

[V^{IV},V^{IV}] complex. However, a rapid purge of excess O₂ following the initial binding in the [V^{III}, V^{IV} O₂⁻] intermediate allows the observation of a slow re-formation of some V₂O(ttha)²⁻. In the process a pool of the [V^{III},V^{IV}] complex is created either by reduction of all [V^{III},V^{IV}O₂⁻] species to [V^{III},V^{IV}] or by dismutation of the superoxo complex into a peroxo complex and finally to

[V^{III},V^{IV}]. The cross-electron-transfer reaction then regenerates up to 50% of V₂O(ttha)²⁻.

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Formation of [(CN)₅Ru^{II}-CN-Ru^{III}(CN)₅]⁶⁻ by Chemical Oxidation, Electrochemical Oxidation, and Photooxidation of Ru(CN)₆⁴⁻

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Electron transfer to a ligand field excited state of tris(glycinato)cobalt(III) by hexacyanoruthenium(II) was observed in pH 5 acetate-buffered aqueous solution. A product of the reaction is a species that has an intervalence transfer band at $9.1 \times 10^3 \text{ cm}^{-1}$ (1094 nm) with a molar absorptivity of about $7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The same spectroscopic band results from chemical oxidation (H₂O₂, Ce⁴⁺), anodic oxidation (Pt electrode), and excited-state electron transfer to tris(2,2'-bipyridine)ruthenium(II). Steady-state analysis of the kinetics of the reaction leads to an estimation of the lifetime of the excited state of tris(glycinato)cobalt(III) as $23 \pm 4 \text{ ns}$. The most likely species responsible for the infrared band is the cyanide-bridged dimer [(CN)₅Ru^{II}-CN-Ru^{III}(CN)₅]⁶⁻. The kinetics of its formation from hexacyanoruthenium(II) and -(III) are rapid (second-order rate constant $\sim 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) in contrast to recent observations on nonphotochemical reactions of hexacyanoruthenium(III).

Introduction

Our laboratory is interested in the development of photoelectrochemistry as an analytical tool.^{1,2} This technique uses an EC catalytic mechanism of electron transfer from an electrode to an acceptor (quencher) in solution via a photoexcited Ru(bpy)₃²⁺.²⁻⁹ In the course of investigations into the suitability of tris(amino acid) complexes of Co(III) as quenchers of Ru(bpy)₃²⁺ and of Ru(CN)₆⁴⁻ as an electron-transfer mediator between Ru(bpy)₃²⁺ and a cathode, we have found evidence that a nonluminescent ligand field excited state of tris(glycinato)cobalt(III), Co(gly)₃, undergoes electron transfer with Ru(CN)₆⁴⁻. Our observations are particularly significant in view of the fact that the bimolecular electron-transfer photochemistry of nonluminescent excited states is known only in a few cases¹⁰⁻¹³ and the methods for studying these reactions are difficult. The findings and methodology described below, though not always applicable, have the potential to allow investigations of other nonluminescent states. Furthermore, the result of photolysis is a spectroscopic band with the characteristics¹⁴ of an intervalence charge-transfer band ($\nu_{IT} = 9.1 \times 10^3 \text{ cm}^{-1}$). The simplest species that could give rise to this feature is the cyanide-bridged binuclear complex [(CN)₅Ru^{II}-CN-Ru^{III}(CN)₅]⁶⁻ (I).

Experimental Section

Materials. Preparation of Co(gly)₃ is described in ref 1. Ru(CN)₆⁴⁻ (Alfa Products), NaCN (Fisher), and Ru(bpy)₃²⁺ (G. F. Smith) were used as received. All solutions were prepared in 0.1 M acetate buffer, pH 5.00 \pm 0.05, prepared in distilled-deionized water. Ru(CN)₆³⁻ was prepared according to Crean and Schug.¹⁵ Ru(CN)₅OH₂³⁻ was prepared according to Johnson and Shepherd.¹⁶

Methods. (a) **Electrochemistry.** Cyclic voltammetric experiments were performed by using a BAS CV-1A potentiostat and data were recorded on an X-Y recorder (Houston Instruments). Constant-potential electrolysis of Ru(CN)₆⁴⁻ was carried out by using a PAR 173 potentiostat-galvanostat. Absorbance was determined with an IBM 9420 UV-vis spectrophotometer. The electrochemical cells used were either a spectrophotometer cuvette or a vial with a conventional three-electrode configuration. An Ag/AgCl (3 M NaCl) reference electrode and a Pt-wire auxiliary electrode were used. The working electrode was a glassy-carbon button (0.07 cm²). The working electrode in the spectroelectrochemical experiment was a Pt wire. All experiments were carried out in 0.1 M acetate, pH 5.00 \pm 0.05, electrolyte.

