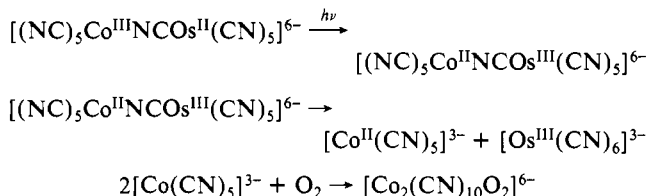


$[(\text{NC})_5\text{Co}^{\text{III}}\text{NCOs}^{\text{II}}(\text{CN})_5]^{6-}$ is less instructive since it is rather featureless at short wavelength in the UV region. However, the MMCT assignment of the band at $\lambda_{\text{max}} = 359 \text{ nm}$ (Table I) is supported by the spectra of the analogous complexes $[(\text{NC})_5\text{Co}^{\text{III}}\text{NCM}^{\text{II}}(\text{CN})_5]^{6-}$ with $\text{M} = \text{Fe}$ and Ru . Within the series $\text{M} = \text{Fe}$ ($\lambda_{\text{max}} = 385 \text{ nm}$),¹⁰ Os , and Ru ($\lambda_{\text{max}} = 312 \text{ nm}$)¹⁰ the MMCT bands move to higher energies since the reducing power of $\text{M}(\text{CN})_6^{4-}$ decreases in this direction.

Photochemistry. The binuclear complexes $[(\text{NH}_3)_5\text{Os}^{\text{III}}\text{NCM}^{\text{II}}(\text{CN})_5]^-$ with $\text{M} = \text{Fe}$, Ru , and Os are not light-sensitive upon MMCT excitation. The redox isomers $[(\text{NH}_3)_5\text{Os}^{\text{II}}\text{NCM}^{\text{III}}(\text{CN})_5]^-$, which are formed upon CT excitation, are certainly not very labile toward substitution. A rapid back electron transfer regenerates apparently the starting $\text{Os}^{\text{III}}/\text{M}^{\text{II}}$ complexes.

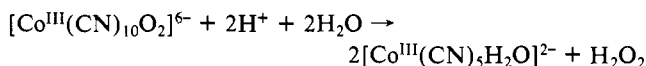
Upon MMCT excitation ($\lambda_{\text{irr}} = 366 \text{ nm}$) the complex $[(\text{NC})_5\text{Co}^{\text{III}}\text{NCOs}^{\text{II}}(\text{CN})_5]^{6-}$ underwent a photolysis in aqueous solution in analogy to the related ions $[(\text{NC})_5\text{Co}^{\text{III}}\text{NCM}^{\text{II}}(\text{CN})_5]^{6-}$ with $\text{M} = \text{Fe}$ and Ru .¹⁰ When the photolysis was carried out in basic solution (1 M KOH) and in the presence of oxygen, the spectral changes during the photolysis (Figure 2) indicated the formation of the superoxo complex $[\text{Co}_2(\text{CN})_{10}\text{O}_2]^{5-}$ ($\lambda_{\text{max}} = 310 \text{ nm}$, $\epsilon = 24\,800 \text{ M}^{-1} \text{ cm}^{-1}$).²⁵ The absorption of this complex is so intense that it obscures bands of other photoproducts. In acidic solution (10^{-4} M HCl) the superoxo complex is not formed. The spectral variations during the photolysis were consistent with the formation of $[\text{Os}(\text{CN})_6]^{3-}$, which shows absorption maxima at 412, 332, 307, and 280 nm.¹⁷

The quantum yield for the formation of $[\text{Os}(\text{CN})_6]^{3-}$ in acidic solution was $\Phi = 0.32$ at $\lambda_{\text{irr}} = 366 \text{ nm}$. According to these observations and in agreement with previous results that were obtained with $[(\text{NC})_5\text{Co}^{\text{III}}\text{NCM}^{\text{II}}(\text{CN})_5]^{6-}$ ($\text{M} = \text{Fe}$ and Ru), the photolysis should proceed by the following mechanism:

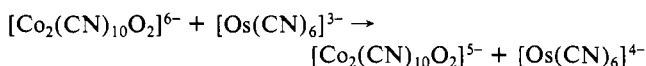


The redox isomer $\text{Co}^{\text{II}}/\text{Os}^{\text{III}}$ produced in the primary photochemical step is certainly strongly distorted at Co^{II} .¹⁰ This distortion and the electrostatic repulsion of both anionic components of the redox isomer apparently facilitates the dissociation into the mononuclear complexes. The dissociation then competes successfully with back electron transfer within the redox isomer.

