end of dipole of the metal chelate cations is near the N–H protons.

The sequence of decreasing mobility acac > acacBr > $acacNO_2$ is consistent with the view that the solvation is stronger for the cation with the substituents Br and NO_2 due to their increasing polarity, in addition to the increase in the van der Waals volume ($cm^3\ mol^{-1}$): H, 3.5; Br, 14.6; NO_2, 16.8.[15]

Registry No. $[Co(acac)_2(en)]ClO_4$, 15611-02-6; $[Co(acacBr)_2(en)]ClO_4$, 88610-49-5; $[Co(acacNO_2)_2(en)]ClO_4$, 88610-51-9; en, 107-15-3.

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Contribution from the Departments of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616,
and Saint Xavier College, Chicago, Illinois 60655

Decomposition of Aqueous Hexacyanoruthenate(III) Ions

FRANCES M. CREAN*[1a,b] and KENNETH SCHUG*[1a]

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Oxidation of aqueous $K_4Ru(CN)_6$ by Ce(IV) followed by ion-exchange treatment produces aqueous solutions containing only $Ru(CN)_6^{3-}$, K^+, and sulfate as solute species. These solutions were used to study the spontaneous decomposition and several related reactions of the $Ru(CN)_6^{3-}$ ion. The decomposition has been interpreted as involving (1) aquation ($Ru(CN)_6^{3-} + H_2O \rightarrow Ru(CN)_5OH_2^{2-}$), (2) dimerization ($(Ru(CN)_5(OH_2)^{2-,3-} \rightarrow$ CN-bridged dimers), and (3) ligand oxidation ($2Ru(CN)_6^{3-} + 2OH^- \rightarrow Ru(CN)_6^{4-} + Ru(CN)_5(CNO)^{4-} + H_2O$). In addition, the reduction of $Ru(CN)_6^{3-}$ by free CN^- and its reaction with several oxidants (Ce^{IV}, MnO_4^-, PbO_2) are described.

Introduction

The study of the aqueous solution chemistry of the $Ru^{III}(CN)_6^{3-}$ ion is complicated by its spontaneous decomposition. Thus, Deford and Davidson[2] have reported that solutions of $Ru^{III}(CN)_6^{3-}$ prepared by reacting $Ru^{II}(CN)_6^{4-}$ with strong oxidizing agents (e.g., acidic cerium(IV)) are unstable under the following conditions: (a) ruthenium concentrations greater than 1 mM; (b) moderate acidity (e.g., 0.05 M HCl); and (c) presence of excess oxidant (viz., Ce^{4+}, H_2O_2, BiO_3^-, and Cl_2). Furthermore, isolation of a solid salt of $Ru^{III}(CN)_6^{3-}$ from aqueous solutions has not been reported, although solid $(Et_4N)_3[Ru^{III}(CN)_6]$ has been reported[3] as a product of the photooxidation of $(Et_4N)_4[Ru^{II}(CN)_6]$ in $CHCl_3$.

We report here the results of a study of the decomposition of aqueous $Ru(CN)_6^{3-}$, which establish that aquation, dimerization, and redox reactions all contribute to the observed decomposition.

Experimental Section

Materials and Apparatus. All chemicals were of reagent grade unless otherwise specified. Doubly deionized water was used for all solutions. $K_4Ru(CN)_6{\cdot}3H_2O$ (Alfa products) analysis: percent weight loss on drying 10.8 (±0.2), calcd 11.6; percent Ru (atomic absorption using a carbon-rod atomizer) 20.53 (±1.43), calcd 21.61 for trihydrate. The Serfass method for cyanide[4] yielded less than half the calculated cyanide, a result not unexpected for a substitution-inert cyano complex.

Aqueous solutions containing the $Ru(CN)_6^{3-}$ ion at known concentrations were prepared by the Ce(IV) (from $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$) oxidation of aqueous $K_4Ru(CN)_6$ in dilute (~0.005 M) sulfuric acid followed by ion-exchange (Dowex 50W-X8 in K^+ form) removal of Ce^{3+} and H^+. The entire process can be completed in from 5 to 25 min, depending on the volume of solution. Use of equimolar amounts of reactants and concentrations below 10^{-3} M produced $Ru(CN)_6^{3-}$ solutions with UV–vis spectra in good agreement with previous reports[3,5] and minimized the side reactions that occur in acidic solutions or at higher ruthenium concentrations. The resultant solutions, containing only K^+, SO_4^{2-}, and $Ru(CN)_6^{3-}$, have been used as the starting material for most of our studies. We have been unsuccessful in preparing a pure solid compound of known composition containing the ruthenicyanide ion and have not developed a reliable analytical method for determination of total cyanide in these solutions.

Instrumentation used was as follows: IR, Beckman Model 20AX and Perkin-Elmer Model 257; UV–vis, Cary Models 14 and 15; pH, Coleman Model 10; atomic absorption, Varian Techtron Model 1200.

