mononuclear species (Table I) and is apparently under the kinetic control of eq A (Scheme I). In addition, the reduction behavior of the bromide systems is simpler, on the whole, in the bromide media where equilibrium A will be displaced to the right and the concentration of bromide-bound species enhanced.

The above points suggest that the redox-active *mononuclear* species in all *three* bromide systems (*including [MoO(SAL-OPHEN)(MeOH)]Br*) is halide-bound [Mo^{V}OLBr], as postulated for the [MoO(SALPN)Cl] system:

$$[Mo^VOLX] + e^- \rightarrow [Mo^{IV}OLX] \qquad (E)$$

It must also be mentioned that the postulated kinetic control could be exercised by reactions B$_1$ and B$_2$ and not by reaction A. In that case, reduction of the *polynuclear* species is involved as observed in the [MoO(SALPN)Cl] system (Figure 4; Scheme II). In any case, the main possibilities appear to be covered by Schemes I and II.

Reactions subsequent to electron transfer also occur in the bromide systems. For example, the reduction peak current, $I_{pc}C^{-1}$, for 1 mM [MoO(SALEN)(MeOH)]Br in the Br$^-$ medium is similar to that for the other two compounds (Table III), but the oxidative component $I_{pa}C^{-1}$ is much lower, leading to $I_{pa}I_{pc}^{-1} = 0.3$–0.5. Reactions involving the *reduced* species may well be involved (Scheme II), or alternatively the reduced species are unstable to further chemical reaction on the cv time scale.

In summary, it appears that the halide-bound complexes are electroactive and the halide-free species electroinactive at the potentials being considered.

Coulometry. Despite the complexity of the polarographic and CV results for the present systems, the evidence strongly suggests that the redox processes involve one electron per molybdenum atom (Scheme II). Coulometric *n* values of between 0.5 and 1 (Table II) suggest that additional reactions are occurring on the longer time scale of controlled-potential electrolysis. Presumably, reactions of reduced species with the oxidized starting materials are occurring, leading to *n* values less than 1.0.
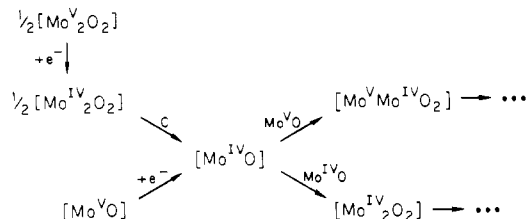
Conclusions. It can be seen that dissolution of the four compounds examined in this study in DMF leads to equilibria between mononuclear and binuclear or more highly condensed species (Scheme I). The behavior in other solvents such as CH$_2$Cl$_2$ and MeCN is even more complex, and it is not surprising that synthetic aspects of these systems can also be complex.[4] The electrochemistry of the DMF solutions are complicated by the equilibria, and a totally convincing interpretation is not possible from the present (quite extensive) data. In fact, deceptively simple behavior can be inferred from a preliminary data set. However, the major features are consistent with Scheme II; in particular, while the electrochemistry of the bromo compounds *trans*-[MoOL(MeOH)]Br in DMF are essentially that of mononuclear species, the corresponding properties of [MoO(SALPN)Cl] are dominated by polynuclear species. Very similar behavior characterizes the redox chemistry of oxomolybdenum(V) thiolate species,[18] where spin-paired binuclear forms for Mo^V are favored thermodynamically while for Mo^{IV}, low-spin, mononuclear forms are favored.

Registry No. *trans*-[MoO(SALOPHEN)(MeOH)]Br, 78891-61-9; *trans*-[MoO(SALPN)(MeOH)]Br, 78891-62-0; *trans*-[MoO(SAL-EN)(MeOH)]Br, 78891-63-1; [MoO(SALPN)Cl], 64085-33-2; Et$_4$NPF$_6$, 429-07-2; Et$_4$NBr, 71-91-0; Et$_4$NCl, 56-34-8; NaBr, 7647-15-6; Hg, 7439-97-6.