The anion $[\text{Co}(\text{CN})_5]^{3-}$ generated in the dissociation of the redox isomer is intercepted by oxygen. The peroxo complex that is formed in this reaction is known to decompose in acidic solution:



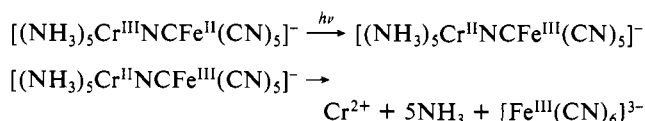
Since $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ has only rather weak absorption bands at long wavelengths,¹⁰ the spectrum of the photolyzed solution is dominated by $[\text{Os}(\text{CN})_6]^{3-}$. In basic solution the peroxo complex does not hydrolyze but is oxidized by $[\text{Os}(\text{CN})_6]^{3-}$ to yield the superoxo complex:



The complex $[(\text{NH}_3)_5\text{Cr}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_5]^-$ underwent also an efficient photolysis in aqueous solution upon MMCT excitation ($\lambda_{\text{irr}} = 366 \text{ nm}$). The accompanying spectral changes (Figure 3) are consistent with the formation of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ ($\lambda_{\text{max}} = 420 \text{ nm}$, $\epsilon = 10\,500 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁷ At this wavelength a shoulder develops. When the irradiation is continued, a secondary photolysis or thermal side reactions take place as indicated by the disappearance

of the isosbestic points. However, the spectral features of $[\text{Fe}(\text{CN})_6]^{3-}$ can then be recognized much better. The fate of the chromium complex is not known. The disappearance quantum yield of the starting complex was approximately $\Phi = 0.1$.

It is suggested that the photolysis proceeds according to



The redox isomer $\text{Cr}^{\text{II}}/\text{Fe}^{\text{III}}$ generated by MMCT excitation is expected to decompose since ammine complexes of $\text{Cr}(\text{II})$ are well-known to be kinetically very labile.²⁶ The ligand displacement at the $\text{Cr}(\text{II})$ center of the $\text{Cr}(\text{II})/\text{Fe}(\text{III})$ redox isomer is apparently fast enough to compete successfully with the back electron transfer. Finally, $\text{Cr}(\text{II})$ is oxidized by oxygen.

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Electrogenerated Chemiluminescence of Hexacyanochromate(III) and Tris(2,2'-bipyridine)chromium(III) in Aprotic Solvents

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The number of examples of chemiluminescence involving reactions of transition-metal (TM) complex species is still relatively small. Of increasing interest in recent years¹⁻¹² is the identification of chemiluminescent TM systems other than the well-documented case of $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine).¹³⁻¹⁵ Literature examples of $\text{Cr}(\text{III})$ chemiluminescence appear to date back to only

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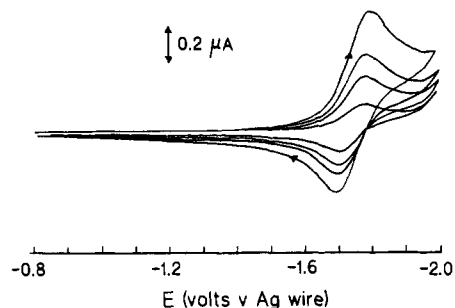
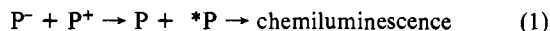


Figure 1. Cyclic voltammogram of a 2 mM $\text{Cr}(\text{CN})_6^{3-}/\text{Me}_2\text{SO}/0.05 \text{ M TBAP}$ solution, for scan rates of 20, 100, 200, and 500 mV s^{-1} (hanging mercury drop working electrode).

1981^{3,4} and involve oxidation of the analogous Cr(II) species with a strong oxidizing agent. To date, such reports for Cr(III) have been restricted to polypyridine systems,³⁻⁶ and in only one instance has electrogenerated chemiluminescence (ECL) been reported (involving the persulfate ion as oxidant).⁶ The success with Cr polypyridine systems rests in part on the solution integrity of the Cr(II) species (established by cyclic voltammetry) and the relatively strong phosphorescence displayed by the Cr(III) complexes in room-temperature solution.

We wish to report here two examples of alternating current (ac) electrogenerated chemiluminescence involving the complexes $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{bpy})_3^{3+}$ in aprotic solvents. In most cases of ac-ECL reported for TM systems a parent species P of strong luminescent character is reduced and oxidized to P^- and P^+ , respectively, at the cathodic and anodic limits employed. The subsequent thermal back-electron-transfer reaction is then sufficiently exoergonic for one of the parent molecules to be regenerated in its luminescent excited state:



A scheme such as reaction 1 is unlikely to be demonstrated for Cr(III) systems due to the general inaccessibility of Cr(IV) species in solution. However, an alternative oxidant to P^+ may under suitable circumstances be produced at the anodic pulse limit, and this latter method has been employed in the present report.

