

explanation for the increase in rate seen experimentally.

The explanation that has been previously set forth is that the enhanced rate of attack of CuOH^+ is due to the formation of some type of hydrogen-bonded or hydroxide-bridged intermediate which imparts an added degree of stability to the intermediate. In the present system, the free acetate arm on the portion of ligand still bonded to nickel would be an excellent nucleophile, far stronger than anything that exists in any of the other systems. The strength of any type of hydrogen bond between the carboxyl group and the hydroxide bonded to copper would cause considerable increases in stability of the intermediate, which would be reflected in the $k^{\text{NiL}}_{\text{CuOH}}/k^{\text{NiL}}_{\text{Cu}}$ ratio. Thus, as the data show, the factor of 1240 increase would be unique to the ligand with a free acetate arm.

The effect of substituting a methyl group on each acetate arm, a seemingly inert substitution, has profound effects on the mechanism. A comparison of the stability constants of (ethylenediaminemonoacetato)nickel(II) (NiEDMA) and NiEDDP shows a gain of only 57 for EDDP, the ligand possessing an additional acetate arm with an α -methyl group.⁴ If it is assumed that one of the acetate arms of EDDP is uncoordinated in the nickel complex, an electrostatic attraction of 3.16 would nevertheless exist such that the added acetate arm of EDDP contributes an increase of only about 20 to the stability of the NiEDDP complex compared to the case for NiEDMA. Thus, the addition of an α -methyl group on the acetate arms of EDDP results in a nickel complex with either two nitrogens and one acetate coordinated or the second acetate only very weakly bonded. As EDDP unwraps from nickel, only one nickel-nitrogen bond need rupture, followed by cleavage of the other acetate arm from nickel, in order to achieve structure **2** of Figure 3, the precursor of the dinuclear intermediate. This would cause k_{12} to be considerably faster for NiEDDP compared to that for NiEDDA, where all four dentate sites are strongly coordinated in the metal complex and where an entire glycine segment must dissociate to get to the dinuclear intermediate precursor.

This very weak coordination or lack of coordination of an acetate arm causes the stability of the nickel complex of EDDP

to be lowered by a factor of 30 relative to that for NiEDDA.⁴ The drop in stability of the initial complex and the lack of acetate coordination seen in the dinuclear intermediate lowers the stability of the dinuclear intermediate relative to that for NiEDDA-Cu. Hence, as eq 7 shows, the rate constant for the metal-exchange pathway is lower.

The two effects discussed above result in an interesting change in mechanism for the EDDP system compared to the EDDA system.⁵ The NiEDDA-Cu system shows a shift in order with respect to copper as the copper concentration is increased, yet NiEDDP-Cu does not. In order for the shift in order with respect to copper to be seen, $k_{45}[\text{species } 4]$ must exceed the value of k_{12} as copper concentration increases. The concentration of species **4** depends upon the copper concentration as can be seen in Figure 3. Experimentally, no order shift was seen with the conclusion that k_{12} for NiEDDP is larger than that of NiEDDA or [species **4**] in the EDDP system is less than that of the EDDA system or both. As previously discussed, weak acetate coordination to nickel causes k_{12} for NiEDDP to be larger than that for NiEDDA. Further, the rate constant $k^{\text{NiL}}_{\text{Cu}}$ for either system can be written as $k_{45}[\text{species } 4]$. It is reasonable to assume that the value of k_{45} , rupture of a nickel-nitrogen bond, is about the same for both systems. The experimental decrease of 10 seen in comparing $k^{\text{NiL}}_{\text{Cu}}$ for EDDP to that for EDDA can be attributed to a lower stability for the NiEDDP-Cu dinuclear intermediate and thus indicates that [species **4**] for EDDP compared to that for EDDA makes it impossible for $k_{45}[\text{species } 4] > k_{12}$ for the EDDP system, resulting in first-order behavior in copper over the entire copper concentration range studied.

The interesting effect of the α -methyl substituents has prompted further studies involving other substituent groups on an EDDA base ligand, which are currently being carried out in our laboratories.

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Heteronuclear Ferrocene-Ruthenium Mixed-Valence Ions. Bi- and Trinuclear Species Based on the 1,1'-Dicyanoferrrocene Ligand

NORMAN DOWLING and PATRICK M. HENRY*¹

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The heterotrimetallic ion $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5](\text{PF}_6)_4$ as well as the corresponding heterobinuclear complex $[(\text{NH}_3)_5\text{RuNCFcCN}](\text{PF}_6)_2$ containing one less ruthenium center have been prepared from the 1,1'-dicyanoferrrocenyl moiety. The similarity between the spectral and electrochemical properties of the mixed-valence species derived from both the trinuclear ion and its binuclear congener indicates the presence of weak electronic interaction between the ferrocene center and ruthenium nuclei in these complexes, with no evidence for end-to-end interaction in the monooxidized trinuclear species, $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{5+}$. The unsymmetrical nature of the charge transfer in these ferrocene-ruthenium ions has been used to advantage to determine the effect of the electrostatic contribution to the intervalence transfer transition energies in these species. The absence of electronic interaction between the terminal ruthenium sites in the (2,2,3) ion allowed the correlation of the experimentally observed electrostatic stabilization for this species with the theoretically determined value, without recourse to estimating a value for a contribution due to ground-state stabilization. The result of this correlation is in keeping with the previous suggestion of an underestimation of the electrostatic contribution by the theoretical expression.

Introduction

Discrete mixed-valence complexes have now received significant attention in the literature since the initial theoretical work by Hush,² describing the properties of the related thermal

and optical electron-transfer processes that occur in weakly coupled mixed-valence systems. A number of studies have

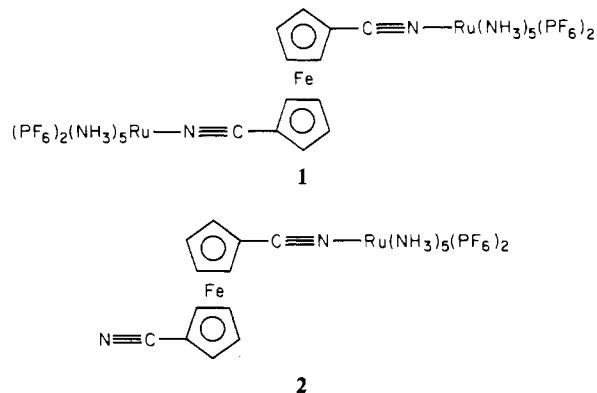
(1) To whom correspondence should be addressed at the Department of Chemistry, Loyola University of Chicago, Chicago, IL 60626.