Effects of Substituted Polar Groups on Ionic Association of Bis(β-diketonato)(ethylenediamine)cobalt(III) Perchlorate Complexes in Nitrobenzene

KAZUAKI ITO,[†] HIROYUKI ISONO, ETSURO IWAMOTO, and YUROKU YAMAMOTO*

The conductances of [Co(β-dik)$_2$(en)]ClO$_4$, where β-dik is 2,4-pentanedionato (acac), 3-bromo-2,4-pentanedionato (acacBr), and 3-nitro-2,4-pentanedionato (acacNO$_2$), were studied in nitrobenzene at 25 °C. It was found that the degree of ionic association increases in the order [Co(acac)$_2$(en)]$^+$ < [Co(acacBr)$_2$(en)]$^+$ < [Co(acacNO$_2$)$_2$(en)]$^+$, whereas the order of the ionic mobility of the chelate cations is of opposite trend. The relative acidity of the N–H protons of the ligand ethylenediamine, determined from the rate of H–D exchange, increases in the same order as for the ionic association. These effects of the substituents were electronic and the Hammett relationship was found to hold true for the ionic association and the rate of H–D exchange. The increasing association was explained in terms of enhanced polarity of the cations and hydrogen-bond interactions between N–H protons and the perchlorate ion.

Introduction

The ligand X in the fragment H–N–M^{n+}–X of octahedral complexes involving amine, where X is Cl$^-$, Br$^-$, etc. and M^{n+} are metal ions, polarizes the complexes and affects labilization of the N–H protons via the central metal ions.[1,2] Hydro-gen-bonding interactions between the N–H protons in the metal complexes and the associating anions are important in the ionic association.[2,3] We previously reported that, for the

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Table I. Molar Concentrations (C/mol dm^{-3}) and Molar Conductances (Λ/S cm^2 mol^{-1}) in Nitrobenzene at 25 °C

[Co(acacBr)$_2$(en)]ClO$_4$		[Co(acacNO$_2$)$_2$(en)]ClO$_4$	
C/10^{-4}	Λ	C/10^{-4}	Λ
Data a			
31.925	24.931	25.492	23.449
28.209	25.306	23.984	23.671
24.775	25.688	19.963	24.309
21.111	26.116	16.738	24.888
16.385	26.743	13.243	25.581
13.340	27.203	10.158	26.293
9.476	27.851	7.480	26.984
5.680	28.619	5.779	27.484
Data b			
24.665	25.660	20.854	24.198
20.748	26.138	18.863	24.541
17.596	26.543	16.041	25.055
14.676	26.963	13.225	25.627
10.430	27.647	11.066	26.103
6.356	28.454	8.656	26.698
		5.602	27.569

Figure 1. Plot of logarithm of intensity of ^{1}H NMR against time for the N–H protons in [Co(β-dik)$_2$(en)]ClO$_4$. β-dik: 1, acac; 2, acacBr; 3, acacNO$_2$.

cobalt complexes [Co(acac)$_2$(diamine)]X, where the nitrogen protons of diamine (en) are replaced by the methyl group and X is Br$^-$ or ClO$_4^-$, the ionic association constants decrease with the decrease in the number of N–H protons in nitrobenzene and 1,2-dichloroethane.[4]

The coordinated acac is of aromatic character[5] and may have electron-mediating ability. In this study, our interest lies in determining the effect of changes in substituent at the C-3 position of the acac ligand for the metal chelate electrolytes [Co(acacX)$_2$(en)]ClO$_4$ (X = H, Br, NO$_2$) on the ionic association and the rate of H–D exchange of the N–H protons in nitrobenzene.

Experimental Section

[Co(acac)$_2$(en)]ClO$_4$ was prepared by the method of Archer et al.[6] [Co(acacBr)$_2$(en)]ClO$_4$ was prepared by the bromination of [Co-(acac)$_2$(en)]ClO$_4$: [Co(acac)$_2$(en)]ClO$_4$ (2.0 g, 4.8 mmol) was dissolved in 25 mL of dimethylformamide containing N-bromosuccinimide (3.58 g, 14.4 mmol), and the resultant mixture was stirred at room temperature for 30 min. A gray-brown precipitate was obtained upon addition of ether with cooling and was recrystallized from water/acetone mixtures (volume ratio 1:5). Anal. Calcd: C, 25.09; H, 3.52; N, 4.88. Found: C, 25.18; H, 3.61; N, 4.81.

[Co(acacNO$_2$)$_2$(en)]ClO$_4$ was prepared by nitration[7] of [Co-(acac)$_2$(en)]ClO$_4$: [Co(acac)$_2$(en)]ClO$_4$ (3.0 g, 7.2 mmol) was dissolved in 450 mL of acetic anhydride containing Cu(NO$_3$)$_2$·3H$_2$O (5.1 g); the resultant mixture was stirred for 1 h and then concentrated. A brown-red precipitate was obtained upon addition of aqueous 6 M NaClO$_4$ and recrystallized from water/acetone mixtures (volume ratio 1:5). Anal. Calcd: C, 28.44; H, 3.99; N, 11.06. Found: C, 28.59; H, 4.05; N, 11.05.