Analytical Procedures. Three methods were used to determine free cyanide ion concentration: high-concentration stock solutions, titrimetrically with $AgNO_3$ (*p*-(dimethylamino)benzalrhodamine indicator);[6] 0.04–1.1 mM solutions, electrochemically by use of an Orion cyanide ion selective electrode; 0.5–10 μm solutions, spectrophotometrically by the pyridine–pyrazalone method using cyaniVer cyanide Reagent Powder Pillows.[7] Cyanogen was determined[8] by flushing the reactant solution with nitrogen or argon, removing any HCN present by an aqueous $AgNO_3$ trap, collecting the C_2N_2 in 1 M NaOH, and analyzing for the CN^- produced in the base-catalyzed disproportionation. Cyanate solutions were standardized[9] by a modified Volhard titration and determined in reactant solutions by acid hydrolysis[6] (0.1 M H_2SO_4 at 95 °C for 1 h) to produce NH_4^+ followed by conversion to NH_3 and use of an Orion NH_3 specific electrode at pH 12 or 12.5. The method was checked with standard KOCN solutions. The CO_2 was determined with an Orion CO_2 electrode.

O_2/H_2O_2 Studies. Stoichiometric studies involving O_2 (and H_2O_2 after conversion to O_2 by addition of MnO_2) were carried out in two ways: (a) by gas chromatography on a Carle 6500 T instrument equipped with a 4-ft column containing 5-Å molecular sieves and (b) by a modification of the Winkler method[10] for dissolved oxygen.

Results and Discussion

Ruthenocyanide Spectra. The electronic spectrum (200–1200 nm) of dilute aqueous $K_4Ru(CN)_6$ (pH 3–10) has

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0020-1669/84/1323-0853$01.50/0

Table I. Selected Spectral Data on $Ru(CN)_6{}^{3-}$

this work[a]		lit. values[b]	
λ, nm	ϵ, M^{-1} cm^{-1}	ϵ,[c] M^{-1} cm^{-1}	ϵ,[d] M^{-1} cm^{-1}
205	~5100		
268 (min)	840		(842)
298 (max)	2150		2046
313 (min)	1860	(1770)	(1583)
328 (max)	2370	2160	2184
348 (min)	1430	(1230)	(1367)
356 (max)	1570	(1250)	1455
396 (min)	320	(215)	(211)
460 (max)	1020	920	875

[a] Estimated uncertainty less than 5% except for λ = 205 nm. [b] Numbers in parentheses calculated from figures in references cited. [c] Reference 5. [d] Reference 3.

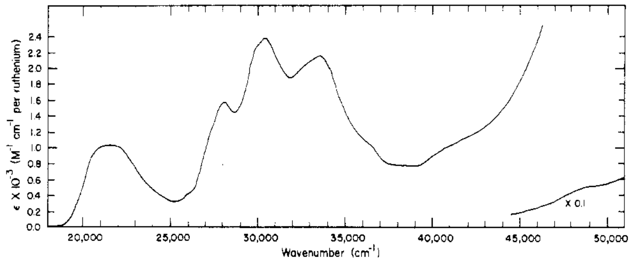


Figure 1. Electronic absorption spectrum of $K_3Ru(CN)_6$ in unbuffered neutral solution, obtained by extrapolation of time-dependent spectra of $Ru(CN)_6{}^{3-}$ to the time of addition of Ce^{IV} to $K_4Ru(CN)_6$.

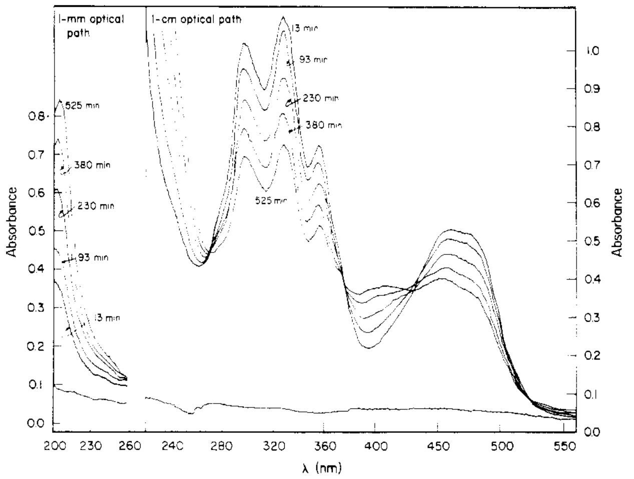
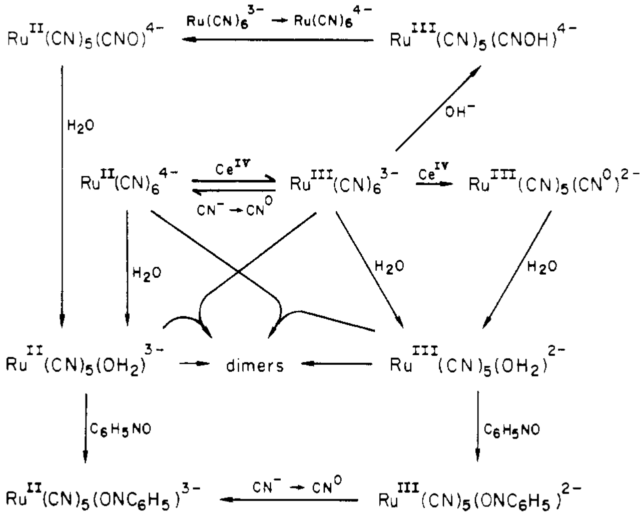