(b) **Steady-State Photolysis.** A 2-mL aliquot of a given reaction mixture was continuously photolyzed by using the 441.6-nm beam of a nominally 40-mW CW He-Cd laser. All solutions were continuously stirred during photolysis with a magnetic stirrer. The base-line-corrected difference (photolyzed minus unphotolyzed) absorption spectra were recorded on an IBM 9420 UV-vis spectrophotometer. Results shown in Figure 1 were recorded on a Cary-14 UV-vis-IR spectrophotometer. Incident light intensity was monitored on a Spectra Physics power meter (401 B). All experiments were carried out at ambient temperature, 22 \pm 1 °C.

(c) **Errors.** All errors reported represent 95% confidence intervals determined from a linear least-squares treatment.

Results and Discussion

Quenching of the Nonluminescent Excited State of Co(gly)₃ and Formation of the Binuclear Complex. Irradiation of a solution of $1.0 \times 10^{-3} \text{ M}$ Co(gly)₃ in 0.1 M acetate, pH 5, buffer leads to no spectral change in a 10-min photolysis. Likewise a solution $1.0 \times 10^{-2} \text{ M}$ in Ru(CN)₆⁴⁻ suffers no spectral change when photolyzed for 10 min. When these two solutions are mixed, either

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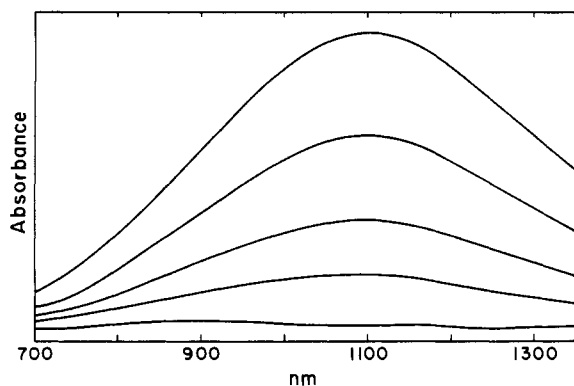


Figure 1. Spectra of photolyzed solutions containing 0.01 M $\text{Ru}(\text{CN})_6^{4-}$ and 0.0010 M $\text{Co}(\text{gly})_3$ in 0.1 M pH 5 acetate buffer. The times of the photolyses are, from the bottom, 0, 1, 2, 4, and 7 min.

before photolysis or after each has been irradiated individually, there is no spectral change. However, when a solution containing both of the above species is photolyzed there is the production of a broad band at 1094 nm ($9.1 \times 10^3 \text{ cm}^{-1}$), see Figure 1. The band intensity increases with photolysis time as shown in Figure 1. The breadth of the band ($\Delta\nu_{1/2} = 4.5 \times 10^3 \text{ cm}^{-1}$) is in agreement with that expected for a type II intervalence complex.¹⁴ Furthermore, the rate of band formation is linear (seven experiments covering a 50-fold intensity range; correlation coefficient = 0.9994) with respect to the incident light intensity, indicating that a single photon process is responsible for the observed results.

The near-IR band is not due to a Co-containing species as evidenced by the following results. The addition of H_2O_2 or Ce^{4+} to a solution of $\text{Ru}(\text{CN})_6^{4-}$ leads to the same band in the spectrum. The electrolysis of a solution of $1.0 \times 10^{-2} \text{ M Ru}(\text{CN})_6^{4-}$ in the aforementioned buffer at +1.0 V (vs. Ag/AgCl, 3 M NaCl) at Pt with an isolated auxiliary electrode leads to the same band. The spectra obtained do not bear any resemblance to ion-paired or cyanide-bridged Ru(II),Co(III) species.^{17,18} We conclude that the species formed contains Ru as the only metal and that it can be formed photochemically in the presence of $\text{Co}(\text{gly})_3$. The identity of the compound yielding the spectrum will be discussed, and then a discussion of the mechanism of its formation will follow.

