ions (Eq. (5)).

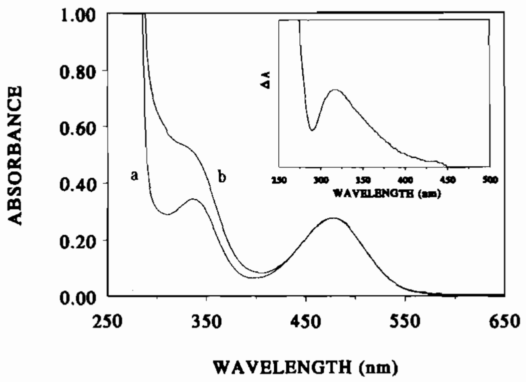


Fig. 2. Electronic absorption spectra of $[Co(NH_3)_6](BPh_4)_3$ in methanol at 20 °C: a, 4.99×10^{-4} M in 10 cm cell; b, 4.99×10^{-3} M in 1 cm cell. Inset shows the difference spectrum of a and b.

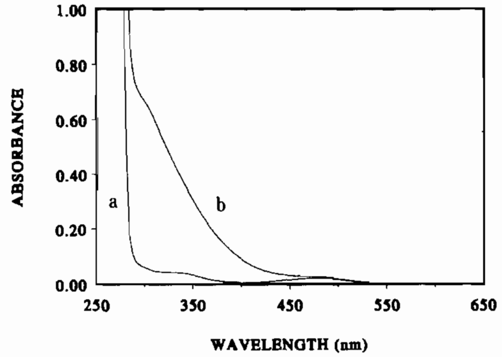


Fig. 3. Electronic absorption spectra of $[Co(NH_3)_6](BPh_4)_3$ in different solvents at 20 °C: a, methanol; b, 1:9 (vol./vol.) methanol/dichloromethane.

$$Co(NH_3)_6{}^{3+} + BPh_4{}^- \rightleftharpoons [Co(NH_3)_6{}^{3+},BPh_4{}^-] \quad (5)$$

Fig. 3 illustrates the influence of solvent polarity on the position of the ion pair equilibrium. Changing from methanol to the less polar mixture of 1:9 (vol./vol.) methanol/dichloromethane (dielectric constant at 20 °C: CH_3OH, 33.6; CH_2Cl_2, 9.1 [19]) causes a large increase in the intensity of the IPCT absorption band. This result reflects the stronger Coulombic attraction that exists between oppositely charged ions in the less polar medium and the resulting higher concentration of ion pairs.

As seen in Fig. 4, the absorption spectrum of $[Co(en)_3](BPh_4)_3$ in methanol closely resembles that of $[Co(NH_3)_6](BPh_4)_3$, and identical assignments apply.

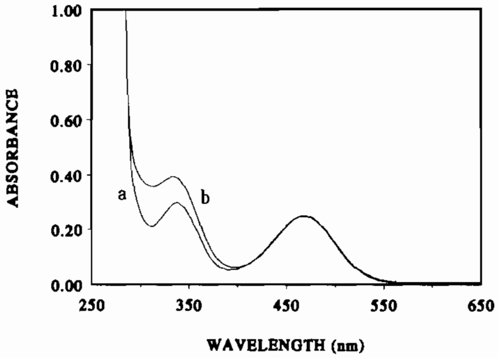


Fig. 4. Electronic absorption spectra of $[Co(en)_3](BPh_4)_3$ in methanol at 20 °C: a, 3.00×10^{-4} M in 10 cm cell; b, 3.00×10^{-3} M in 1 cm cell.

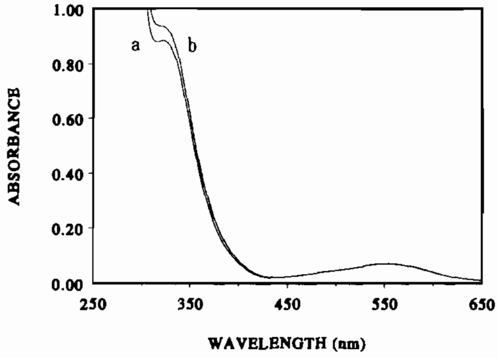


Fig. 5. Electronic absorption spectra of $[Co(NH_3)_5Br](BPh_4)_2$ in methanol at 20 °C: a, 1.21×10^{-4} M in 10 cm cell; b, 1.21×10^{-3} M in 1 cm cell.