Figure 2. First 9 h of time-dependent electronic absorption spectra of 0.45 mM $K_3Ru(CN)_6$ in unbuffered neutral solution.

Scheme I



as its main feature an intense peak (ϵ = 3.7×10^4 M^{-1} cm^{-1}) at 205 nm (in good agreement with that previously reported[11]) that remains essentially unchanged for months, although small spectral changes occur slowly on the long-wavelength side of this peak (e.g., ϵ_{295} increased from 0 to 680 in 3 weeks at ambient temperatures in a typical 4×10^{-4} M solution at pH 6). Aquation of $Ru(CN)_6{}^{4-}$ may be contributing to this spectral change since it has been reported[12,13] that $Ru^{II}(CN)_5(OH_2)^{3-}$ has an absorption maximum near 310 nm.

As the pH is increased above 10, the spectra of fresh solutions correspond to the sum of the absorptions of $Ru(CN)_6{}^{4-}$ and the OH^- blank, finally becoming indistinguishable from the OH^- blank alone.

In acidic solutions (pH <3) the spectra undergo a variety of changes that depend on the acid concentration and on the presence or absence of air. Briefly, argon-flushed solutions develop a shoulder between 270 and 370 nm (ϵ_{app} ~1200) with a steep rise toward shorter wavelengths and a long tail extending to 800 nm; these solutions eventually form white precipitates. In the presence of air, the spectra initially resemble those described above; but on aging (up to 80 days), the steeply rising UV slope moves toward the visible and a pronounced (but poorly reproducible) absorption develops at much longer wavelengths (780–1200 nm), accompanied by formation of dark blue particles in the solutions.

Although these systems have not been studied in detail, it is likely that polymerization reactions are occurring, culminating in cyano-bridged polymers containing Ru(II) and/or Ru(III) centers.

Ruthenicyanide Spectra. The spectrum of a freshly prepared dilute $Ru(CN)_6{}^{3-}$ solution contains several distinctive peaks in the 300–500-nm region. The ϵ values (Table I and Figure 1) are based on the assumption that the conversion of $Ru(CN)_6{}^{4-}$ to $Ru(CN)_6{}^{3-}$ is quantitative; corrections have been made for the slow ($t_{1/2}$ ~ 10 h at pH 5) decomposition reaction by extrapolation back to the time of addition of the Ce(IV) oxidant.

Qualitatively, the spectrum closely resembles those of $Fe(CN)_6{}^{3-}$ and $Os(CN)_6{}^{3-}$ reported and discussed by Alexander and Gray.[14] Furthermore, our ϵ_{max} values for $Ru(CN)_6{}^{3-}$ are 5–17% higher than those previously reported[3,5] in studies using less direct preparative methods (viz., photochemical oxidation of $Ru(CN)_4{}^{6-}$ in aerated chloroform[3] and oxidation of the same species by hydroxyl radicals produced by pulse radiolysis[5]). Reproducibility of ϵ_{max} values was about ±5% except near 205 nm (where $Ru(CN)_6{}^{4-}$ has a very large absorption peak).

Decomposition of $Ru(CN)_6{}^{3-}$. The spectral behavior of a freshly prepared solution of $Ru(CN)_6{}^{3-}$ depends strongly on the pH of the solution and on the concentration of the complex. Because experimental difficulties, e.g., precipitate formation, are encountered at higher concentrations, most of the work to be described has been limited to concentrations below 10^{-3} M in $Ru(CN)_6{}^{3-}$. For these solutions at room temperature, a qualitative summary of spectral changes is as follows: at high acidity ($[H^+] > 0.1$ M), an intensely blue intractable solid forms within a few hours; from pH 2 to 6, a slow decomposition (3–4 days) occurs; above pH 6, the rate of decomposition increases with pH until at pH 12 the $Ru(CN)_6{}^{3-}$ spectrum disappears in a few minutes. The principal feature of the spectral change at pH 2 and above is a decrease in the $Ru(CN)_6{}^{3-}$ peaks with eventual loss of the initial isosbestic points