Our first example involves the species $\text{Cr}(\text{CN})_6^{3-}$, which to our knowledge represents the first case of chemiluminescence from a non-polypyridyl Cr(III) complex. We also report results for $\text{Cr}(\text{bpy})_3^{3+}$ in acetonitrile solution. In both instances ECL is observed on pulsing the potential of a Pt working electrode between approximately +2.2 and -2.0 V ($\text{Cr}(\text{CN})_6^{3-}$) or -1.6 V ($\text{Cr}(\text{bpy})_3^{3+}$) vs. a Ag-wire quasi reference electrode.

Experimental Section

Instrumentation. Cyclic voltammetry experiments were carried out with a Princeton Applied Research (PAR) Model 173 potentiostat and a PAR Model 175 universal programmer. The same electrochemical equipment was employed for electrogenerated chemiluminescence (ECL) studies. The three-electrode PAR electrochemical cell was placed in the cell compartment of an Aminco-Bowman spectrofluorimeter (SPF) equipped with a red-sensitive R446S photomultiplier tube. The Pt-wire working electrode was inserted in the center of the cell, while the Pt-wire auxiliary electrode and Ag-wire quasi reference electrode were off to the side. The cell was blackened such that only light from the working electrode could enter the inlet slit of the detection monochromator. Conventional photoluminescence spectra of the complexes under investigation were recorded on the same Aminco-Bowman SPF. All experiments were performed at room temperature ($\sim 22^\circ\text{C}$) on solutions deaerated by N_2 bubbling.

Chemicals. The Cr(III) complexes $\text{Cr}(\text{CN})_6^{3-}$ and $\text{Cr}(\text{bpy})_3^{3+}$ were used in the forms of their tetrabutylammonium and perchlorate salts, respectively. Polarographic grade tetrabutylammonium perchlorate (TBAP) and reagent grade tetrabutylammonium tetrafluoroborate ($(\text{TBA})\text{BF}_4$) were used as received (Fisher). Spectroscopic grade dimethylformamide (DMF) and acetonitrile were used as solvents.

Results and Discussion

A. $\text{Cr}(\text{CN})_6^{3-}$. Cyclic voltammetry (CV) data for $\text{Cr}(\text{CN})_6^{3-}$ in Me_2SO with a hanging mercury drop electrode (HMDE) as working electrode (Figure 1) provide evidence for close to fully

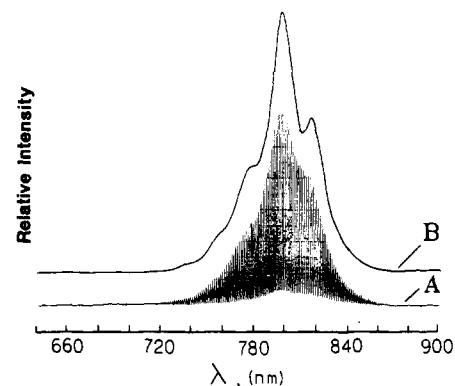


Figure 2. (A) ECL spectrum of a 2.5 mM $\text{Cr}(\text{CN})_6^{3-}/\text{MeCN}/0.1 \text{ M TBAP}$ solution (pulsing limits +2.2 and -2.0 V vs. Ag quasi reference electrode at 0.5 Hz; Pt working and auxiliary electrodes). (B) Photoluminescence spectrum of a 2.5 mM $\text{Cr}(\text{CN})_6^{3-}$ solution in MeCN on 365-nm excitation.

reversible electrochemical behavior for the $\text{Cr}(\text{CN})_6^{3-/4-}$ redox couple. The standard reduction potential vs. the Ag-wire quasi reference electrode is estimated to be -1.75 V. Even at a sweep rate of 20 mV/s, the current associated with the return anodic wave is almost equal in size to that of the corresponding cathodic wave. Although CV data for this redox couple in aprotic solvents reveal irreversible type behavior for Pt as the working electrode, sufficiently rapid $\text{Cr}(\text{CN})_6^{4-}$ formation should occur in an ac-ECL experiment on stepping a Pt working electrode to a cathodic limit of ≥ 2.0 V (vs. Ag wire).¹⁶ Furthermore, these CV data suggest $\text{Cr}(\text{CN})_6^{4-}$ is long enough lived in aprotic solvents that it might be oxidized by a solvent or backing-electrolyte-originated oxidant on subsequently stepping to a potential of approximately +2.2 V (where a significant background anodic current is observed in a CV scan employing Pt as the working electrode).