been conducted by Taube and co-workers³ on symmetrical Ru(II)–Ru(III) complexes of the type $[(\text{NH}_3)_5\text{RuLRu}(\text{NH}_3)_5]^{5+}$ involving a variety of bridging groups, while several reports have appeared on the mixed-valence properties of binuclear ferrocene–ferrocenium derivatives.^{4–6} Meyer has also studied the symmetrical Ru(II)–Ru(III) complexes $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})]^{3+7}$ and $[(\text{bpy})_2(\text{py})\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{py})(\text{bpy})_2]^{5+8}$ of a slightly different nature (pyz = pyrazine; bpy = 2,2'-bipyridine; 4,4'-bpy = 4,4'-bipyridine; py = pyridine) and has further demonstrated typical class II behavior⁹ for unsymmetrical systems of the type $[(\text{NH}_3)_5\text{RuLRuCl}(\text{bpy})_2]^{4+10,11}$. A primary initiative in the study of mixed-valence compounds has been the information that can be obtained from the light-induced intervalence-transfer (IT) absorption properties of these species, with regard to the extent of ground-state delocalization as well as the rate of the related thermal electron-transfer process.¹²

A number of investigations have also appeared on the properties of polynuclear mixed-valence species in an attempt to observe the possible multisite interactions that might exist in these complexes. The essential difference between the polynuclear ions and analogous binuclear mixed-valence species is the intermediacy of one or more metal centers in the intervalence bridge mediated electron delocalization pathway. The trimeric ruthenium ions $[(\text{NH}_3)_5\text{RuLRu}(\text{bpy})_2\text{LRu}(\text{NH}_3)_5]^{6+}$, studied by Meyer,^{11,13} gave no indication of end-to-end interaction through the bridging ruthenium atom in the monooxidized mixed-valence (2,2,3) ion. In contrast, Taube has reported electrochemical and intervalence-transfer properties consistent with the presence of end-to-end interaction in the linear trinuclear mixed-valence ion $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_4(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{7+}$, indicating the feasibility of intervalence electron transfer through a bridging metal center.¹⁴ Included also in the studies of this type is the investigation of the 1,1'-polyferrocenyl derivatives 1,1'-terferrocene and 1,1'-quaterferrocene.¹⁵ The presence simply of localized interactions between adjacent sites in the incompletely oxidized forms of both these species was inferred from the IT properties of the mixed-valence states.

Our interest in this field centers on the study of discrete heteronuclear mixed-valence species. Attention has been directed to this area in an attempt to ultimately take advantage of the unique electron-transfer properties of mixed-valence species in the design of possible multielectron redox catalysts.

We have recently communicated the results of our initial study on heteronuclear ferrocene–ruthenium mixed-valence ions.¹⁶ The ions $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCR}]^{3+}$ (R = Fc and *trans*-FcCH=CH; Fc = ferrocenyl), were found to possess intervalence-transfer properties in agreement with the predictions of the Hush model. We report here the preparation and properties of the heterotrimeric ion $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5](\text{PF}_6)_4$ (**1**) and related binuclear complex $[(\text{NH}_3)_5\text{RuNCFcCN}](\text{PF}_6)_2$ (**2**) based on the 1,1'-dicyanoferrrocenyl ligand, as well as the spectral and electrochemical properties of the mixed-valence species derived from these ions.



The trinuclear ion $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{4+}$ may be formally considered as a symmetrical ruthenium(II) dimer bridged by a 1,1'-dicyanoferrrocenyl group. As such it was of interest to study the properties of the mixed-valence species derived from this complex, in relation to those of the previously reported trinuclear species, and so obtain information on the bridging properties of the ferrocenyl moiety.

Experimental Section

Materials. Tetrabutylammonium hexafluorophosphate (TBAH) was prepared by the published procedure,^{17a} recrystallized from ethanol–water, and finally dried under vacuum at 100 °C for 24 h prior to use. Acetonitrile (Burdick and Jackson, Spectrograde) was further dried by passing down an alumina (neutral, B.A. 1) column. Distilled water was purified by passage through an Ion X-changer (Cole-Parmer) water purification system, and all other solvents were used without further purification. Ruthenium(II) complexes were chromatographed on controlled-pore glass beads (Sigma, PG240-200).^{17b} Argon was scrubbed by passing it through either an Oxisorb (Aircro Industrial Gases) canister of a chromous bubbler.

Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrometer as Nujol mulls in the range 4000–600 cm^{-1} . Ultraviolet–visible spectra were recorded on a Cary Model 118 spectrophotometer on deaerated solutions of the complexes at room temperature. Near-infrared spectra were run on approximately 6×10^{-4} M solutions on a Cary Model 14 spectrophotometer over the wavelength range 2000–800 nm. Samples of the mixed-valence ions for spectral determinations were generated electrochemically by controlled-potential electrolysis in a 0.1 M solution of TBAH in acetonitrile. Solutions of known concentrations of the ruthenium(II) complexes in deaerated solvent were prepared directly in the electrochemical cell. After exhaustive electrolysis the solutions were transferred by syringe technique to an argon-flushed 1-cm quartz cell fitted with a special Teflon inert valve.

Syntheses. **1,1'-Fe(C₅H₄CN)₂.** 1,1'-Dicyanoferrrocene was prepared by a four-step synthesis from commercially available 1,1'-ferrocenedicarboxylic acid, dimethyl ester (Strem). 1,1'-Bis(hydroxymethyl)ferrocene was obtained in 86% yield by lithium aluminum hydride reduction of 1,1'-ferrocenedicarboxylic acid, dimethyl ester, according to the procedure of Nesmeyanov et al.¹⁸ The 1,1'-bis-

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(hydroxymethyl) derivative was converted by the method of Osgerby and Pauson,¹⁹ via the 1,1'-dicarboxaldehyde (64%) and 1,1'-dialdoxime (66%) derivatives, to 1,1'-dicyanoferrrocene (87%), after purification by column chromatography on Florisil with benzene as the eluant; mp 168–169 °C (lit. mp 166–167 °C). Anal. Calcd for C₁₂H₈FeN₂: C, 61.06; H, 3.42; N, 11.87. Found: C, 60.80; H, 3.29; N, 11.54. (¹H NMR (CDCl₃): apparent triplets δ 4.85 (H_α), δ 4.63 (H_β).

[(NH₃)₅RuCl]Cl₂. This complex was prepared by the method of Vogt et al.²⁰ and recrystallized from warm (40 °C) 0.1 M HCl.

[(NH₃)₅Ru(H₂O)](PF₆)₂. The procedure outlined by Kuehn and Taube²¹ was used for the synthesis of this complex.

[(NH₃)₅RuNCFcCN](PF₆)₂. [(NH₃)₅Ru(H₂O)](PF₆)₂ (32 mg, 0.065 mmol) in deaerated acetone (5 mL) was added slowly to a solution of 1,1'-dicyanoferrrocene (0.304 g, 1.29 mmol; 20-fold excess) in deaerated acetone (20 mL). The reaction was allowed to proceed for 2 h, during which time the solution was agitated by a slow stream of argon. Addition of ether to the reaction mixture precipitated the product (36.6 mg, 78%) as an orange solid, which was filtered under an argon atmosphere, washed with ether, and suction-dried. Anal. Calcd for [(NH₃)₅RuNCC₅H₄FeC₅H₄CN](PF₆)₂: C, 20.24; H, 3.25; N, 13.77. Found: C, 20.14; H, 3.31; N, 13.55.

A similar preparation using a 5:1 ratio of 1,1'-dicyanoferrrocene to [(NH₃)₅Ru(H₂O)](PF₆)₂ gave an identical product in 35% yield after column chromatography (CH₂Cl₂-acetone, 1:1) and recrystallization (see below).