In the spectroelectrochemistry experiment described above the initial rate of production of the band is linear with time and the electrolysis current is constant. From the electrolytic current and the change in absorbance with time, if one assumes $n = 1$ electron and that each oxidation leads to one molecule of I, then one can calculate a molar absorptivity of $(7.14 \pm 0.5) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. This compares favorably with the Fe(II),Fe(III) analogue of I, $(\text{CN})_5\text{Fe}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}(\text{CN})_5$ ($\epsilon = 2.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; $\nu_{\text{IT}} = 7.7 \times 10^3 \text{ cm}^{-1}$),¹⁹ and the Ru(II),Fe(III) analogue,²⁰ ($\epsilon = 3.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; $\nu_{\text{IT}} = 12.4 \times 10^3 \text{ cm}^{-1}$). The spectrum of the complex formed is not consistent with spectra from species such as Prussian blue or its ruthenium analogue.^{21,22}

Attempts to confirm the suspected (1:1) stoichiometry by using mole ratio plots in which the principal species were $\text{Ru}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{CN})_6^{3-}$ led to values near 30:1 (II:III). Titration of $\text{Ru}(\text{CN})_6^{4-}$ by Ce^{4+} confirmed this. We do not understand the reason for these results, but we suspect that cyanide ion and its reaction products play a role in limiting the concentration of the reaction product. To avoid the complication caused by the released CN^- , the compound $\text{Ru}(\text{CN})_5(\text{OH}_2)^{3-}$ was prepared¹⁶ and reacted with $\text{Ru}(\text{CN})_6^{3-}$. Owing to the instability of both of the starting materials and the lack of certainty concerning the concentrations of the starting materials (they are both prepared as solutions and

used as such), it is difficult to be certain of the stoichiometry of the compound yielding the intervalence band. For both the method of continuous variations and the mole ratio method, the data are consistent with a 1:1 stoichiometry. Incidentally, we believe the molar absorptivity of $\text{Ru}(\text{CN})_5(\text{OH}_2)^{3-}$ in pH 5 sodium acetate buffer is incorrectly reported.²³ Our data indicate $\epsilon(\lambda = 311 \text{ nm}) = 4.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

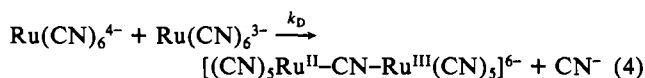
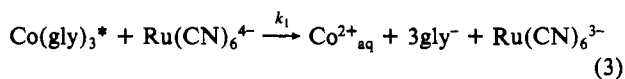
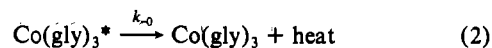
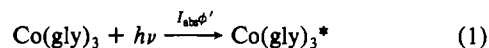
Calculations based on theoretical grounds¹⁴ support the conclusion reached above. A brief discussion of available data on iron and ruthenium cyanide compounds is followed by a discussion of the putative ruthenium dimer I. Observations of E_{opt} , the optical energy for the intervalence charge-transfer transition, for a series of $\text{M}(\text{CN})_6^{4-}, (\text{NH}_3)_5\text{RuL}^{3+}$ ion pairs have been made.²⁴ Taking the set of four pairs of data in which $\text{M} = \text{Fe}$ and Ru and L is the same for each ion pair, one obtains an average ΔE_{opt} of $4.64 \times 10^3 \text{ cm}^{-1}$. There are several contributions to this number, but the largest are the ΔE° values for $\text{M}(\text{CN})_6^{3-/4-}$ ($\text{M} = \text{Fe}, \text{Ru}$) and $\Delta\lambda$, where λ is the reorganizational energy. A significant factor in the latter is the difference in the energies of the $\text{M}(\text{CN})_6^{3-}$ $d^5(\text{A})$ and $d^5(\text{E})$ states resulting from spin-orbit coupling.²⁴ $\Delta E_{1/2}$ is $4.14 \times 10^3 \text{ cm}^{-1}$,²⁴ and $\Delta\lambda$ due to spin-orbit effects is about $0.7 \times 10^3 \text{ cm}^{-1}$.^{24,25} The sum of these is $4.84 \times 10^3 \text{ cm}^{-1}$ in reasonable agreement with $\Delta E_{\text{opt}} = 4.64 \times 10^3 \text{ cm}^{-1}$ calculated from the data of Curtis and Meyer.²⁴

Cyanide-bridged complexes with Fe(III) as the acceptor and Fe(II)¹⁹ or Ru(II)²⁰ as the donor have been mentioned above. ΔE_{opt} between these two compounds is $4.72 \times 10^3 \text{ cm}^{-1}$. Thus, for this small set of compounds, the replacement of Fe(II) with Ru(II) has a predictable effect on the optical spectrum.