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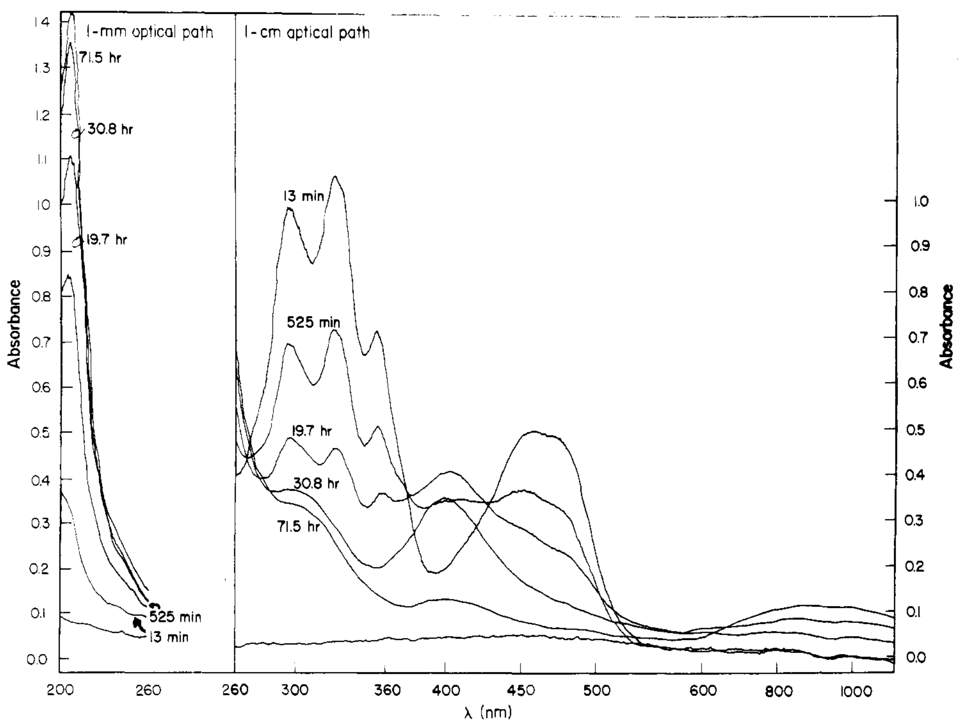

Figure 3. First 3 days of time-dependent electronic absorption spectra of 0.45 mM $K_3Ru(CN)_6$ in unbuffered neutral solution.

as shown in Figures 2 and 3.

An explanation of the qualitative behavior of aqueous $Ru(CN)_6^{3-}$ described above clearly requires the occurrence of at least two decomposition reactions. Three plausible primary decomposition paths are (a) aquation of the cyano ligand, (b) reduction or disproportionation of Ru^{III}, and (c) oxidation of the cyanide ligand. Following these primary processes, secondary decomposition steps can include additional reactions (aquation, oxidation–reduction, polymerization) of the species formed in the primary steps. The experiments described below lead to a consistent and plausible reaction scheme for the decomposition of dilute $Ru(CN)_6^{3-}$ in weakly acidic, neutral, and basic solutions. The proposed reactions are summarized in Scheme I.

Reduction of $Ru(CN)_6^{3-}$. Over the pH range 2–12 the following common features have been established from spectral studies on aqueous $Ru(CN)_6^{3-}$: (a) disappearance of the absorption peaks associated with $Ru(CN)_6^{3-}$; (b) appearance of new peaks at 205 nm (sh), ~400 nm (br), and 1100 nm (vbr); (c) reappearance of $Ru(CN)_6^{3-}$ peaks on reoxidation of aged solutions.

These observations establish that $Ru(CN)_6^{4-}$ is an important reaction product in the spontaneous decomposition of $Ru(CN)_6^{3-}$. Further insight into the nature of this reduction is provided by experiments with added OH^- and with added CN^-.

Addition of aqueous NaOH to freshly prepared ruthenicyanide solution causes a rapid disappearance of the ruthenicyanide peaks and appearance of a new peak at 205 nm, with 90% or more of the absorption expected for complete conversion to ruthenocyanide. Treatment of this solution with a stoichiometric amount of acidic Ce(IV) converts the spectrum to that of the original ruthenicyanide in about 85% "yield". These observations strongly support the occurrence of highly efficient redox reactions of the hexacyanoruthenium species with retention of coordinated cyanide. The simplest explanation for the effect of added hydroxide would be that OH^- acts as a reducing agent for $Ru(CN)_6^{3-}$ in alkaline solution:

$$Ru(CN)_6^{3-} + OH^- \xrightarrow{?} Ru(CN)_6^{4-} + (^1/_2H_2O_2 \text{ or } ^1/_4O_2) \tag{1}$$

Experiments carried out to test this hypothesis, however, showed that neither O_2 nor H_2O_2 is produced when $Ru(CN)_6^{3-}$ is converted (with at least 95% efficiency) to $Ru(CN)_6^{4-}$ in 0.01 M NaOH. A more detailed discussion of the reaction in alkaline solution appears in a later section.