[(NH₃)₅RuNCFcCNRu(NH₃)₅](PF₆)₄. 1,1'-Dicyanoferrrocene (40 mg, 0.17 mmol) and [(NH₃)₅Ru(H₂O)](PF₆)₂ (184 mg, 0.37 mmol; 10% excess) in deaerated acetone (5 mL) gave by a procedure similar to that already outlined a crude product in 92% yield. The expected product was isolated chromatographically on eluting with acetone after discarding the previous CH₂Cl₂-acetone (2:1 and 1:1) fractions (100 mg, 50%) after recrystallization. Anal. Calcd for [(NH₃)₅RuNCC₅H₄FeC₅H₄CNRu(NH₃)₅](PF₆)₄: C, 12.13; H, 3.22; N, 14.14. Found: C, 12.19; H, 3.13; N, 13.85.

The trinuclear ion was also prepared in 57% yield by reacting the binuclear complex [(NH₃)₅RuNCFcCN](PF₆)₂ and [(NH₃)₅Ru(H₂O)](PF₆)₂ in a stoichiometric ratio.

Chromatography. Samples of the crude ruthenium(II) complexes up to 100 mg were chromatographed on a 8 mm × 8 cm column packed with controlled-pore glass beads.^{17b} A slow inverted argon flow was passed through the packed column prior to dry loading the solid to be chromatographed. Elution was achieved with the appropriate methylene chloride-acetone deaerated-solvent mixture, and the entire operation was carried out in an argon-flushed glovebag.

Unreacted aquopentaammineruthenium(II) was removed initially with CH₂Cl₂-acetone (2:1), and the remaining ferrocene-ruthenium(II) complexes were eluted with solvent mixtures containing higher acetone contents. The fractions were quickly evaporated to dryness and recrystallized under an argon atmosphere by dissolving in a minimum volume of deaerated acetone-water (1:3) and reprecipitating by addition of NH₄PF₆.

Electrochemistry. Cyclic voltammetry was performed with a Bioanalytical Systems (BAS) Model CV-1A voltammetry control unit. Current-potential curves were displayed on a Nicolet Explorer IIIA digital oscilloscope equipped with a Model 201 two-channel plug-in unit and permanent traces run off on a standard X-Y recorder. Controlled-potential coulometry was performed using the same basic system by feeding the potentiostat output through a voltage-to-frequency converter and making use of the counting capability of our laboratory Rockwell Aim 65 microcomputer to integrate the resultant proportional frequency with respect to time. Differential pulse voltammetry was performed on a PAR Model 174A polarographic analyzer.

All electrochemical experiments were performed in a conventional three-compartment electrochemical cell equipped with a Pt-flag working electrode and Pt-wire auxiliary electrode. Cyclic voltammetric formal potentials were determined relative to an internal standard at 22 ± 2 °C and the recorded values corrected relative to the potential of +0.340 V vs. the saturated calomel electrode for the ferrocene/ferrocenium couple in acetonitrile. Potentials determined in this

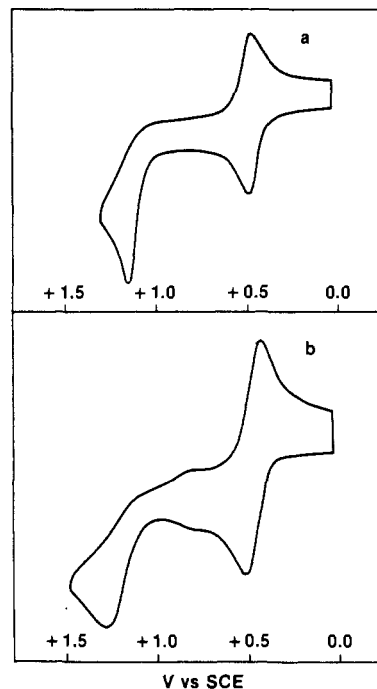


Figure 1. Cyclic voltammograms of (a) [(NH₃)₅RuNCFcCN](PF₆)₂ and (b) [(NH₃)₅RuNCFcCNRu(NH₃)₅](PF₆)₄ in 0.1 M TBAH in CH₃CN vs. SCE at a scan rate of 200 mV/s.

manner were found to be highly reproducible due to elimination of random variations in liquid-junction potentials and reference electrode degradation in individual experiments.²²

Measurements were carried out on millimolar concentrations of the complexes in acetonitrile solution containing 0.1 M TBAH as supporting electrolyte. $E_{1/2}$ values were taken where possible as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the peak-to-peak separation (ΔE_p) for the complementary anodic and cathodic cyclic voltammetric waves relative to the theoretically predicted value of 59 mV for a reversible one-electron redox process. Chemical irreversibility was inferred from a plot of the peak potential, E_p , relative to the scan rate function $\ln v^{1/2}$.²³

Current decay curves for controlled-potential coulometric experiments were routinely monitored and experiments terminated after the current had essentially decayed to zero. Coulometric n values were then determined by using the equation $Q = nNF$.

Differential pulse voltammetry was performed at a scan rate of 2 mV/s with a pulse amplitude of 10 mV. Values of the peak width at half-height were determined, and peak potentials were again corrected relative to an internal standard and found to be consistent with previous cyclic voltammetric results. Near-theoretical behavior for the peak width at half-height (94 vs. 90.9 mV)²⁴ was confirmed in both 0.1 M TBAH in acetonitrile at a Pt electrode and 1 N HCl at a carbon-paste electrode with use of the one-electron standard [(NH₃)₅RuNCPH](PF₆)₂.

Kinetics. Pseudo-first-order rate constants for the loss of the 1,1'-dicyanoferrrocenium cation as a function of the water concentration in acetonitrile were determined by cyclic voltammetry from the peak current ratio (i_{pc}/i_{pa}) with use of the appropriate working curve.²³ Cathodic peak currents were measured to the extension of the anodic curve, as interference from the electrochemical breakdown of the added water at the anodic limit of +1.5 V vs. SCE used in the experiment prevented the use of the more straightforward equation developed by Nicholson.²⁵

As a result of electrode fouling on oxidation of the 1,1'-dicyanoferrrocene molecule, the working electrode was cleaned after each successive scan by flaming.

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Results

Electrochemistry. Cyclic voltammograms of the fully reduced heteronuclear ions in 0.1 M TBAH in acetonitrile, shown in Figure 1, exhibited two waves in the potential range 0.0 to +1.5 V vs. the saturated calomel electrode (SCE). Oxidation of free 1,1'-dicyanoferrrocene as well as the ferrocene oxidations in both ruthenium complexes, assigned to the higher potential wave by analogy to the free-ligand oxidation, appeared as chemically irreversible processes in cyclic voltammetry experiments at a scan rate of 200 mV/s. Potentials for this step are therefore reported as anodic peak potentials, E_{pa} , as the true half-wave potentials can only be estimated.