Regarding the putative cyanide-bridged Ru dimer, one should be able to predict its E_{opt} from either the Fe(II),Fe(III) compound (using $\Delta\lambda_{\text{spin-orbit}}$) or the Ru(II),Fe(III) compound (using ΔE°). Both computations yield similar calculated ΔE_{opt} values for Ru-(II),Ru(III) compound, $\sim 8.3\text{--}8.4 \times 10^3 \text{ cm}^{-1}$. The experimental value of $9.14 \times 10^3 \text{ cm}^{-1}$ is in reasonable agreement with this. The difference is probably due to two small effects. One is the difference in the redox potential shift for Fe and Ru complexes in changing a cyanide to an isocyanide ligand, and the other is the difference in inner- and outer-sphere reorganizational energies for Fe(III) and Ru(III) cyanide complexes.

It is possible that the dicyano-bridged compound is responsible for the observed spectra. The near-infrared spectra of the analogous singly and doubly bridged iron compounds are very similar,^{19,26} E_{opt} differing by only $0.1 \times 10^3 \text{ cm}^{-1}$. The fact that the complex we observe is rapidly formed from the monoquo complex reacting with a hexacyano complex, rather than being formed from a pair of monoquo complexes,²⁶ leads us to believe that the monocyano bridge is more likely responsible for the observed spectra.

If we turn now to a consideration of the mechanism, the photochemical formation of the complex must come from the oxidation of $\text{Ru}(\text{CN})_6^{4-}$ by $\text{Co}(\text{gly})_3^*$ or a species derived from aquation of $\text{Co}(\text{gly})_3$. We propose the following scheme to explain our results:



Reaction 1 is the excitation of the cobalt complex. The complex has a molar absorptivity at 442 nm of $22 \text{ M}^{-1} \text{ cm}^{-1}$. The prob-

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Table I. Effect of CN^- on Formation of I

	ϕ/ϕ'
no CN^- ^a	0.36
CN^- after photolysis	0.12
CN^- during photolysis	0.036

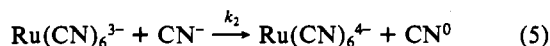
$$^a [\text{CN}^-] + [\text{HCN}] = 1.0 \times 10^{-1} \text{ M.}$$

ability of populating the reactive excited state following photon absorption is ϕ' , and I_{abs} is photons absorbed (M) per second. As reactions 3 and 4 indicate, photolysis in unbuffered solution should yield a basic shift in pH. This is observed experimentally. The chemistry of $\text{Ru}(\text{CN})_6^{3-}$ in aqueous solutions is complex. It has recently been studied in some detail.¹⁵ Under the conditions employed in our work (pH 5), the half-life of $\text{Ru}(\text{CN})_6^{3-}$ is reported to be 10 h.¹⁵ However aquation of the complex, ligand oxidation and conversion to cyanate have been observed. The charge-transfer band at 1094 nm was also seen¹⁵ after solutions of $\text{Ru}(\text{CN})_6^{3-}$ were aged for 3 days. We have not observed the spectrum of $\text{Ru}(\text{CN})_6^{3-}$ in our photolyzed solutions, but we did see an absorbance in the 400–500-nm region that could be attributed to $\text{Ru}(\text{CN})_6^{3-}$ after the addition of H_2O_2 to $\text{Ru}(\text{CN})_6^{4-}$. It is interesting that our conditions favor rapid reaction of $\text{Ru}(\text{CN})_6^{3-}$ while those employed by Crean and Shug¹⁵ did not. An investigation of the reaction kinetics was carried out.