These expectations appear to have been borne out. For $2.5 \times 10^{-3} \text{ M}$ solutions of $\text{Cr}(\text{CN})_6^{3-}$, strong ECL signals of comparable intensity were observed in DMF and acetonitrile solvents. The ECL spectrum in acetonitrile when the working electrode potential is stepped from +2.2 to -2.0 V is shown in Figure 2A. The intensity of the ECL signal was approximately 1/200th that of an equimolar acetonitrile solution of $\text{Ru}(\text{bpy})_3^{2+}$ pulsed between +1.7 and -1.4 V vs. Ag-wire quasi reference electrode (uncorrected for differences in photomultiplier tube wavelength response).¹⁹ The corresponding ECL spectrum for $\text{Cr}(\text{CN})_6^{3-}$ in Me_2SO was approximately 1/10th as intense, which may be attributed in part to the weaker steady-state photoluminescence observed in this solvent. For all three solvents the ECL signal was maintained for several hours, although the intensity did decrease slowly with time and some deposition on the Pt working electrode was observed. The ECL spectrum in each case matched closely the corresponding photoluminescence spectrum of $\text{Cr}(\text{CN})_6^{3-}$ (Figure 2B), although the former had somewhat poorer resolution due to the wider slits employed. The ECL is therefore clearly associated with production of the $^2\text{E}_g$ excited state of $\text{Cr}(\text{CN})_6^{3-}$.²⁰

Formation of this Cr(III) excited-state product presumably results from the reaction of $\text{Cr}(\text{CN})_6^{4-}$ (produced on stepping to

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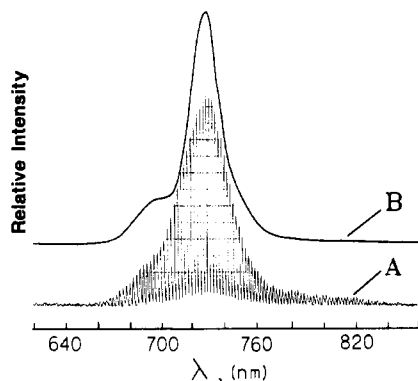


Figure 3. (A) ECL spectrum of a 4 mM $\text{Cr}(\text{bpy})_3^{3+}/\text{MeCN}/0.1 \text{ M}$ TBAP solution (pulsing limits +2.2 and -1.6 V vs. Ag quasi reference electrode at 0.5 Hz; Pt working and auxiliary electrodes). (B) Photoluminescence spectrum of a 1 mM $\text{Cr}(\text{bpy})_3^{3+}$ solution in MeCN on 436-nm excitation.

-2.0 V) with an oxidant generated on stepping the voltage to approximately +2.2 V. ECL were *not* observed when anodic limit potentials of less than +2.0 V were employed—a result in harmony with CV data, which revealed significant background anodic currents only at potentials $>+2.0$ V. The identity of the oxidant generated at potentials in excess of +2.0 V is as yet unclear, although it is unlikely to be $\text{Cr}(\text{CN})_6^{2-}$ due to the general absence of electrochemical evidence for Cr(IV) species in solution.⁶ Doubling the supporting electrolyte concentration slightly decreased the ECL intensity, which suggests that TBAP is not the source of the oxidant. Similar results were obtained with $(\text{TBA})\text{BF}_4$ as the backing electrolyte. We therefore tentatively assign an adventitious solvent impurity as the origin of the $\text{Cr}(\text{CN})_6^{4-}$ oxidant.²¹ It is noteworthy that the light pulses were generally observed only upon stepping to the cathodic limit (Figure 2A). This result is consistent with the $\text{Cr}(\text{CN})_6^{4-}$ produced in the -2.0 V pulse having a shorter lifetime than the oxidant formed at the anodic limit. The strongest ECL signals were observed in DMF and acetonitrile with a pulse width of 0.5 s, and 1 s for Me_2SO solution.

In view of the rather negative potential for the $\text{Cr}(\text{CN})_6^{3-/4-}$ couple and the unusually low energy of the $\text{Cr}(\text{CN})_6^{3-} {}^2\text{E}_g$ excited state (~ 800 nm emission, 1.5 eV),²⁰ a range of oxidants might potentially be capable of generating chemiluminescence via reaction with $\text{Cr}(\text{CN})_6^{4-}$. We are presently exploring these possibilities further.