Confirmation of chemical irreversibility was obtained from a plot of E_p vs. $\ln v^{1/2}$ for 1,1'-dicyanoferrrocene, which was linear with a slope of 37.5 mV; this is, however, larger than the theoretically predicted slope of 26 mV.²³ Only for the case of the free ligand was it possible to clearly observe the cathodic counterpart of the ferrocene oxidation wave on increasing the scan rate to 10 V/s, which is the limit of our present instrumentation.

The peak-to-peak separation ($\Delta E_p = E_{pa} - E_{pc}$) of 69 mV for the ruthenium oxidation–reduction wave at 0.466 V in the cyclic voltammogram of the binuclear complex indicated essentially electrochemical reversibility for this redox process. The larger than theoretical value of 59 mV likely arises as a result of uncompensated solution resistance. The corresponding wave in the cyclic voltammogram of the trinuclear ion at 0.467 V displayed a larger separation with a ΔE_p of 99 mV. Coulometry on the diffusion plateau of this wave for the trinuclear ion $[(NH_3)_5RuNCFcCNRu(NH_3)_5]^{4+}$ however gave an n value close to 2, consistent with oxidation of both ruthenium(II) centers. The corresponding coulometric experiment on the binuclear ion $[(NH_3)_5RuNCFcCN]^{2+}$ indicated the presence of only one center for this wave.

The value of 0.467 V for the composite first wave in the cyclic voltammogram of the trinuclear ion is not representative of the true half-wave potential for either of the individual electrode processes occurring in that wave. Accurate values of the half-wave potentials for oxidation of the two ruthenium(II) centers in the trinuclear ion $[(NH_3)_5RuNCFcCNRu(NH_3)_5]^{4+}$ were determined instead from a measurement of the peak width at half-height, $W_{1/2} = 119$ mV, and peak potential 0.444 V of the differential pulse voltammogram for this ion in 0.1 M TBAH in acetonitrile and by making use of the equations

$$E_{1/2}(2) = E_c + \frac{\Delta E_{1/2} + E_{pul}}{2}$$

$$E_{1/2}(1) = E_{1/2}(2) - \Delta E_{1/2}$$

where E_c represents the peak potential in this case, $E_{pul} = 10$ mV is the pulse amplitude used in the differential pulse experiment, and the separation between the half-wave potentials $\Delta E_{1/2} = 58$ mV as determined from a working curve of $W_{1/2}$ vs. $\Delta E_{1/2}$.²⁶

Voltammetric data for the heteronuclear ions as well as the free ligand are presented in Table I.

Near-Infrared Spectra. The half-oxidized binuclear mixed-valence complex $[(NH_3)_5Ru^{III}NCFcCN]^{3+}$ together with the doubly oxidized trinuclear mixed-valence species $[(NH_3)_5Ru^{III}NCFcCNRu^{III}(NH_3)_5]^{6+}$, and a solution containing the singly oxidized $[(NH_3)_5Ru^{II}NCFcCNRu^{III}(NH_3)_5]^{5+}$ ion, exhibited similar low-energy electronic bands in acetonitrile in the borderline visible–near-infrared spectral region. These bands, which are absent from the spectra of the fully reduced complexes, have been assigned to IT tran-

Table I. Electrochemical Data for the Heteronuclear Complexes^a

| complex | $E_{1/2}^-$ (Ru ^{III/II}), V | E_{pa}^- (Fc ⁺⁰), ^b V |
|-------------------------------------|--|--|
| $[(NH_3)_5RuNCFcCN]^{2+}$ | 0.466 | 1.186 |
| $[(NH_3)_5RuNCFcCNRu(NH_3)_5]^{4+}$ | 0.420 ^c | 1.277 |
| | 0.478 ^c | |
| NCFcCN ^d | | 1.092 |

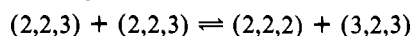
^a Pt working electrode in 0.1 M TBAH in acetonitrile vs. SCE.

^b Chemically irreversible process at a scan rate of 200 mV/s. Peak potentials reported are for the initial scan with a flamed working electrode. ^c Determined by differential pulse voltammetry.

^d Voltammetric half-wave potential of 1.111 V vs. SCE determined at a scan rate of 10 V/s.

sitions between the dissimilar ferrocene and ruthenium(III) centers in the molecules.²⁷

Determination of the band parameters for the IT absorption associated with the (2,2,3) ion was complicated by the disproportionation equilibrium



which on the basis of the separation of 58 mV between the potentials for the two ruthenium centers indicates only 60% of the material to be in the (2,2,3) form. Contributions to the overall absorption in this region are expected from the IT absorption in the (3,2,3) ion and tailing from the intense MLCT band in the (2,2,2) species, as well as the tailing from the residual MLCT transition within the (2,2,3) ion. An attempt to apply the corrections for the contributions due to the (3,2,3) and (2,2,2) species to the approximate band maximum of 820 nm in the spectrum of the solution containing a single equivalent oxidized sample of the (2,2,3) ion provided an upper limit of 690 M⁻¹ cm⁻¹ for the extinction coefficient of the IT band in the (2,2,3) species.

Relevant band parameters for the long-energy absorptions in the (3,2,3) and (2,3) species in acetonitrile are provided in Table II.

Electronic Spectra. Ultraviolet–visible spectral data for the ions $[(NH_3)_5RuNCFcCNRu(NH_3)_5]^{4+}$ and $[(NH_3)_5RuNCFcCN]^{2+}$ in acetonitrile, together with data for the corresponding mixed-valence 6+ and 3+ ions and free 1,1'-dicyanoferrrocene are summarized in Table III. The spectra of the ruthenium(II) ions could be explained on the basis of the individual ferrocene and ruthenium(II) components of each complex. Comparison with the free-ligand spectrum in Table III, as well as previous results,²⁸ showed the ultraviolet bands to be the result of ferrocene-based charge-transfer transitions. The 450-nm shoulder observed in the spectrum of the binuclear ion $[(NH_3)_5RuNCFcCN]^{2+}$ probably has as its origin the moderately weak band at 437 nm in the spectrum of the free ligand, which can also be assigned on the basis of previous work as arising from the ferrocene-based spin-allowed d–d transitions.²⁸

Infrared Spectra. The infrared spectrum of the sample of 1,1'-dicyanoferrrocene prepared was identical with that reported by Osgerby and Pauson,¹⁹ with a nitrile stretching frequency of 2225 cm⁻¹ (Nujol). The absence of the structurally significant 9–10- μ m bands served to confirm the heteroannularly disubstituted nature of the synthesized ferrocene derivative.²⁹ The infrared spectra of the ruthenium(II) complexes are essentially identical and displayed the characteristic ammine

(27) No attempt was made to determine the near-infrared spectra of the fully oxidized species in view of the chemically irreversible nature of the ferrocene oxidation step.

(28) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(29) Rosenblum, M. "Chemistry of the Iron Group Metalloenes: Ferrocene, Ruthenocene, Osmocene"; Wiley: New York, 1965; p 38.