A steady-state analysis of the above reaction scheme leads to a linear correlation between the inverse of the quantum yield²⁷ of the formation of I, ϕ^{-1} , and $[\text{Ru}(\text{CN})_6^{4-}]^{-1}$ with intercept $1/\phi'$ and slope $k_{-0}/k_1\phi'$. This correlation is experimentally confirmed. The value of the intercept yields $\phi' = 0.116 \pm 0.021$. The slope divided by the intercept yields $k_{-0}/k_1 = (6.09 \pm 1.16) \times 10^{-3} \text{ M}$. Assuming that k_1 is diffusion controlled ($7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for two 3-Å radius molecules using the Stokes–Einstein and Smoluchowski relationships), we estimate that $k_{-0} = (4.3 \pm 0.9) \times 10^8 \text{ s}^{-1}$. This corresponds to an excited-state lifetime of $23 \pm 4 \text{ ns}$. This seems long for a nonluminescent state, but it has been demonstrated that $\text{Co}(\text{en})_3^{3+}$ has a nonluminescent excited state with a 10-ns lifetime.¹²

The fact that $\phi' \neq 1$ perhaps may be interpreted as evidence for a chemical intermediate coming from $\text{Co}(\text{gly})_3^*$ that reacts with $\text{Ru}(\text{CN})_6^{4-}$, rather than the reaction occurring with the excited state. Flash photolysis studies would help elucidate this aspect of the reactivity of $\text{Co}(\text{gly})_3^*$.

If the reaction mechanism outlined in reactions 1–4 is correct, then the addition of NaCN to the mixture being photolyzed should decrease color formation. The system is complex, and several possible reactions (5 and 6) should be considered in addition to the reverse of reaction 4.



Two points cause less importance to be given to the reversal of reaction 4. The dissociation of the analogue $[(\text{CN})_5\text{Ru}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}(\text{CN})_5]^{6-}$ is extremely slow; a dissociation rate constant on the order of 10^{-9} s^{-1} can be estimated from data in ref 20. Also, our own data, if treated assuming that reaction 4 is a reversible equilibrium, yield very poor statistics. In order to see the influence of CN^- , large concentrations were required, and for the highest concentration of CN^- used in our experiments, (0.175 M) the pH was 10.0. This means that the protonation of CN^- is not acting to pull reaction 4 to the right, making the equilibrium appear irreversible at lower pH.

To help elucidate the roles of reactions 5 and 6, photolysis of the $\text{Co}(\text{gly})_3-\text{Ru}(\text{CN})_6^{4-}$ -acetate mixture was done in the absence of CN^- and the presence of CN^- , and then CN^- was added to the

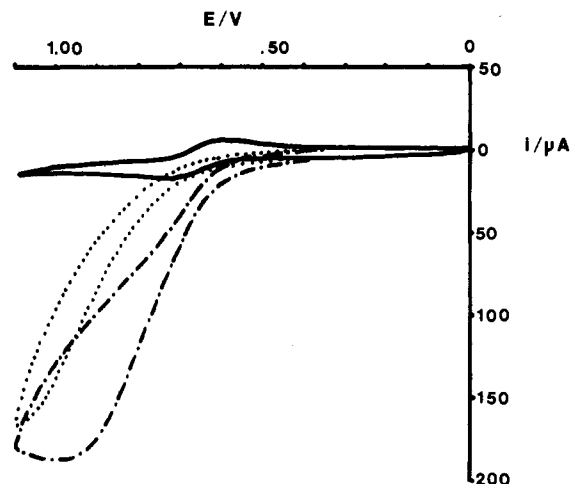


Figure 2. Cyclic voltammetry: (a) $\text{Ru}(\text{CN})_6^{4-}$ (0.0010 M) in pH 5 acetate buffer (—); (b) 0.050 M CN^- in 0.1 M acetate (pH 9.2) (---); (c) 0.0010 M $\text{Ru}(\text{CN})_6^{4-}$ and 0.050 M CN^- (pH 9.2) in 0.1 M acetate (-·-·-). The maximum difference between the latter two curves (occurring near $E = 0.85\text{--}0.90 \text{ V}$ vs. Ag/AgCl, 3 M NaCl) was taken to represent the catalytic current due to the oxidation of CN^- by $\text{Ru}(\text{CN})_6^{3-}$.