Ion pair formation is clearly evident from the appearance of a concentration-dependent IPCT band at ~320 nm. Ion pairing should be less important for $[Co(NH_3)_5Br](BPh_4)_2$ owing to the smaller charge on the cation. Nonetheless, it does occur as evidenced in Fig. 5 by the IPCT band that appears near 320 nm as a shoulder on the intense Br → Co charge transfer band.

3.2. Luminescence quenching studies

When photoexcited at 290 nm, BPh_4^- emits a broad π–π^* fluorescence [18] with a maximum at 335 nm in deaerated methanol at 20 °C. The luminescence decays with a concentration-independent (over the range 1.2–12×10^{-3} M) lifetime of 8.5 ns. While the freely solvated BPh_4^- ions present in a methanol solution of $[Co(NH_3)_6](BPh_4)_3$ (Eq. (5)) also emit this fluorescence, the luminescence intensity decreases with increasing $Co(NH_3)_6^{3+}$ concentration. This quenching by the cationic cobalt(III) complex was analyzed by means of the Stern–Volmer relationship in Eq. (6) [20], where I_0 and I denote the intensities measured in the absence and presence, respectively, of $Co(NH_3)_6^{3+}$, k_q is the bimolecular quenching rate constant, and τ is the unquenched fluorescence lifetime of BPh_4^-. As seen in Fig. 6, the relative fluorescence intensity, I_0/I, obeys this linear relationship below a $Co(NH_3)_6^{3+}$ concentration of $\sim1.5\times10^{-3}$ M. At higher concentrations, however, the data exhibit an upward curvature.

$$I_0/I = 1 + k_q\tau[Co(NH_3)_6^{3+}] \qquad (6)$$

We attribute this non-linear Stern–Volmer behavior to the presence in solution of both freely solvated and ion-paired BPh_4^-, and the consequent operation of the two quenching pathways outlined in Scheme 1. Path A dominates in the low-concentration regime where free BPh_4^- absorbs nearly all of the exciting light. Under these conditions the π–π^* fluorescence of the anion competes with diffusional redox quenching by $Co(NH_3)_6^{3+}$. From the slope of the linear portion of the Stern–Volmer plot in Fig. 6 and the measured fluorescence lifetime, we calculate a value of 1.4×10^{11} M^{-1} s^{-1} for k_q. Path B reflects the increasing importance of ion pairing at higher $Co(NH_3)_6^{3+}$ concentrations. Photoexcitation of BPh_4^- to the π–π^* excited state is followed by highly efficient static quenching by its ion-paired partner. In addition, competitive absorption by the IPCT band of the ion pair (Fig. 2) decreases the fraction of the incident radiation available to excite BPh_4^-. Both factors effectively lower the fluorescence intensity in the high-concentration regime and thereby

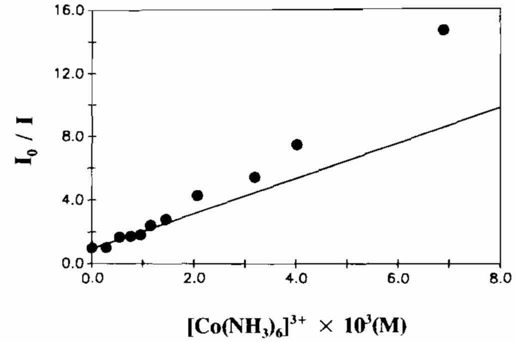
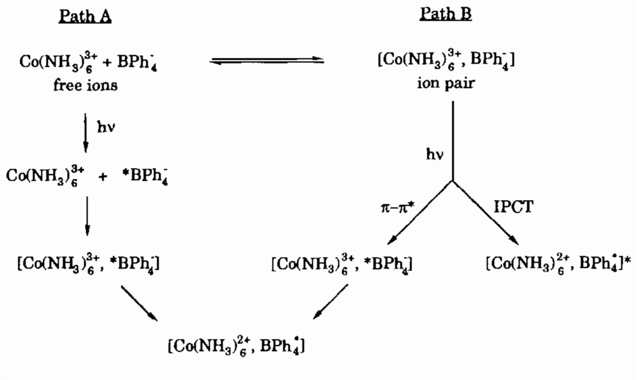