Table II. Intervalence-Transfer-Band Properties for the Mixed-Valence Ions in Acetonitrile

| complex | λ_{\max} , nm | $10^{-3} \bar{\nu}_{\max}$, cm^{-1} | $10^{-3} \Delta \bar{\nu}_{1/2}$, cm^{-1} | ϵ_{\max} , $\text{M}^{-1} \text{cm}^{-1}$ |
|--|-----------------------|---|---|--|
| $[(\text{NH}_3)_5\text{RuNCFcCN}]^{3+ a}$ | ~840 | ~11.9 | ~6.5 | <336 |
| $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{6+}$ | 818 | 12.22 | 6.5 | 827 |

^a Band appears as a well-defined shoulder for this complex.

Table III. Ultraviolet-Visible Spectral Data for Heteronuclear Ferrocene-Ruthenium(II) and -Ruthenium(III) Complexes in Acetonitrile^a

| complex | λ_{\max} , nm | $10^{-3} \epsilon_{\max}$, $\text{M}^{-1} \text{cm}^{-1}$ |
|--|-----------------------|--|
| $[(\text{NH}_3)_5\text{RuNCFcCN}]^{2+}$ | 450 sh | 4.03 |
| | 380 | |
| | 280 sh | |
| $[(\text{NH}_3)_5\text{RuNCFcCN}]^{3+ b}$ | 248 | 22.1 |
| | 450 sh | |
| | 365 | |
| $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{4+}$ | 380 | 9.90 |
| | 290 sh | |
| | 247 | |
| $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{6+ b}$ | 525 sh | 30.3 |
| | 365 | |
| | 437 | |
| NCFcCN | 325 sh | 0.242 |
| | 261 sh | |
| | 246 | |
| | 246 | |

^a Spectra were recorded at room temperature in argon-purged solutions. ^b Solutions also contained 0.1 M TBAH, present as background electrolyte in the electrochemical generation of these species.

bands^{30,31} at 3370 and 3297 ($\nu(\text{NH}_3)$), 1625 ($\delta(\text{NH}_3)$ (deg)), 1272–1280 ($\delta(\text{NH}_3)$ (sym)), and 740–745 cm^{-1} ($\rho(\text{NH}_3)$) (Nujol). The broad PF_6^- band masked the 800–900- cm^{-1} region. The trinuclear ion $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{4+}$ exhibited a single nitrile stretching band at 2214 cm^{-1} at lower wavenumber than that of the free ligand, consistent with ruthenium(II) coordination of both nitrile functions of the 1,1'-dicyanoferrrocenyl moiety.³² As expected, the monoruthenium(II) binuclear complex $[(\text{NH}_3)_5\text{RuNCFcCN}]^{2+}$ displayed two nitrile stretching bands, one at approximately the free-ligand value of 2226 cm^{-1} and the other at 2214 cm^{-1} at lower wavenumber characteristic of a ruthenium(II)-bound nitrile.

Stability of the Complexes. Solutions of the oxidized (3,2,3), (2,2,3), and (2,3) species derived from both the trinuclear and binuclear complexes were found to be unstable on standing for a period of 24 h. This instability was characterized by the growing in of a band at slightly higher energy than the IT absorptions in these species in the 700-nm region and could also be detected visually by a deepening green coloration imparted to the solutions. Cyclic voltammograms of the oxidized species run subsequently to generation by controlled-potential electrolysis did not however exhibit any change from cyclic voltammograms recorded on the original fully reduced complexes.

Neither the nature of the decomposition reaction nor the species responsible for the characteristic transition was investigated. However, in view of the hydrolytic instability of Ru(III)-nitrile complexes,³³ it is probable that hydrolysis of the nitrile function in these species would be a likely source for the observed instability. This solution instability did not however interfere with the reported spectral measurements.

Kinetics. A plot of the pseudo-first-order rate constants for loss of the 1,1'-dicyanoferrrocenium cation, determined by cyclic

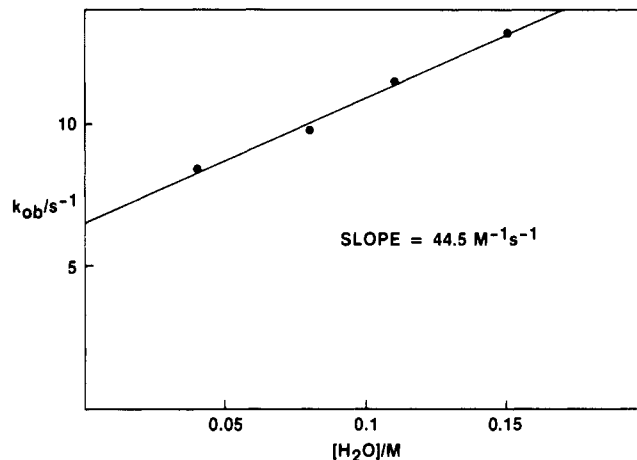


Figure 2. Plot of pseudo-first-order rate constants, k_{obs} , vs. $[\text{H}_2\text{O}]$. k_{obs} was determined for the loss of the 1,1'-dicyanoferrrocenium cation from the current ratio $i_{\text{pc}}/i_{\text{pa}}$ by cyclic voltammetry.

voltammetry, against the concentration of added water is shown in Figure 2. The experimental points cover a range up to 0.15 M $[\text{H}_2\text{O}]$; beyond this concentration current ratios became difficult to establish and irregular behavior was noted. The plot in Figure 2 represents the best fit straight line by least-squares analysis. The second-order hydrolysis rate constant was determined to be 44.5 $\text{M}^{-1} \text{s}^{-1}$ from the slope of the plot.

Discussion

Initial Site of Oxidation. Initial oxidation of the ruthenium centers in the heteronuclear ions $[(\text{NH}_3)_5\text{RuNCFcCN}]^{2+}$ and $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{4+}$ was supported by both the redox potential data from these ions as well as the electronic spectral data for the corresponding (2,3) and (3,2,3) mixed-valence ions.

The visible spectra of the ruthenium(II) complexes exhibited intense bands at 380 nm assigned to $(\text{Ru}(\text{II}))d\pi-\pi^*(\text{L})$ charge-transfer (MLCT) transitions. The appearance of MLCT transitions in the complexes of ruthenium(II) with π -acceptor ligands has been well documented.^{30,32} Oxidation to the mixed-valence (2,3) and (3,2,3) species resulted in the loss of the 380-nm Ru(II) MLCT transition, indicating the initial site of oxidation to be essentially localized on the ruthenium centers in the molecules.

A similar result is also evident from the redox potential data for the heteronuclear ions, as shown by the assignments of the potentials to the oxidation of a particular metal center in the molecules in Table I. The reported assignments are based on the measured potential of 0.498 V for oxidation of the ruthenium(II) center in the complex $[(\text{NH}_3)_5\text{RuNCFcCN}]^{2+}$, as well as the observed anodic peak potential of 1.092 V for oxidation of the free ligand in acetonitrile.

The low-energy oxidation state isomers generated on partial oxidation of the heteronuclear ions therefore have the structures $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCFcCN}]^{3+}$, $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCN}-\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$, and $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{6+}$ containing ruthenium sites in the oxidized 3+ state.

Intervalence Transfer. The mixed-valence (2,3) species $[(\text{NH}_3)_5\text{RuNCFcCN}]^{3+}$ obtained on half-oxidation of the binuclear complex exhibited a broad low-energy absorption

(30) Ford, P. C. *Coord. Chem. Rev.* 1970, 5, 75.