former solution. These data are shown in Table I. It can be seen that the presence of CN^- during photolysis, lowering the steady-state concentration of $\text{Ru}(\text{III})$ species (competition of reactions 4 and 5), leads to a lower rate of formation of the IT band than in the absence of CN^- . However, it is also true that the CN^- lowers the extent of formation of the IT band when added after the photolysis, indicating a direct reaction with the species responsible for the IT band. Thus both reactions 5 and 6 take place. An analysis of the kinetics in the presence of cyanide, assuming $[\text{CN}^-] \gg [\text{I}]$, and with steady states in $\text{Co}(\text{gly})_3^*$ and $\text{Ru}(\text{CN})_6^{3-}$ yields

$$[\text{I}] = \frac{f([\text{CN}^-])}{k_3[\text{CN}^-]} [1 - e^{-k_3[\text{CN}^-]t}] \quad (7)$$

where

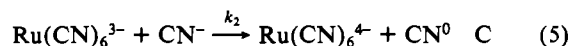
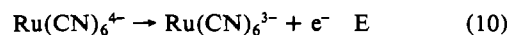
$$f([\text{CN}^-]) = \frac{k_1 k_D I_{\text{abs}} \phi [\text{Ru}(\text{CN})_6^{4-}]^2}{(k_{-0} + k_1 [\text{Ru}(\text{CN})_6^{4-}]) (k_D [\text{Ru}(\text{CN})_6^{4-}] + k_2 [\text{CN}^-])} \quad (8)$$

Our data indicate a linear growth in [I] for at least several minutes. Therefore $k_3[\text{CN}^-]t \ll 1$ (i.e., reaction 5 is more important than reaction 6) and

$$[\text{I}] = f([\text{CN}^-])t \quad (9)$$

Equation 9 leads to a linear relationship between $1/\phi$ and $[\text{CN}^-]$. The linear relationship holds well with slope = $k_2(k_{-0} + k_1[\text{Ru}(\text{CN})_6^{4-}])/k_D[\text{Ru}(\text{CN})_6^{4-}]^2 k_1 \phi'$ and an intercept = $(k_{-0} + k_1[\text{Ru}(\text{CN})_6^{4-}])/[\text{Ru}(\text{CN})_6^{4-}] k_1 \phi'$. The values obtained are slope = $104 \pm 8.9 \text{ M}^{-1}$ and intercept = 14.6 ± 0.8 . The intercept is made up of terms determined previously, and indeed, substitution of the known values of k_{-0} , k_1 , $[\text{Ru}(\text{CN})_6^{4-}]$, and ϕ' yields 14.6. The slope:intercept ratio and $[\text{Ru}(\text{CN})_6^{4-}]$ yield a value of $k_2/k_D = (6.38 \pm 0.64) \times 10^{-2}$.

The fact that $\text{Ru}(\text{CN})_6^{4-}$ can be electrochemically oxidized allows the determination of k_2 by using the following EC catalytic mechanism:

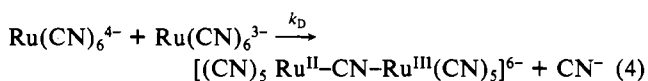
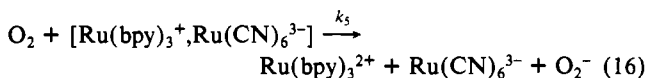
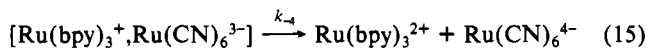
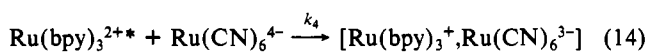
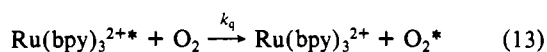
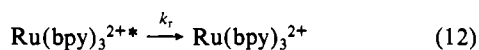
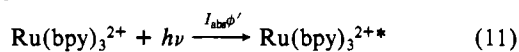


Under pseudo-first-order conditions ($[\text{CN}^-] + [\text{HCN}] = 0.05 \text{ M}$ and $[\text{Ru}(\text{CN})_6^{4-}] = 0.0010 \text{ M}$) the voltammetry at a glassy-carbon electrode is not ideal (see Figure 2). The major interference is from the direct oxidation of CN^- at the electrode surface. At large positive potentials, the direct anodic oxidation of CN^- lowers the concentration of CN^- near the electrode, decreasing