B. $\text{Cr}(\text{bpy})_3^{3+}$. In keeping with earlier reports,²² the CV of $\text{Cr}(\text{bpy})_3^{3+}$ in acetonitrile exhibited reversible electrochemical behavior on Pt for the $\text{Cr}^{3+/2+}$, $\text{Cr}^{2+/+}$, and $\text{Cr}^{+/0}$ couples. The reduced species $\text{Cr}(\text{bpy})_3^{2+}$, $\text{Cr}(\text{bpy})_3^+$, and $\text{Cr}(\text{bpy})_3^0$ might all therefore be considered as potential redox precursors to chemiluminescence from the ${}^2\text{E}_g$ excited state of $\text{Cr}(\text{bpy})_3^{3+}$. ac-ECL is in fact observed on pulsing a 4.0×10^{-3} M solution of $\text{Cr}(\text{bpy})_3^{3+}$ between +2.2 and -1.6 V, and the ECL spectrum agrees closely with the photoluminescence spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ (Figure 3). Electrogeneration of the ${}^2\text{E}_g$ (O_h) excited state of $\text{Cr}(\text{bpy})_3^{3+}$ is thus clearly established.²³

The intensity of the ECL signal was markedly dependent on the voltage employed as the cathodic limit for the working electrode. At potentials that produce $\text{Cr}(\text{bpy})_3^{2+}$ (-0.2 to -0.5 V)

and $\text{Cr}(\text{bpy})_3^+$ (-0.7 to -1.1 V) only very weak signals were observed. A much larger ECL signal was generated on stepping to -1.6 V, where CV data predict formation of $\text{Cr}(\text{bpy})_3$. At present we can offer no ready explanation for this interesting intensity dependence on cathodic potential. Finally, the identity of the oxidant in this system has again not been established, although a solvent impurity is considered the most probable source of this species. The ECL signal was maintained for several hours, and only minor deposition on the Pt electrode surface was detected. Once again, emission pulses were observed only as the system was stepped to the cathodic limit, and the strongest signals were detected for a pulse width of 0.5 s.

Acknowledgment. We gratefully acknowledge the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The financial support of the Camille and Henry Dreyfus Foundation is also gratefully acknowledged.

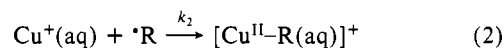
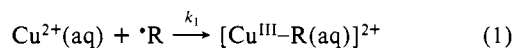
Contribution from the Nuclear Research Center Negev, Chemistry Department, and Coal Research Center, Ben-Gurion University of the Negev, Beer-Sheva, Israel

Kinetics of the Reaction of Copper(I) and Copper(II) Ions with 2,5-Dioxacyclohexyl Free Radicals and Homolysis of the Aqua-Copper(II)-2,5-Dioxacyclohexyl Complex in Aqueous Solutions. A Pulse Radiolysis Study

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The effect of copper ions on the product composition in catalytic free-radical processes in aqueous solutions was interpreted as indicating that short-lived intermediates with copper-carbon bonds are formed in these processes.^{2,3} Recently it was shown that indeed the reactions



can be followed in aqueous solutions by using pulse radiolysis or flash photolysis techniques⁴⁻⁸ (where $\cdot\text{R}$ is an aliphatic free radical). These techniques enable also the study of the properties of the $[\text{Cu}^{\text{III}}\text{-R}(\text{aq})]^{2+}$ and $[\text{Cu}^{\text{II}}\text{-R}(\text{aq})]^+$ complexes. We have recently shown⁸ that one can extend the range of reactions² that can be studied by preparing solutions of $\text{Cu}^+(\text{aq})$ via



By use of this reaction solutions containing $[\text{Cu}^+(\text{aq})]/[\text{Cu}^{2+}(\text{aq})] \leq 0.2$ can be easily prepared and kept for several hours.⁹ As k_2 is in many systems over 2 orders of magnitude larger than k_1 , reaction 2 can be directly followed. (The reactions of $\text{Cr}^{\text{III}}(\text{aq})$

- (21) The results obtained on intentional contamination of solutions with small amounts of O_2 and H_2O exclude these species as the oxidant source. In both cases some emission quenching occurred, the effect being especially marked in the case of H_2O . Prior studies have shown that both species also quench $\text{Cr}(\text{CN})_6^{3-}$ photoluminescence.²⁰ A reviewer also suggested the Pt electrode itself may function as the oxidant in these systems. Although an electrode oxidant might result in ECL on stepping to positive potentials, this mechanism will not account for the much greater emission intensity observed on stepping to the cathodic limit potential.
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