(31) Allen, A. D.; Senoff, C. V. *Can. J. Chem.* 1967, 45, 1337.

(32) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* 1970, 9, 227.

(33) Diamond, S. E.; Taube, H. *J. Chem. Soc., Chem. Commun.* 1974, 622.

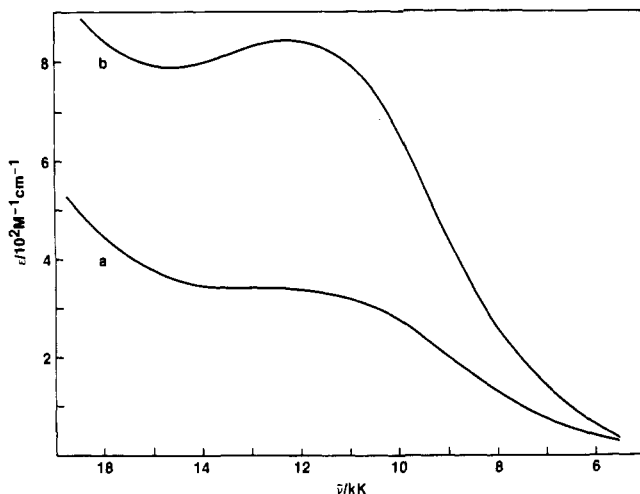
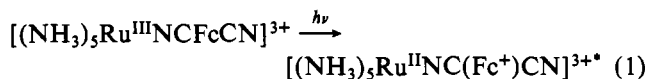


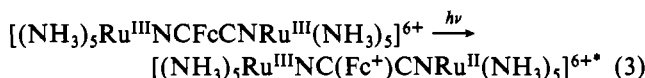
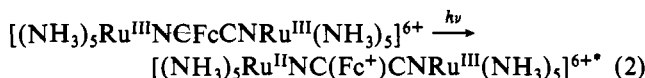
Figure 3. Intervalence-transfer bands for (a) the singly oxidized $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCFcCN}]^{3+}$ and (b) the doubly oxidized $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{6+}$ ions in 0.1 M TBAH in CH_3CN .

at ~ 840 nm ($\epsilon < 336 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 3) assigned to the IT transition



involving light-induced electron transfer between the dissimilar ferrocene and ruthenium(III) nuclei. Similar IT transitions have previously been shown to exist in the analogous heterobinuclear mixed-valence ions $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCCH}=\text{CHFc}]^{3+}$.¹⁶ The appearance of the IT band for the (2,3) ion at sufficiently high energy to permit overlap with a visible-based transition reduced the accuracy with which the band parameters could be determined. The assignment of this band as an IT absorption, however, also receives support from the larger optical transition energy for the (2,3) species relative to that for the analogous mixed-valence ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$.³⁴

The corresponding absorption in the doubly oxidized (3,2,3) mixed-valence species $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{6+}$ occurs at 818 nm ($\epsilon = 827 \text{ M}^{-1} \text{ cm}^{-1}$) at slightly higher energy than that of the (2,3) ion. This absorption in the spectrum of the (3,2,3) ion in which both ruthenium centers are in the oxidized 3+ state is similarly assigned to the two equivalent IT transitions that can occur in this complex (eq 2 and 3). In



(34) The difference in optical transition energies is expected to reflect the difference in E_0 values for the two ions $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCN}]^{3+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$, given that the Franck-Condon contributions χ_i and χ_0 are expected to remain essentially constant (eq 5), in view of the similarity in coordination environments, bridging ligand, and internuclear separation for these two species. From the expression $E_0 = \Delta E + \Delta E_{\text{el}} = \Delta G + T\Delta S + \Delta E_{\text{el}}$, this difference translates into the difference in ΔG ($=E_{1/2}(\text{D}) - E_{1/2}(\text{A})$) values, for constant $T\Delta S$ and ΔE_{el} terms. The values of ΔG from redox potential measurements are as follows: $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCN}]^{3+}$, $\Delta G \approx 5.2 \times 10^3 \text{ cm}^{-1}$; $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$, $\Delta G \approx 2.1 \times 10^3 \text{ cm}^{-1}$.³⁵ The difference of $3.1 \times 10^3 \text{ cm}^{-1}$ is in excellent agreement with the difference in optical transition energies of $\sim 3.0 \times 10^3 \text{ cm}^{-1}$.

(35) The potentials originally reported in ref 16 have been reassessed relative to an internal standard (see Experimental Section of this paper), and the following values found in 0.1 M TBAH in CH_3CN vs. the SCE: $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$ $E_{1/2}(1) + 0.442 \text{ V}$, $E_{1/2}(2) + 0.840 \text{ V}$; FcCN $E_{1/2} + 0.701 \text{ V}$; $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCCH}=\text{CHFc}]^{2+}$ $E_{1/2}(1) + 0.434 \text{ V}$, $E_{1/2}(2) + 0.610 \text{ V}$; $\text{trans-FcCH}=\text{CHCN}$ $E_{1/2} + 0.514 \text{ V}$.

view of the identical bridging ligand and similar coordination environments of the two dissimilar metal centers involved in the intervalence transfer in the (2,3) and (3,2,3) ions, the nature of the IT transition in both these species would not be expected to be greatly different, the major factor in this respect being the degeneracy of the transition in the case of the latter ion. This expectation is borne out by the similar transition energies, $\bar{\nu}_{\text{max}}$, and bandwidths at half-height, $\Delta\bar{\nu}_{1/2}$, for the two ions in acetonitrile (Table II).

The bandwidth at half-height for an unsymmetrical mixed-valence ion can be determined from the expression (4),

$$\bar{\nu}_{\text{op}} - \bar{\nu}_0 = (\Delta\bar{\nu}_{1/2})^2 / 2.31 \quad (\bar{\nu} \text{ in } 10^3 \text{ cm}^{-1}) \quad (4)$$

where $\bar{\nu}_{\text{op}}$ is the energy of the IT transition and $\bar{\nu}_0$ is the internal energy difference between the two oxidation-state isomers (eq 6 and 7). As a result of the irreversibility of the ferrocene oxidation step in these compounds, the method of estimating $\bar{\nu}_0$ from the difference between the potentials in the complex could not be used.³⁶ Reasonable estimates for $\bar{\nu}_0$ in the two ions were obtained instead from the difference between the $E_{1/2}$ values for the free-ligand couple and the potential for oxidation of the ruthenium center in the complex³⁷ (Table I), $E_{1/2}(2)$ in the case of the trinuclear ion, together with the respective calculated electrostatic work terms (see below). The sum of these contributions afforded values of 5.7×10^3 and $6.2 \times 10^3 \text{ cm}^{-1}$ for the (2,3) and (3,2,3) ions, which gave on applying eq 4 calculated bandwidths at half-height, $\Delta\bar{\nu}_{1/2}$ (calcd), of 3.8×10^3 and $3.7 \times 10^3 \text{ cm}^{-1}$ for these ions, respectively. Comparison with the corresponding observed values, $\Delta\bar{\nu}_{1/2}(\text{obsd})$, of $6.5 \times 10^3 \text{ cm}^{-1}$ for both ions, showed $\Delta\bar{\nu}_{1/2}(\text{obsd}) \approx 1.7[\Delta\bar{\nu}_{1/2}(\text{calcd})]$. Class II or weakly interacting mixed-valence ions have generally been found to exhibit bandwidths at half-height greater than those predicted on the basis of the Hush model.^{3b,6,7,10a} However, a slightly better order of agreement between observed and calculated values has normally been found than that reported for these ions.