The effect of added NaCN on $Ru(CN)_6^{3-}$ solutions was studied by (a) spectral observations in the 200–800-nm range, (b) monitoring the free CN^- concentration, and (c) isolation and identification of reaction products. Addition of NaCN in equimolar or greater amounts (in solutions buffered at pH 6) causes an immediate decrease in all $Ru(CN)_6^{3-}$ peaks and the appearance of a strong new peak at 205 nm. Addition of $Ru(CN)_6^{3-}$ solution directly from the preparative cation-exchange resin column into buffered solutions containing a 4- to 10-fold molar excess of CN^- produced solutions spectrally indistinguishable from $Ru(CN)_6^{4-}$ in greater than 95% yield. These solutions could then be oxidized with acidic Ce^{IV} to regenerate $Ru(CN)_6^{3-}$. Twenty-six experiments were conducted (seventeen with $[Ru(CN)_6^{3-}] = 4 \times 10^{-4}$ M and nine with $[Ru(CN)_6^{3-}] = 2 \times 10^{-4}$ M) with added CN^- (from equimolarity to 8-fold excess) in which final free cyanide was determined. The average value for $\Delta[CN^-]/[Ru]_0$ was 0.96 ± 0.16 (0.99 ± 0.11 with the four most discrepant points removed). These results provide strong support for a reaction of $Ru(CN)_6^{3-}$ with CN^- having a 1:1 stoichiometry in neutral solutions; a possible reaction sequence is[15]

$$Ru(CN)_6^{3-} + CN^- \rightarrow Ru(CN)_6^{4-} + CN^0 \tag{2}$$

$$2CN^0 \rightarrow C_2N_2 \text{ (and other products?)} \tag{3}$$

Cyanogen determinations (0.4 mM $Ru(CN)_6^{3-}$, 1.5–4 mM total cyanide, 1.5–5 h reaction time at pH 6) gave results corresponding to 12–43% conversion of CN^0 to C_2N_2. Control experiments using Cu(II) and CN^- yielded ~40% of the C_2N_2 expected on the basis of the equation $Cu^{2+} + 2CN^- \rightarrow CuCN + {}^1/_2C_2N_2$. It is not known whether the low yield of C_2N_2 is due to analytical difficulties, side reactions of the CN^0 radical, or hydrolysis of C_2N_2.[16] Evidence for the complexity

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[15] Sawyer, D. T.; Day, R. J. *J. Electroanal. Chem.* **1963**, *5*, 195.

[16] Cyanogen yields of ~41% for the $Cu^{II} + CN^-$ reaction have been reported by: Janz, G. J. *Inorg. Synth.* **1970**, *5*, 43–8.

of the aqueous chemistry of the CN radical is provided by electrochemical studies[17] that quantitatively established one-electron oxidation of CN^- but were unsuccessful in establishing the overall stoichiometry (ammonia being the only reported product).

Spontaneous Decomposition of $Ru(CN)_6^{3-}$. Solutions of $Ru(CN)_6^{3-}$ that have been allowed to decompose for several days under neutral conditions differ from those that have decomposed at pH 12 (or those with added CN^- at pH 6) as follows: (a) They contain a broad, fairly strong absorption peak near 400 nm. (b) On reoxidation with Ce(IV), only about 75% of the $Ru(CN)_6^{3-}$ is regenerated and the final spectrum contains additional absorption peaks.

Since aquation is a plausible decomposition pathway, experiments were performed with added Hg(II) (as $HgCl_2$), which is known to accelerate aquation of other metal–cyano complexes.[18] In solutions buffered at pH 6 that were 4×10^{-4} M in $Ru(CN)_6^{3-}$ and 2×10^{-4} M in $HgCl_2$, spectral changes similar to those observed in the absence of Hg(II) occurred, but with a fourfold increase in rate. (Attempts to conduct this experiment at a higher concentration of either reactant were unsuccessful due to precipitate formation within a few minutes of mixing.) The most obvious difference between the Hg(II)-containing and control solutions was a much stronger absorption near 400 nm in the presence of mercury. This observation, plus the analogy with the $Fe(CN)_6^{3-}/Fe(CN)_5(OH_2)^{2-}$ system,[19] suggests strongly that the 400-nm absorption is due to the monoaquated species $Ru(CN)_5(OH_2)^{2-}$ and that the principal change occurring in the presence of mercury is

$$Ru^{III}(CN)_6^{3-} + Hg(II) \rightarrow Ru^{III}(CN)_5(OH_2)^{2-} + HgCN^+ \text{ (or } {}^1/_2Hg(CN)_2) \quad (4)$$