(27) The quantum yields ϕ are defined as the rate of formation of I divided by the absorbed intensity, I_{abs} . The latter is related to I_{incident} as $I_{\text{abs}} = I_{\text{incident}} [1 - 10^{-\epsilon C l}]$, where C is the concentration of photosensitive species, l is the path length, and ϵ (442 nm) = $22 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Co}(\text{gly})_3$ and $1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Ru}(\text{bpy})_3^{2+}$.

the rate of reaction 5. Nonetheless at less positive potentials a large increase in the oxidation current due to reactions 10 and 5 can be seen. The maximum difference in current between voltammograms b and c in Figure 2 was taken as the catalytic current.²⁸ From this datum the estimate of k_2 is $6.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$. From this an estimate of k_D is $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The kinetics of the formation of the dimer are therefore relatively rapid. The half-life of $\text{Ru}(\text{CN})_6^{3-}$ under our conditions of $[\text{Ru}(\text{CN})_6^{4-}] = 0.01 \text{ M}$ would be about 0.01 s. This clearly explains why we do not see spectroscopic evidence for $\text{Ru}(\text{CN})_6^{3-}$. In stark contrast, Crean and Shug¹⁵ report that $\text{Ru}(\text{CN})_6^{3-}$ is aquated in a slow step and then that species reacts with $\text{Ru}(\text{CN})_6^{4-}$ in a "very slow" step yielding blue product(s).

Quenching of the Charge-Transfer Excited State of $\text{Ru}(\text{bpy})_3^{2+}$ and the Formation of I. To determine the generality of these events we decided to study the formation of such a complex by electron transfer to the luminescent state of $\text{Ru}(\text{bpy})_3^{2+}$. The excited state is known to be reductively quenched by $\text{Ru}(\text{CN})_6^{4-}$ ²⁹ with $k \sim 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution and 0.5 M NaCl. Thus, photolysis of an aerated solution containing $1.0 \times 10^{-5} \text{ M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and $1.0 \times 10^{-2} \text{ M}$ $\text{Ru}(\text{CN})_6^{4-}$ in 0.1 M acetate pH 5 buffer leads to the formation of an IT band, which is the same in all respects to that obtained during the photolysis of the non-luminescent $\text{Co}(\text{gly})_3$ in the presence of $\text{Ru}(\text{CN})_6^{4-}$. This band grows in intensity with increasing photolysis time. When another solution containing the same species is purged with N_2 (10 min), it does not lead to the formation of observable IT bands even after 15 min of continuous photolysis. These results are consistent with the following reaction scheme:



In this scheme most of the reactions are known. In reaction 11 the efficiency of population of the charge-transfer excited state, ϕ' , is 1.³⁰ The excited-state lifetime is 620 ns,⁹ and k_q is $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁹ Reaction 14 has not been studied in detail, but in one report k_4 is given as $\sim 0.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ²⁹ at an ionic strength of 0.5 M. Since we saw no production of I in the absence of oxygen, it must mean that the thermal back-reaction between $\text{Ru}(\text{bpy})_3^+$ and $\text{Ru}(\text{CN})_6^{3-}$ is rapid, which is reasonable given the exergicity of the reaction. Also, the tendency for electrostatic attraction between them would be large. The reaction between $\text{Ru}(\text{bpy})_3^+$ and O_2 is also expected to be fast.

With the assumption of a steady state in $\text{Ru}(\text{bpy})_3^{2+*}$, $[\text{Ru}(\text{bpy})_3^+, \text{Ru}(\text{CN})_6^{3-}]$, and $\text{Ru}(\text{CN})_6^{3-}$ one arrives at the following equation for $d[\text{I}]/dt$:

$$\frac{d[\text{I}]}{dt} = \frac{k_4[\text{Ru}(\text{CN})_6^{4-}]}{k_r + k_q[\text{O}_2] + k_4[\text{Ru}(\text{CN})_6^{4-}]} \left(\frac{k_5[\text{O}_2]}{k_{-4} + k_5[\text{O}_2]} \right) I_{\text{abs}}\phi' \quad (17)$$