Fig. 6. Stern–Volmer plot showing quenching of BPh_4^- fluorescence by $Co(NH_3)_6^{3+}$ ($\lambda_{ex}=290$ nm, $\lambda_{em}=400$ nm).



* denotes electronic excitation

Scheme 1.

contribute to the upward deviation from linearity of the Stern–Volmer plot.

3.3. Photochemistry in solution

Continuous 313 nm irradiation of $[Co(NH_3)_6](BPh_4)_3$ in deaerated methanol induces the spectral changes illustrated in Fig. 7. Analysis of the photolyte revealed the presence of solvated Co^{2+} and biphenyl. These products result from a sequence of reactions initiated by the photoinduced transfer of an electron from BPh_4^- to $Co(NH_3)_6^{3+}$ (Eq. (7)). Both members of the initially formed radical pair, $[Co(NH_3)_6^{2+},BPh_4^{\cdot}]$, undergo rapid thermal reactions that compete effectively with back-electron transfer. Thus $Co(NH_3)_6^{2+}$ sheds its ligands to yield Co^{2+}(solv.), while the tetraphenylboranyl radical, $BPh_4^{\cdot}$, produces biphenyl (Ph–Ph) via a pathway that involves the coupling of phenyl radicals [21] or the reaction of a substituted cyclohexadienyl radical [22,23]. Production of the strongly absorbing biphenyl ($\lambda_{max}=252$ nm, $\epsilon=18\,300$ M^{-1} cm^{-1} [24]) contributes to the general rise in the UV absorbance of the system as photolysis proceeds (Fig. 7).

$$Co(NH_3)_6^{3+} + BPh_4^- \xrightarrow{h\nu} [Co(NH_3)_6^{2+},BPh_4^{\cdot}] \longrightarrow Co^{2+}(solv.) + 6NH_3 + Ph\text{–}Ph + \text{other products} \qquad (7)$$

Referring to Scheme 1, we note that both free ions (path A) and ion pairs (path B) can participate in photoinduced redox chemistry. The relative contribution of each species is governed by the experimental conditions. Increasing the $[Co(NH_3)_6](BPh_4)_3$ concentration, for example, favors ion pair formation, and the accompanying growth of the IPCT absorption band (Fig. 2) results in an increase of the extinction coefficient at 313 nm (Fig. 8(a)). Significantly, the photoredox quantum yield, $\phi_{Co^{2+}}$, measured at this wavelength exhibits the same trend (Fig. 8(b)), suggesting that ion pairs undergo net photoredox decomposition more efficiently than the free ions. Additional evidence for the important photochemical role played by $[Co(NH_3)_6^{3+},BPh_4^-]$ ion pairs is provided by the quantum yield data compiled in Table 1. Under otherwise identical conditions, the largest values of $\phi_{Co^{2+}}$ result from irradiation at 313 nm, a wavelength that corresponds to direct excitation of the IPCT transition of the ion pair. Moreover, the increase in ion pair concentration that occurs upon switching solvents from methanol to the less polar 1:9 methanol/dichloromethane produces a concomitant rise in $\phi_{Co^{2+}}$.

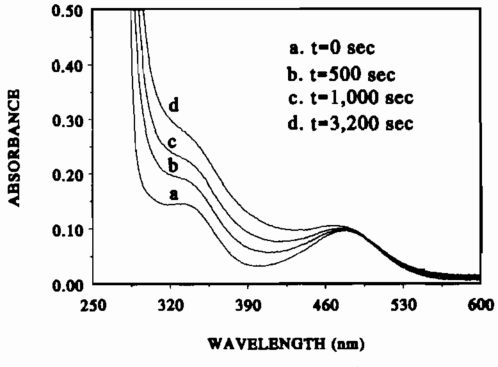


Fig. 7. Spectral changes observed upon 313 nm photolysis of $[Co(NH_3)_6](BPh_4)_3$ in methanol as a function of irradiation time. Zero-time spectrum corresponds to unirradiated complex.