From solutions in which $Ru(CN)_6^{3-}$ peaks have just disappeared, it is possible to estimate $\epsilon \geq 1500$ M^{-1} cm^{-1} at $\lambda_{max} = 400$ nm for $Ru^{III}(CN)_5(OH_2)^{2-}$. (For comparison, $Fe^{III}(CN)_5(OH_2)^{2-}$ has $\lambda_{max} = 394$ nm (ϵ 743)[19] and $Fe^{II}(CN)_5(OH)^{3-}$ has $\lambda_{max} = 390$ nm (ϵ 1740).[20])

One other relevant observation on neutral solutions of $Ru(CN)_6^{3-}$ is that as the absorption near 400 nm decreases on long standing, new absorptions appear at about 1100 nm, suggestive of bridged dinuclear species involving charge-transfer transitions between Ru(II) and Ru(III) centers.

In summary, the reaction scheme (5)–(7) (where eq 6 = eq 2 + eq 3) is proposed to account for the spectral and chemical behavior of $Ru(CN)_6^{3-}$ in neutral solution.

$$Ru^{III}(CN)_6^{3-} + H_2O \xrightarrow{\text{slow}} Ru^{III}(CN)_5(OH_2)^{2-} + CN^- \quad (5)$$

$$Ru^{III}(CN)_6^{3-} + CN^- \xrightarrow{\text{fast}} Ru^{II}(CN)_6^{4-} + {}^1/_2C_2N_2 \text{ (etc.)} \quad (6)$$

$$Ru^{II}(CN)_6^{4-} + Ru^{III}(CN)_5(OH_2)^{2-} \xrightarrow{\text{very slow}} (NC)_5Ru^{II}CNRu^{III}(CN)_5^{6-} + H_2O \quad (7)$$

Further support for the above sequence is provided by experiments in which acidic (pH ~2) aqueous $Ru(CN)_6^{3-}$ is allowed to decompose in the presence of excess nitrosobenzene (C_6H_5NO) while both the spectrum and the free cyanide concentration are monitored. It is known[21] that $Ru^{II}(CN)_5(OH_2)^{3-}$ reacts rapidly and irreversibly with nitrosobenzene to produce $Ru^{II}(CN)_5(ONC_6H_5)^{3-}$ with an absorption maximum at 475 nm. We have obtained $\epsilon_{475} = 7600$ M^{-1} cm^{-1} for this species from solutions prepared from $Ru(CN)_6^{4-}$, $HgCl_2$, and nitrosobenzene. It was found that in the presence of nitrosobenzene the spectral peaks attributed above to dimer formation did not appear and that on long standing (25 days) all the original ruthenium could be accounted for as $Ru^{II}(CN)_5(ONC_6H_5)^{3-}$; in addition, 0.5 mol of CN^- was produced/mol of $Ru(CN)_6^{3-}$ taken. The $Ru^{II}(CN)_5(ONC_6H_5)^{3-}$ peak appeared more rapidly in $Ru^{III}(CN)_6^{3-}$ solutions than in $Ru^{II}(CN)_6^{4-}$ solutions of the same concentration. These observations can be explained if $Ru^{III}(CN)_5(OH_2)^{2-}$ is converted to $Ru^{II}(CN)_5(ONC_6H_5)^{2-}$ faster than to dimer. We propose a sequence of reactions in which (5) and (2) are followed by substitution (8) and (9), Ru^{III} reduction by CN^- (10), and CN^0 disproportionation (11):

$$Ru^{III}(CN)_5(OH_2)^{2-} + C_6H_5NO \rightarrow Ru^{III}(CN)_5(ONC_6H_5)^{2-} + H_2O \quad (8)$$

$$Ru^{II}(CN)_6^{4-} + C_6H_5NO \rightarrow Ru^{II}(CN)_5(ONC_6H_5)^{3-} + CN^- \quad (9)$$

$$Ru^{III}(CN)_5(ONC_6H_5)^{2-} + CN^- \rightarrow Ru^{II}(CN)_5(ONC_6H_5)^{3-} + CN^0 \quad (10)$$

$$2CN^0 + H_2O \rightarrow HCN + HOCN \quad (11)$$

The net reaction in the presence of nitrosobenzene then becomes

$$2Ru^{III}(CN)_6^{3-} + 2C_6H_5NO + H_2O \rightarrow 2Ru^{II}(CN)_5(ONC_6H_5)^{3-} + HCN + HOCN \quad (12)$$

Oxidation Studies. Addition of Ce(IV) to solutions of $Ru(CN)_6^{3-}$ (or addition of more than 1 mol of Ce(IV)/mol of $Ru(CN)_6^{4-}$) produces a rapid decrease in the $Ru(CN)_6^{3-}$ peaks and an increase near 400 nm; the simplest explanation for this is a one-electron oxidation of a CN^- ligand followed by a rapid aquation.

$$Ru^{III}(CN)_6^{3-} + Ce(IV) \rightarrow Ru^{III}(CN)_5(CN^0)^{2-} + Ce(III) \quad (13)$$

$$Ru(CN)_5(CN^0)^{2-} + H_2O \rightarrow Ru^{III}(CN)_5(OH_2)^{2-} + CN^0 \quad (14)$$

$$2CN^0 \rightarrow C_2N_2 + \text{other products}$$

Qualitatively similar observations have been made in systems in which MnO_4^- or solid PbO_2 were used as oxidants.