For [Co(acacBr)$_2$(en)]ClO$_4$ and [Co(acacNO$_2$)$_2$(en)]ClO$_4$, the peak of the methine proton in the NMR spectrum of the acac ligand (δ 5.56), which was observed for [Co(acac)$_2$(en)]ClO$_4$ in dimethyl-d_6 sulfoxide (Me$_2$SO-d_6) relative to tetramethylsilane as an internal reference, was not detected.

The purification of nitrobenzene and the conductivity measurements were done as described previously.[4] ^{1}H NMR spectra were obtained on a Hitachi Model R-20 high-resolution spectrometer (60 MHz) at room temperature. Deuterium oxide (D$_2$O, 99.8 atom % D min-
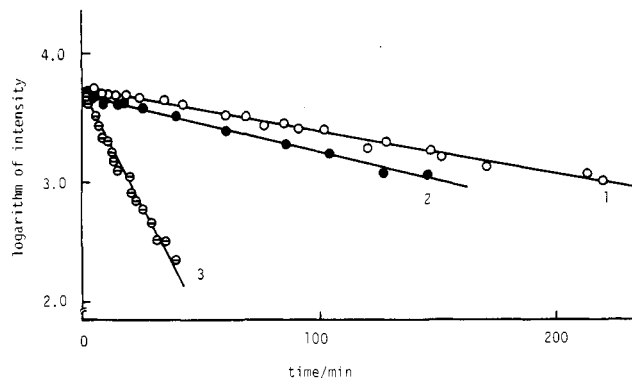
imum) and dimethyl-d_6 sulfoxide (99.5 atom % D minimum) were purchased from Merck and used as received.

The dielectric constant (34.82) and the viscosity of solvent (0.01847 P) were used for conductance analyses.

Results and Discussion

The measured conductances, Λ (S cm^2 mol^{-1}), and the corresponding concentrations, C (mol dm^{-3}), of [Co-(acacBr)$_2$(en)]ClO$_4$ and [Co(acacNO$_2$)$_2$(en)]ClO$_4$ in nitrobenzene at 25 °C (Table I) were analyzed by the Fuoss–Hsia equation with $E = E_1\Lambda_0 - 2E_2$ in the form[8]

$$\Lambda = \Lambda_0 - SC^{1/2}\gamma^{1/2} + EC\gamma \log C\gamma + J_1C\gamma + J_2C^{3/2}\gamma^{3/2} - K_aC\gamma f_\pm^2 \quad (1)$$

where K_a refers to ionic association constant and other symbols have their usual meanings. The results obtained are given in Table II. The changes in substituent at the 3-position of the acac ligands promote ionic association in the order [Co-(acac)$_2$(en)]$^+$ < [Co(acacBr)$_2$(en)]$^+$ < [Co(acacNO$_2$)$_2$(en)]$^+$ while these decrease the ionic mobility in the opposite order.

In this type of metal chelate cations, the acac ligand has electron-mediating ability due to its pseudoaromatic character with a ring current.[5] Therefore, the effect of the electron-withdrawing ability of the substituents Br and NO$_2$ on the labilization of N–H protons in ethylenediamine would be expected through the pseudoaromatic chelate ring although these are far from the N–H protons.

Thus, we have examined by NMR the rate of hydrogen exchange of N–H protons for the three metal chelate cations. A deuterium oxide/dimethyl-d_6 sulfoxide mixture (weight ratio 1:3.9) was used as the solvent because of the low solubility of the solutes in deuterium oxide and nitrobenzene. Figure 1 shows the logarithm of intensity of proton signal against time, and Table III gives the chemical shift and the rate constant of H–D exchange (k_{H-D}). The rate constant increases in the sequence acac < acacBr < acacNO$_2$, in accordance with that of electron-withdrawing tendency of the substituents.

The rate of hydrogen exchange in cobalt(III) amine complexes has been examined in connection with trans and cis effects of a substituent.[1b] When the electron density on the nitrogen atom decreases for some reason, this leads to a labilization of the nitrogen protons. Therefore, it can be said that the substituents, Br and NO$_2$, which are at the para position to the central metal, withdraw the electron on the nitrogen atom via the central metal.