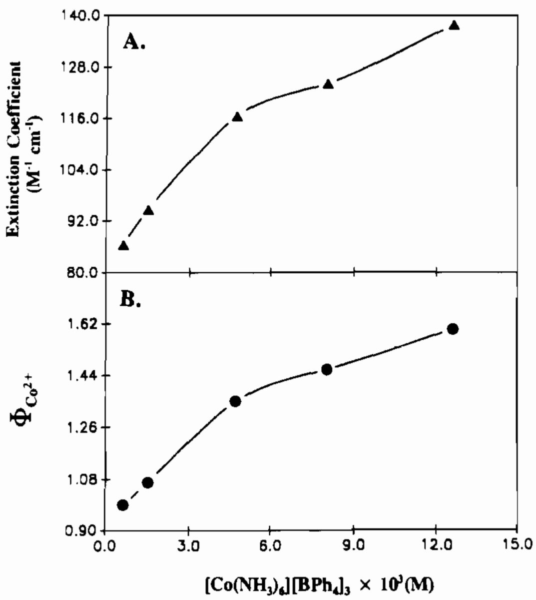


Fig. 8. Dependence of 313 nm extinction coefficient (panel A) and 313 nm photoredox quantum yield (panel B) upon concentration of $[Co(NH_3)_6](BPh_4)_3$ in methanol.

Table 1
Photoredox quantum yield data for $[Co(NH_3)_6](BPh_4)_3$ in solution

Excitation wavelength (nm)	Reaction conditions	$\phi_{Co^{2+}}$ [a] MeOH [b]	$\phi_{Co^{2+}}$ [a] $MeOH:CH_2Cl_2/1:9$ [c]
254	N_2 bubbling	1.10 ± 0.02 [d]	1.28 ± 0.02
313	N_2 bubbling	1.37 ± 0.03	1.81 ± 0.06
	air saturated	0.89 ± 0.04	1.48 ± 0.07
	O_2 bubbling	0.71 ± 0.05	1.34 ± 0.05
365	N_2 bubbling	0.83 ± 0.04	1.45 ± 0.08
436	N_2 bubbling	0.18 ± 0.02	1.12 ± 0.08

[a] Measured at ≤ 10% reaction; temperature was 20 °C.
[b] Initial complex concentration of $3.5\text{–}4.5 \times 10^{-3}$ M.
[c] Initial complex concentration of $1.5\text{–}2.5 \times 10^{-3}$ M.
[d] Error limits represent mean deviation of two or more determinations.

As seen in Table 1, the photoredox decomposition of $[Co(NH_3)_6](BPh_4)_3$ in solution can occur with a quantum yield appreciably above unity. We attribute this behavior to the photochemical production of species that can thermally reduce the parent complex. Most likely, these species are radicals formed from the decomposition of BPh$_4^{\bullet}$ [21–23]. Scavenging of these radicals by O_2 inhibits the thermal reduction process and thereby lowers the $\phi_{Co^{2+}}$ values measured in non-deaerated solutions.

Data summarized in Table 2 reveal the marked difference between the photoreactivities of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6](BPh_4)_3$ in a 4:1 methanol/water solvent mixture (the chloride salt is insoluble in pure methanol). The absorption spectrum of a 5×10^{-3} M solution of the former complex contains no features above 300 nm attributable to free Cl^- or a $[Co(NH_3)_6{}^{3+},Cl^-]$ ion pair. Consequently, excitation at 313 nm directly populates a ligand field excited state whose only reaction is very inefficient ligand substitution [25]. In contrast, absorption of 313 nm radiation by free BPh_4^- ions and $[Co(NH_3)_6{}^{3+},BPh_4^-]$ ion pairs results in highly efficient redox decomposition by the dual pathways shown in Scheme 1.