To obtain more detailed information on the species present in aged neutral solutions of $Ru(CN)_6^{3-}$, a series of experiments was carried out in which varying amounts of Ce(IV) were added to such aged solutions (Ce^{IV}:Ru ratios of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 1.0). Only in the ratio range 0.3–0.8 were plots of absorbance vs. added Ce^{IV} at λ = 298, 328, 356, and 460 nm linear with the slope expected for conversion of $Ru(CN)_6^{4-}$ to $Ru(CN)_6^{3-}$. This result is consistent with the presence in aged $Ru(CN)_6^{3-}$ solutions of about 50% of the total ruthenium as $Ru(CN)_6^{4-}$; it also requires that at least two other oxidations occur, one (or more) more readily than $Ru(CN)_6^{4-}$ and one (or more) less readily. A possible sequence for these oxidations is the Ru^{II} dimer to the Ru^{II}/Ru^{III} dimer and the mixed dimer to the Ru^{III} dimer.

Reaction of $Ru(CN)_6^{3-}$ + H_2O_2. The failure to detect H_2O_2 or O_2 as reaction products in the reaction of $Ru(CN)_6^{3-}$ with OH^- could arise from a rapid reaction between these products and the parent complex. Since $Ru(CN)_6^{3-}$ in the presence of O_2 does not undergo spectral change at an appreciable rate, a rapid reaction with O_2 can be eliminated. Experiments carried out with added H_2O_2, however, showed that addition of small amounts of H_2O_2 to dilute solutions of $Ru(CN)_6^{3-}$ significantly accelerates spectral changes. Since H_2O_2 could in principle function as a reductant ($Ru^{III} \rightarrow Ru^{II}$), an oxidant

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(17) Adamson, A. W. *J. Phys. Chem.* **1952**, *56*, 858–62. A stoichiometry of 2 $Fe(CN)_6^{3-}/CN^-$ was observed in this analogous system under different reaction conditions (pH ~9, $[CN^-]$ ~ 0.1 M).

(18) E.g.: Espenson, J. H.; Bushey, W. R. *Inorg. Chem.* **1971**, *10*, 2457–63.

(19) Espenson, J. H.; Wolenuk, S. G. *Inorg. Chem.* **1972**, *11*, 2034–41.

(20) Davies, G.; Garafalo, A. *Inorg. Chem.* **1976**, *15*, 1101–6.

(21) Emschwiller, G. *C. R. Hebd. Seances Acad. Sci.* **1959**, *248*, 959–61.

($CN^- \rightarrow CNO^-$), or a catalyst ($Ru^{III}/CN^- \rightarrow Ru^{II}/CNO^-$), experiments were performed to measure the yield of O_2. It was found that 0.5 mol of O_2 was produced/mol of H_2O_2 used, the result expected if H_2O_2 produces O_2 only via disproportionation to H_2O and O_2. It is therefore proposed that a reaction sequence similar to the following occurs in alkaline solutions containing $Ru(CN)_6^{3-}$ and H_2O_2.

$$Ru(CN)_6^{3-} + H_2O_2 \rightarrow Ru(CN)_6^{4-} + HO_2 + H^+$$

$$Ru(CN)_6^{3-} + HO_2 \rightarrow (NC)_5Ru(CNOOH)^{3-}$$

$$(NC)_5Ru(CNOOH)^{3-} + H_2O \rightarrow (NC)_5Ru(CNO)^{4-} + H_2O_2 + H^+$$

$$\text{net: } 2Ru(CN)_6^{3-} + H_2O \rightarrow Ru(CN)_6^{4-} + (NC)_5Ru(CNO)^{4-} + 2H^+$$

The hydrogen peroxide is simultaneously decomposed by disproportionation via catalysis by an appropriate Ru^{II}/Ru^{III} couple.