From the above results the increase in the ionic association constant with substituents can be interpreted in two ways: (a)

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Table II. Derived Parameters in Nitrobenzene at 25 °C

electrolyte		Λ_0/S cm^2 mol^{-1}	$\lambda_0{}^{+\,a}$	K_a/dm^{-3} mol	d^b/10^{-1} nm	$\sigma_\Lambda{}^c$
[Co(acac)$_2$(en)]ClO$_4{}^d$		31.770 ± 0.007	10.68	56 ± 1	12.0	0.004
[Co(acacBr)$_2$(en)]ClO$_4$	e	30.86 ± 0.01	9.77	75 ± 1	13.9	0.006
	f	30.86 ± 0.02	9.77	76 ± 1	13.6	0.006
[Co(acacNO$_2$)$_2$(en)]ClO$_4$	e	30.38 ± 0.02	9.29	134 ± 1	16.1	0.006
	f	30.38 ± 0.01	9.29	132 ± 1	17.2	0.003

[a] With $\lambda_0(\text{ClO}_4{}^-) = 21.09$ (Iwamoto, E.; Monya, S.; Yamamoto, Y. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 625). [b] Distance parameter with a minimum σ_Λ value in eq 1. [c] Standard deviation of Λ. [d] From ref 4a. [e] Obtained from data a in Table I. [f] Obtained from data b in Table I.

Table III. Chemical Shift (δ) of the N–H Protons of [Co(β-dik)$_2$(en)]ClO$_4$ in Me$_2$SO-d_6 and the Rate of H–D Exchange ($k_{\text{H-D}}$) in D$_2$O/Me$_2$SO-d_6

electrolyte	δ	$10^2 k_{\text{H-D}}$/min^{-1}
[Co(acac)$_2$(en)]ClO$_4$	5.15	0.28 ± 0.02
[Co(acacBr)$_2$(en)]ClO$_4$	5.56	0.43 ± 0.01
[Co(acacNO$_2$)$_2$(en)]ClO$_4$	6.12	3.4 ± 0.2

the increasing polarity of metal chelate cations and (b) the increasing hydrogen-bond interactions between the N–H protons and the perchlorate ion. The effect of increasing polarity (a) results in anion–cation dipole interaction, $E_1 = \mu e/r_1{}^2 \epsilon k T$, in addition to the charge–charge interaction $E = e^2/r \epsilon k T$ of the Fuoss and Bjerrum equations,[9] where r and r_1 are the distance from the center and the dipole center of cations to the anion, respectively, and μ is the dipole moment of cation. Provided that $r = r_1$ is taken as 0.5 nm,[10] the additional association constants compared to that of [Co(acac)$_2$(en)]$^+$ need the corresponding additional dipole moments of 2.2 and 3.4 for [Co(acacBr)$_2$(en)]$^+$ and 6.5 and 10 for [Co(acacNO$_2$)$_2$-(en)]$^+$ from the Fuoss and Bjerrum equations, respectively. However, these additional dipole moments seem to be too large, suggesting interactions other than charge–charge and charge–dipole.

For [Co(NH$_3$)$_5$NO$_2$]SO$_4$, the existence of an "extra" attractive energy is emphasized in explanation of enhanced ionic association in water/dioxane mixtures compared with that calculated from the Bjerrum equation; a dipole moment of 6.3 D units for the cation was estimated.[11] It was also reported that for cations of the type *cis*-[CoXY(en)$_2$]$^+$, where X and Y represent either Cl$^-$ or Br$^-$, association constants in dimethyl sulfoxide decrease in the order *cis*-[CoCl$_2$(en)$_2$]$^+$ > *cis*-[CoClBr(en)$_2$]$^+$ > *cis*-[CoBr$_2$(en)$_2$]$^+$ for association with both chloride and bromide ions, and emphasis was placed on the contribution of increasing dipole moment due to the difference in electronegativity between chlorine and bromine.[2a] However, since the site of ion pairing is within the plane containing the four nitrogen ligand atoms in those complexes and hydrogen-bonding interactions are important for the stronger hydrogen-bond acceptor chloride and bromide ions,[2a] it is likely to also be important that the chlorine of stronger electronegativity more strongly activates the N–H protons to promote association than the bromine.