The extent of ground-state delocalization, α^2 , in the two mixed-valence complexes can also be determined from the equation

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{\text{max}}(\Delta\bar{\nu}_{1/2})}{\bar{\nu}_{\text{op}}d^2}$$

where ϵ_{max} is the molar extinction coefficient and d is the internuclear separation. Using an estimate of 6.2 \AA for the distance between the two metal centers in both ions together with the remaining parameters in Table II gave values of $<2.0 \times 10^{-3}$ and 2.4×10^{-3} for the extent of interaction, per (2,3) unit, in the (2,3) and (3,2,3) ions, respectively, after the expected degeneracy of 2 in the trinuclear (3,2,3) ion had been taken into account. These values are in good agreement with the previous result of 2.3×10^{-3} for α^2 in the analogous mixed-valence heteronuclear ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFc}]^{3+}$, as might be expected from the similar metal centers and bridging ligand delocalization pathway for the intervalence interaction in all three ions.

The energy of the optical transition, E_{op} , for an unsymmetrical mixed-valence ion is given by the expression³⁸

$$E_{\text{op}} = E_{\text{FC}} + E_0 = \chi_i + \chi_0 + \Delta E + \Delta E_{\text{el}} \quad (5)$$

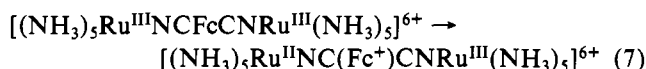
where χ_i and χ_0 are the respective contributions to the Franck-Condon energy from inner- and outer-sphere reorg-

(36) Argument previously outlined as a footnote in ref 16.

(37) This approach ignores any contribution to the $E_{1/2}$ of the ferrocene nuclei in the complexes that may arise from the presence of the appended $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ group(s).

(38) Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Now. J. Chim.* **1980**, *4*, 643.

anizations. E_0 is the internal energy difference between the two ground-state oxidation-state isomers which result from electron transfer between the metal centers, corresponding to the energy change for reactions 6 and 7, for the case of the $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{NCFcCN}]^{3+} \rightarrow [(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NC}(\text{Fc}^+)\text{CN}]^{3+}$ (6)



heteronuclear complexes in the present study. The internal energy difference E_0 term can be expressed in the form of two basic contributions as in eq 5. The first of these, $\Delta E = \Delta G + T\Delta S$, arises as a result of the inherent redox inequivalency of the two metal centers involved in the intervalence electron transfer and can be estimated from the difference between the redox potentials for the donor and acceptor sites, $E_{1/2}(\text{D}) - E_{1/2}(\text{A})$, together with the appropriate entropic term.³⁹ The second contribution, ΔE_{el} , is a direct consequence of the unsymmetrical charge transfer in these ions and is only nonzero for this particular case, having its origin in the difference in electrostatic repulsion following optical excitation.

From consideration of the nature of the IT transitions in the mixed-valence (2,3) and (3,2,3) ions, eq 1 and 2 or 3, as well as the individual contributions to the optical transition energy, eq 5, it might be expected that χ_i , χ_o , and ΔE would all remain essentially constant for a given solvent, in view of the similar coordination environments and internuclear separation of the two centers involved in the intervalence transition in the two ions. The ΔE_{el} term applicable to eq 1 and 2 or 3 can in turn be estimated by making use of the electrostatic free energy equation (8), where Z_1 and Z_2 are the charges on

$$w = \frac{Z_1 Z_2 e^2}{D_s d (1 + \kappa d)} \quad (8)$$

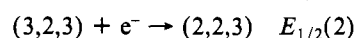
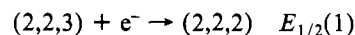
$$\kappa = \left(\frac{8\pi N^2 e^2 \mu}{1000 D_s R T} \right)^{1/2}$$

the metal centers, e is the electronic charge, D_s is the dielectric constant (36.2), d is the internuclear separation (6.2×10^{-8} cm), N is Avogadro's constant, μ is the ionic strength (0.1 M), R is the gas constant, and T is the temperature (298 K). So that the above point charge electrostatic expression could be used for the systems currently being discussed, the iron site in the ferrocene moiety was treated as a neutral center and the existence of a 1+ charge assumed to exist at the iron nucleus in the oxidized ferrocenium state. On this basis the ΔE_{el} contribution for the (2,3) ion was calculated to be 6.35 kJ/mol ($0.53 \times 10^3 \text{ cm}^{-1}$). The presence of the second Ru(III) center in the trinuclear (3,2,3) ion results in an increased ΔE_{el} term for this ion, which was calculated as 12.7 kJ/mol ($1.06 \times 10^3 \text{ cm}^{-1}$).⁴⁰

In view of the expected constancy of the other contributions, the difference in the ΔE_{el} terms for the two ions is expected to be the major contributor to the difference in the energy of the IT transitions in these two mixed-valence species. The experimentally determined values of E_{op} in Table III indicate the optical transition in the (3,2,3) ion to occur at an energy $\sim 0.3 \times 10^3 \text{ cm}^{-1}$ greater than the corresponding transition in the (2,3) ion. This represents a reasonable agreement with the calculated difference, $\Delta E_{\text{el}}(3,2,3) - \Delta E_{\text{el}}(2,3) = 0.53 \times$

10^3 cm^{-1} , given the assumptions inherent in the present treatment.⁴¹ Also of significance is the qualitatively correct prediction for the effect of the electrostatic term ΔE_{el} on the energy of the optical transitions, which as a result of the unsymmetrical charge transfer in these ions allow this factor to be assessed.

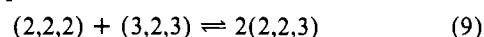
Mixed-Valence Stabilization. On the basis of the coulometric results for the trinuclear ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{4+}$ the two couples



representing oxidation-reduction of the two ruthenium centers in the ion were shown to occur in relatively close proximity. A measure of the actual separation between the potentials $E_{1/2}(1)$ and $E_{1/2}(2)$ for these couples in acetonitrile was determined to be 58 mV from the differential pulse voltammetric results. Application of the equation

$$\log K_c = \frac{n}{0.059} (E_{1/2}(2) - E_{1/2}(1))$$

where $n = 1$, afforded a value of $K_c = 10$ for the comproportionation equilibrium



which is only slightly larger than the statistical value of 4. The appearance of the statistical factor in the $\Delta E_{1/2}$ separation for the comproportionation equilibrium in eq 9 arises from the equivalency of the two ruthenium centers in this complex.