Stoichiometry of $Ru(CN)_6^{3-}$ + OH^-. Failure to detect either H_2O_2 or O_2 as reaction products in alkaline solutions of $Ru(CN)_6^{3-}$ (vide supra) suggests that oxygen is being incorporated into the system via oxidation of a cyano ligand. The reaction sequence (15) and (16) is postulated where L = $(NCOH)^{2-}$

$$Ru^{III}(CN)_6^{3-} + OH^- \rightarrow (NC)_5Ru^{III}(L)^{4-} \qquad (15)$$

$$OH^- + Ru^{III}(CN)_6^{3-} + (NC)_5Ru^{III}(L)^{4-} \rightarrow Ru^{II}(CN)_6^{4-} + Ru^{II}(CN)_5(NCO)^{4-} + H_2O \qquad (16)$$

or $(CNOH)^{2-}$ depending on the position of attack of OH^-. The net reaction thus corresponds to the oxidation by Ru(III) of ligand cyanide to ligand cyanate (or an isomer thereof).

Support for the overall stoichiometry shown in eq 15 and 16 has been obtained by acid hydrolysis of the solutions resulting from the treatment of $Ru(CN)_6^{3-}$ with OH^-; NH_4^+ and CO_2 are produced as would be expected from the known reaction $NCO^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+$. In eight such experiments, recovery of CO_2 ranged from 95 to 101% of the expected amount and of NH_4^+ from 78 to 102% (with five of the eight values in the range 98–102%). These results require that OH^- attack the carbon atom of the cyano ligand (or that attack at nitrogen is followed by isomerization to an N–C–O moiety). Spectral observations (with and without reoxidation by Ce(IV)) also require that the postulated (isocyanato)pentacyanoruthenium(II) and -ruthenium(III) species have UV/vis spectra similar to those of the corresponding hexacyanides.

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Registry No. $(NH_4)_4Ce(SO_4)_4$, 7637-03-8; $Ru(CN)_6^{4-}$, 21029-33-4; $Ru(CN)_6^{3-}$, 54692-27-2; CN^-, 57-12-5; $HgCl_2$, 7487-94-7; $Ru^{III}(CN)_5(OH_2)^{2-}$, 74009-26-0; MnO_4^-, 14333-13-2; PbO_2, 1309-60-0; H_2O_2, 7722-84-1; OH^-, 14280-30-9.

Contribution from the Department of Chemistry,
City University of New York, Queens College, Flushing, New York 11367

Spectroscopic and Electrochemical Properties of the Dimer Tetrakis(2,2′-bipyridine)(μ-2,3-bis(2-pyridyl)pyrazine)diruthenium(II) and Its Monomeric Analogue

CARLOS H. BRAUNSTEIN, A. DAVID BAKER,* THOMAS C. STREKAS,* and HARRY D. GAFNEY*

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The ligand 2,3-bis(2-pyridyl)pyrazine, dpp, has been used to prepare the complexes $Ru(bpy)_2(dpp)^{2+}$ and $(bpy)_2Ru(dpp)Ru(bpy)_2^{4+}$. In contrast to previously synthesized mono- and bimetallic Ru(II) complexes, both $Ru(bpy)_2(dpp)^{2+}$ and $(bpy)_2Ru(dpp)Ru(bpy)_2^{4+}$ are luminescent in room-temperature fluid solution. The resonance Raman spectra of the complexes exhibit a pronounced dependence on excitation wavelength, which indicates that the visible MLCT transitions terminate in different ligands. Luminescence is assigned to a dpp π^*–Ru(II) t_2 transition, and measurements of the relative quantum yields of emission indicate that the emissive state is populated with equal efficiency in both complexes. Analysis of the electrochemical and spectral properties of the complexes indicates that the perturbation introduced by the second $Ru(bpy)_2^{2+}$ moiety in $(bpy)_2Ru(dpp)Ru(bpy)_2^{4+}$ is relatively small and similar to that introduced by substituting a weak electron-withdrawing substituent onto the ligand periphery. This relatively weak interaction, which is thought to be the reason both mono- and bimetallic complexes emit, is attributed to steric constraints imposed by the dpp bridging ligand.

Introduction

Recognition of the photoinduced redox properties of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$,[1] has spurred numerous studies of the complex and related derivatives, which have led to a rather detailed understanding of this chemistry.[2–5] Optical excitation of the complex leads to population of a luminescent metal to ligand charge-transfer (MLCT) state, which can act as an oxidizing or reducing agent.[2,3,5] Current interest centers on minimizing the reverse reaction that follows the photoinduced electron transfer and converting the one-photon, one-electron redox steps into more useful multielectron-transfer reactions. Semiconductors, electron relay reagents, and catalysts are being investigated as a means of storing electrons and initiating subsequent multielectron reactions.[4] Another approach is the use of dimeric Ru(II) complexes, which, if certain lifetime constraints are satisfied, could in principle act as a two-electron-transfer reagent when excited by two photons. Although a number of dimeric Ru(II) complexes have previously been prepared for the purpose of studying the intervalence charge-transfer (IT) transition in the mixed-valence (+5) system,[6–13] none satisfy the criteria

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