Although the perchlorate ion is not usually regarded as a hydrogen-bond acceptor,[2a,12] evidence for hydrogen-bond interactions between the perchlorate ion and the N–H protons of (5(*SR*),7(*RS*),12(*RS*),14(*SR*)-tetramethyl-1,4,8,11-tet-raazacyclotetradecane)nickel(II) was found by the X-ray analysis of the crystals: the N⋯O distance for N–H⋯O–Cl is 0.31 nm.[13]
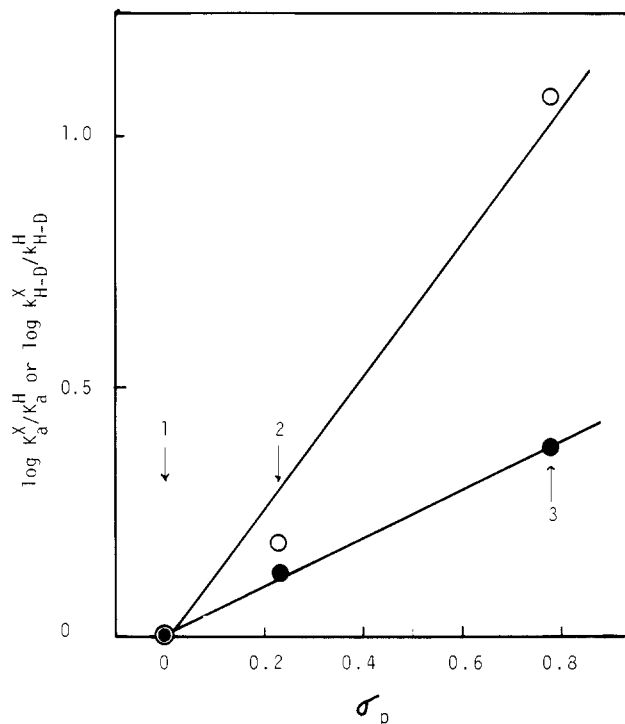
Figure 2. Hammett's relationship for the ionic associaton constant (●) and the rate of H–D exchange (○) for [Co(β-dik)$_2$(en)]ClO$_4$. β-dik: 1, acac; 2, acacBr; 3, acacNO$_2$.

Furthermore, the conductance study of (1,4,8,11-tetraaza-cyclotetradecane)nickel(II) perchlorate in nitrobenzene showed that the first and second association constants are 11 000 and 620, respectively.[14] These large association constants suggest hydrogen-bond interaction of the perchlorate ion even in solution. Although not as favorable sterically as for such a square-planar cation, it seems that the hydrogen-bond interaction can be an important factor of the increasing association for the present octahedral system.

The equilibrium and kinetic influence of the substituents in the para position or the 3-position of the acac ligands cannot be steric but must be electronic in nature. This view is supported by the Hammett correlation shown in Figure 2 where the logarithm of association and exchange rate constants for acacBr and acacNO$_2$ relative to that for acac were plotted against the Hammett σ_p values. There is a linear relationship for the equilibrium constant. Although for the kinetic constant a linear relationship does not seem justified on the basis of the three points, a similar σ_p dependence of the kinetic constants is seen.

We cannot at present say which is predominant of the two factors a or b, but it can be said that the perchlorate ion comes close to the side of N–H protons to associate since the positive

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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]

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Decomposition of Aqueous Hexacyanoruthenate(III) Ions

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Oxidation of aqueous K$_4$Ru(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$_2$O → Ru(CN)$_5$OH$_2^{2-}$), (2) dimerization (Ru(CN)$_5$(OH$_2$)$^{2-,3-}$ → CN-bridged dimers), and (3) ligand oxidation (2Ru(CN)$_6^{3-}$ + 2OH$^-$ → Ru(CN)$_6^{4-}$ + Ru(CN)$_5$(CNO)$^{4-}$ + H$_2$O). 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$_2$O$_2$, 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$_4$N)$_3$[Ru^{III}(CN)$_6$] has been reported[3] as a product of the photooxidation of (Et$_4$N)$_4$[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$_4$Ru(CN)$_6$·3H$_2$O (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$_4$)$_4$Ce(SO$_4$)$_4$·2H$_2$O) oxidation of aqueous K$_4$Ru(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$_2$N$_2$ 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$_2$SO$_4$ 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$_2$O$_2$ Studies. Stoichiometric studies involving O$_2$ (and H$_2$O$_2$ 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$_4$Ru(CN)$_6$ (pH 3–10) has

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