The small value of 58 mV for the separation between $E_{1/2}(1)$ and $E_{1/2}(2)$ in the complex $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{4+}$, together with the resultant value of $K_c = 10$, tends to indicate that electronic delocalization between the terminal ruthenium sites in the ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{5+}$ is probably negligible. The near-infrared spectra of both the monooxidized (2,2,3) and the dioxidized (3,2,3) mixed-valence ions support this result. The similarity of the above spectra to that of the (2,3) mixed-valence ion derived from the binuclear complex $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCN}]^{2+}$ represents the basis for assigning the observed intervalence transitions in the trinuclear mixed-valence ions to that involving the ferrocene and ruthenium nuclei. As such no optical transition originating from the transfer of an electron between the terminal ruthenium sites in the monooxidized (2,2,3) species was observed under the conditions of the present study.

The absence of end-to-end interaction in the singly oxidized $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{5+}$ ion is of particular interest. From the potentials for oxidation of the individual sites in the complex, the difference between the energies of the (2,2,3) and (2,3,2) valence isomers can be estimated to be between 0.8 and 0.9 V. The small extent of mixing of these two states that is therefore likely, proposed by Taube¹⁴ to account for the lack of electronic interaction between the terminal sites in the ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{III}}(\text{bpy})_2(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{7+}$, compared to that in $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{7+}$, presumably also holds in this case.

(39) The usual assumption of $\Delta S \approx 0$ does not appear to be justified in the case of these heteronuclear ions from the results of temperature-dependent redox studies performed on other ferrocene-ruthenium heterobinuclear systems: Dowling, N., unpublished results.

(40) ΔE_{el} was calculated by using $\Delta(Z_1 Z_2)$ in eq 8, where $\Delta(Z_1 Z_2)$ represents the difference in the product of the site charges ($Z_1 Z_2$) for a particular electrostatic interaction in the individual oxidation-state isomers.

(41) While the internuclear separation is expected to be the same in both ions, the effect of the second $(\text{NH}_3)_5\text{Ru}^{\text{III}}$ group in the trinuclear ion on the other factors is less predictable. The ability of this group to act as an acidic center of positive charge enables it to change the redox potential of the ferrocene center in the complex relative to that of the free ligand, thus affecting the ΔE term directly. Also in the calculation of the electrostatic term for the (3,2,3) ion a Ru-Ru separation of 12.4 Å was chosen, which represents the trans arrangement for this ion. Any rotation therefore of the cyclopentadienyl rings away from this conformation will result in a larger Ru-Ru repulsion term and an overall smaller ΔE_{el} contribution for the process $[\text{Ru}^{\text{III}}\text{FcRu}^{\text{III}}]^{6+} \xrightarrow{e^-} [\text{Ru}^{\text{II}}\text{Fc}^+\text{Ru}^{\text{III}}]^{6+}$, leading in turn to an improved quantitative agreement.

The result of negligible interaction between the two terminal ruthenium sites in the (2,2,3) ion can be taken as an indication of a virtual nonexistent contribution to the $\Delta E_{1/2}$ separation ($E_{1/2}(2) - E_{1/2}(1)$) from electronic delocalization in this ion. The remaining contributions to the observed stability of the (2,2,3) state relative to that of the (2,2,2) + (3,2,3) states, a measure of which is provided by the comproportionation equilibrium, can be taken to represent the whole of the observed $\Delta E_{1/2}$ separation. The purely statistical contribution to K_c is represented by $RT/nF \ln 4$, which is equal to 35.6 mV (where 4 is the value of K_c for two equivalent noninteracting centers). The remaining stabilization converted to energy units, of 2.16 kJ/mol (or 1.08 kJ/mol per (2,2,3) unit) should therefore provide a measure of the extent to which the (2,2,3) ion is favored on electrostatic grounds.

A check on the validity of this assumption can be made by calculating the electrostatic contribution from eq 8 with a value of 12.4×10^{-8} cm for d , the internuclear separation, and previously defined quantities. The calculated electrostatic stabilization per (2,2,3) unit was found to be 0.53 kJ/mol, indicating an agreement within a factor of 2 with the experimental value.

A similar approach to the treatment of mixed-valence stabilization has been previously used by Taube in a study on the symmetrical ruthenium(II) dimer $[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{4+}$,⁴² where it was also necessary to estimate the ground-state stabilization due to electron delocalization in the complex. The difference in discrepancies found between calculated and observed electrostatic contributions can probably be traced to the use of different solvent media in the two studies. In both cases, however, the theoretical value was found to represent an underestimate of the experimental result.

Kinetics. The lack of reversibility for the ferrocene-based oxidations in the cyclic voltammetry experiments of both the ruthenium complexes and the free ligand was suspected to derive from the ability to hydrolyze the cyano group. So that hydrolysis could be substantiated as the probable origin of this effect, the rate of disappearance of the 1,1'-dicyanoferricenium cation as a function of water concentration was monitored.

The observed linear water dependence of the pseudo-first-order rate constants determined by cyclic voltammetry for loss of the 1,1'-dicyanoferricenium ion in Figure 2 supports the contention that the chemical irreversibility of the ferrocene oxidation is at least due in part to hydrolysis of the nitrile group. In principle it would also be expected that the similar irreversibility in the case of the ruthenium complexes would

also be due in part to the hydrolytic instability of the nitrile function in these species.

The nonzero intercept in the kinetic plot is of interest as it implies the presence of a second competing decomposition pathway, the rate of which is independent of water concentration. The instability of the ferrocenium ion in dipolar aprotic solvents such as CH_3CN , Me_2SO , and DMF has been previously reported⁴³ and recently attributed to traces of dissolved oxygen.⁴⁴ It seems reasonable therefore to attribute the present observed behavior for the 1,1'-dicyanoferricenium ion to a combination of both a similar decomposition pathway and hydrolysis of the nitrile function.

The presence of a further decomposition pathway for the oxidized 1,1'-dicyanoferricenium derivative is also evident from the unusual coulometric result, which indicated the passage of more than one electron per 1,1'-dicyanoferricenium molecule on exhaustive electrolysis past the ferrocene oxidation wave. The origin of this unusual result is not immediately obvious. However, exhaustive electrolysis past the ferrocene oxidation waves in both the binuclear ion $[(\text{NH}_3)_5\text{RuNCFcCN}]^{2+}$ and trinuclear complex $[(\text{NH}_3)_5\text{RuNCFcCNRu}(\text{NH}_3)_5]^{4+}$ also afforded coulometric n values in excess of the expected value, consistent with the above result.

Conclusion

Class II behavior involving electron delocalization between the dissimilar ferrocene and ruthenium(II) nuclei was observed for the mixed-valence ions reported in this study. The mixed-valence properties of the singly oxidized trinuclear ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{NCFcCNRu}^{\text{III}}(\text{NH}_3)_5]^{5+}$ were shown to be formally analogous to those for the trinuclear ion $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})\text{Ru}^{\text{II}}(\text{bpy})_2(\text{pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{7+}$ previously reported by Meyer,¹³ in that electronic interaction between the terminal ruthenium sites through the bridging ferrocenyl moiety appeared to be negligible. A direct method of probing the electrostatic contribution to the intervalence-transfer transition energies in these heteronuclear ferrocene–ruthenium mixed-valence species was also shown to exist for an appropriate choice of ions.

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