Less detailed studies of the photoredox reactions of $[Co(en)_3](BPh_4)_3$ and $[Co(NH_3)_5Br](BPh_4)_2$ were undertaken. To the extent that comparisons can be made, these complexes behave similarly to $[Co(NH_3)_6](BPh_4)_3$. In particular, each undergoes redox decomposition with high quantum efficiency when irradiated in its IPCT absorption band (Table 2).

Table 2
Photoredox quantum yield data for cobalt(III) complexes in solution

Complex [a]	Solvent [b]	Excitation wavelength (nm)	$\phi_{Co^{2+}}$
$[Co(NH_3)_6](BPh_4)_3$	4:1 $MeOH/H_2O$	313	1.33 ± 0.04 [c]
$[Co(NH_3)_6]Cl_3$	4:1 $MeOH/H_2O$	313	< 0.001
$[Co(NH_3)_5Br](BPh_4)_2$ [d]	MeOH	313	1.12 ± 0.05
$[Co(en)_3](BPh_4)_3$	MeOH	313	1.00 ± 0.05

[a] Initial complex concentration was 4.9×10^{-3} M unless indicated otherwise.

[b] All solutions were deaerated by bubbling with N_2; temperature was 20 °C.

[c] Error limits represent mean deviation of two or more determinations.

[d] Initial complex concentration was 1.7×10^{-3} M.

Table 3
Photoredox quantum yield data for cobalt(III) complexes in COP films

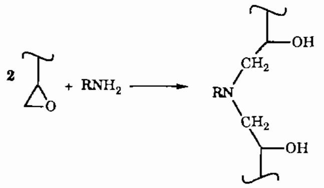
Complexes	$\phi_{Co^{2+}}$ [a]
$[Co(NH_3)_6](BPh_4)_3$	0.34 ± 0.04 [b]
$[Co(NH_3)_5Br](BPh_4)_2$	0.30 ± 0.01
$[Co(en)_3](BPh_4)_3$	0.24 ± 0.03

[a] Excitation wavelength was 254 nm.

[b] Error limits represent mean deviation of two or more determinations.

3.4. Photochemistry in polymer films

Earlier work from this laboratory [26,27] demonstrated that the intramolecular photoredox decomposition of $Co(NH_2R)_5X^{2+}$ complexes (R is H or CH_3; X is Cl^- or Br^-) in thin films of an epoxide-functionalized polymer results in crosslinking of the epoxide groups by liberated base (Eq. (8)). Production of base



(8)

in these systems occurs with low quantum efficiency ($\phi_{Co^{2+}} \sim 0.01$) owing to rapid back-electron transfer between the primary photoproducts in the viscous polymer matrix. This problem should be less serious for cobalt(III) am(m)ine tetraphenylborate complexes since both constituents of the photogenerated radical pair undergo rapid secondary reactions that favor irreversible redox decomposition (Eq. (7)). To test this premise, we prepared thin films of the copolymer of glycidyl methacrylate and ethyl acrylate (COP; Fig. 1) containing $[Co(NH_3)_6](BPh_4)_3$, $[Co(en)_3](BPh_4)_3$ or $[Co(NH_3)_5Br](BPh_4)_2$. The films were irradiated at 254 nm and then analyzed for Co^{2+}. Quantum yield data summarized in Table 3 show that all of the complexes undergo efficient photoredox decomposition in the polymer.

Preliminary photochemical experiments reveal that COP films containing the cobalt(III) am(m)ine tetraphenylborate salts behave similarly to the systems reported in our previous work [26,27]. Thus an irradiated film dissolves away completely when sprayed with a 2-butanone/ethanol developing solution. In contrast, post-irradiation heating at 65–70 °C for 6 min crosslinks the polymer and thereby renders it insoluble in the developer. This insolubilization of the exposed areas of the film affords a mechanism for negative-tone image formation with deep-UV light. Detailed lithographic studies of these interesting photosensitive materials are underway.

Acknowledgements

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