Linear relationships between $d[\text{I}]/dt$ and I_{abs} (altered by changing $[\text{Ru}(\text{bpy})_3^{2+}]$ and between $1/(d[\text{I}]/dt)$ and $1/[\text{Ru}(\text{CN})_6^{4-}]$ are expected. From the latter (inverse) plot the slope ($1.36 \pm 0.18 \times 10^4 \text{ s}$) divided by the intercept ($4.43 \pm 0.82 \times 10^6 \text{ M}^{-1} \text{ s}$) yields $(k_r + k_q[\text{O}_2])/k_4$. Since all the terms in the numerator are known, k_4 can be calculated as $(8.2 \pm 1.9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. It can also be calculated that the efficiency of production of $\text{Ru}(\text{CN})_6^{3-}$ in the presence of O_2 , $k_5[\text{O}_2]/(k_{-4} + k_5[\text{O}_2])$ is 0.016 ± 0.003 . The slope of the former plot gives the overall quantum efficiency as $(9.1 \pm 1.1) \times 10^{-3}$. The intercept is $(3.2 \pm 3.4) \times 10^{-10} \text{ M} \text{ s}^{-1}$, consistent with the expectation of an intercept of zero. The quantum efficiency can be used with the intercept from the inverse plot to yield a second estimate of k_4 , $(3.2 \pm 1.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The reason for the discrepancy in the values of k_4 may be due to ionic strength changes. In the experiment in which $[\text{Ru}(\text{CN})_6^{4-}]$ is altered, the maximum concentration of $\text{Ru}(\text{CN})_6^{4-}$ used was 0.01 M and the background electrolyte was 0.1 M acetate buffer. Because of the high charge on the $\text{Ru}(\text{CN})_6^{4-}$ a shift in ionic strength sufficient to alter the electrostatic influence on the formation of $[\text{Ru}(\text{CN})_6^{4-}, \text{Ru}(\text{bpy})_3^{2+}]$ could have occurred. Likewise, we feel that the value of k_4 is larger than the literature value ($\sim 0.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)²⁹ for reasons of ionic strength. The activity coefficient correction (eq 18) required to compare our

$$2z_a z_b \frac{A\mu^{1/2}}{1 + \mu^{1/2}} \quad A = 0.509 \quad (18)$$

value ($\mu = 0.1$) to that of Juris et al.²⁴ ($\mu = 0.5$) is 26. This is entirely consistent with the results.

The formation of the observed IT band has allowed us to further elucidate the complex chemistry of the cyanide complexes of ruthenium. The observation of redox processes initiated from an LF transition is somewhat unusual. This analysis has at least provided a lifetime measurement for $\text{Co}(\text{gly})_3^*$ (ca. 23 ns). Flash photolysis or transient absorption measurements are really required to understand the details of the events studied.

The formation of the IT band under several different sets of conditions indicates that the minimum requirement for formation of the dimer I is outer-sphere electron transfer from $\text{Ru}(\text{CN})_6^{4-}$ to form $\text{Ru}(\text{CN})_6^{3-}$. The data of Crean and Shug¹⁵ seem to indicate that the sequence of events is $\text{Ru}(\text{CN})_6^{3-} \rightarrow \text{Ru}(\text{CN})_5(\text{OH}_2)^{2-} \rightarrow$ dimer, and this occurs over days. Our data are inconsistent with an aquation requiring at least hours preceding the formation of I.

The $\text{Ru}(\text{CN})_6^{3-}$ absorption band at $21\,500 \text{ cm}^{-1}$ seen by Crean and Shug¹⁵ is very likely due to a ligand-to-metal charge-transfer (LMCT) band in analogy to the analogous $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Os}(\text{CN})_6^{3-}$ bands.³¹ It is known that $\text{Fe}(\text{CN})_6^{3-}$ undergoes substitution reactions, e.g. to $\text{Fe}(\text{CN})_5(\text{OH}_2)^{2-}$, upon illumination in the LMCT band.³² Thus, it is entirely possible that the more rapid effective rates of formation of the 1094-nm charge-transfer band observed by us is due to some photoassistance. However, it should also be pointed out that our experiments also had an excess of $\text{Ru}(\text{CN})_6^{4-}$ and a low concentration of $\text{Ru}(\text{CN})_6^{3-}$, exactly the opposite of Crean and Shug. It is interesting to note that in the analogous iron case Moggi et al.³³ noted a decrease in the rate of formation of a species of the nature of Prussian blue with an increase in the concentration of $\text{Fe}(\text{CN})_6^{3-}$ under photolysis. Further work on the photochemistry of $\text{Ru}(\text{CN})_6^{3-}$ is clearly required.

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