

delineate the mechanisms of ammonia and hydrazine formation from the same bis(dinitrogen) complex.

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(23) On leave from Nebraska Wesleyan University, 1981-1982.

Department of Chemistry
University of Nebraska—Lincoln
Lincoln, Nebraska 68588-0304

Gerald E. Bossard
T. Adrian George*
Daniel B. Howell²³
Lenore M. Koczon
Richard K. Lester

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Articles

Contribution from the Department of Chemistry, University of Guelph, Guelph Campus, The Guelph-Waterloo Center for Graduate Work in Chemistry, Guelph, Ontario N1G 2W1, Canada

Mixed-Valence Ions of Ruthenium Containing Fumaronitrile and Tetracyanoethylene as Bridging Groups

SULTAN I. AMER,^{1a} TARA P. DASGUPTA,^{1b} and PATRICK M. HENRY*^{1a}

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Complexes of the type $[(\text{H}_3\text{N})_5\text{Ru}]_n\text{L}^{2n+}$ (L = Fum, $n = 2$; L = TCNE; $n = 4$) were synthesized and characterized. Cyclic voltammetry of the $[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}^{4+}$ ion in CH_3CN shows two reversible one-electron waves for the stepwise oxidation of the two Ru(II) centers. The potential difference, $\Delta E_{1/2}$, and the appearance of an intervalence transfer (IT) band at 975 nm ($\epsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$) for the mixed-valence ion $[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}^{5+}$ indicate that the [2,3] ion is stable in solution with respect to disproportionation to the 4+ and 6+ ions. The IT half-bandwidth, $\Delta \bar{\nu}_{1/2}$, was found to be broader than calculated. The extent of electron delocalization, α^2 , estimated for the [2,3] ion, was found to be 3×10^{-4} , implying that the ion belongs to class II, weakly coupled systems. The IT band showed the expected solvent dependence. The tetraruthenium TCNE ion displayed five reversible one-electron waves; the negative one corresponds to the TCNE^{0/-} couple. The presence of MLCT and LMCT bands at low energy (800-nm region) indicates strong interaction between Ru(II) and Ru(III) centers, suggesting a strongly coupled ion. The potential differences between the ruthenium couples also support a strongly coupled system. The failure to detect IT bands is believed due to the fact that they appear in the same region as the MLCT and LMCT bands. The doubly oxidized ion $[(\text{NH}_3)_5\text{Ru}]_4\text{TCNE}^{10+}$ was found to be more stable than the 9+ and 11+ ions.

Introduction

The first mixed-valence ion, containing two rutheniums and a pyrazine bridging group, was reported by Creutz and Taube more than a decade ago.² Since then, a number of such ions have been studied. These studies have involved systematic variations of the bridging ligand³⁻⁸ as well as the auxiliary ligand.⁵⁻⁷ Most of the ions reported are homonuclear with two metal centers that are usually ruthenium or ferrocene iron, although ions containing pentacyanoiron^{5,7,9} and platinum and palladium¹⁰ have been reported. There are also a few examples of heteronuclear mixed-valence ions.⁸⁻¹² Mixed-valence ions have been classified by Robin and Day¹³ according to the extent of electronic interaction between the metal centers. Most ions are of class II or weakly interacting systems. Class

II ions have been treated by theories advanced by Hush¹⁴ and Marcus.¹⁵ In particular, class II ions display an intervalence-transfer transition (IT) that corresponds to a light-induced electron transfer between the metal centers. This transition provides evidence for the extent of electron delocalization in the ground state.^{13,14}

Our interest in mixed-valence ions focuses on new bridging groups, heteronuclear ions,¹² and polynuclear ions, especially those with metal ions attached to a common bridging group. To our knowledge, there are only two reports^{16,17} of polynuclear mixed-valence ions containing ruthenium centers both of which were weakly interacting.

In this paper we describe the preparation and characterization of mixed-valence ions containing fumaronitrile (Fum) and tetracyanoethylene (TCNE) bridging ligands. The bimetallic fumaronitrile might be expected to serve as a model for the TCNE complex. However, there might well be differences since TCNE is a better acceptor than fumaronitrile.¹⁸

Experimental Section

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by a literature procedure,¹⁹ recrystallized twice from

- (1) (a) Present address: Department of Chemistry, Loyola University of Chicago, Chicago, IL 60626. (b) Visiting Professor, July 1-Sept 30, 1980; permanent address: University of West Indies, Mona, Kingston 7, Jamaica.
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hot water-ethanol mixture, and vacuum dried at 80° for 12 h. Acetonitrile (Burdick and Jackson Spectrograde) was dried over freshly activated alumina. All other solvents were reagent grade and were dried over molecular sieves. Argon was purified by passing it either through a chromous bubbler or through a commercially available oxygen removal cartridge (Oxisorb, Airco-Industrial Gases). Fumarionitrile and tetracyanoethylene (Aldrich Chemicals) were used as received. Elemental analyses were carried out by Guelph Chemical Laboratories, Guelph, Ontario.

Preparations. The salts $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2^{20}$ and $[\text{Ru}(\text{NH}_3)_5\text{O}(\text{H}_2)(\text{PF}_6)_2]^{21}$ were prepared by literature procedures. All complexes were prepared and collected under argon. The complexes were purified by passing them through a controlled-pore glass-bead column with, initially, a 2:1 CH_2Cl_2 -acetone mixture as eluent. The monoruthenium complexes are eluted first. When the acetone content of the eluent is increased, complexes with higher ruthenium content can be eluted.²² A typical preparation follows.

$[\text{Ru}(\text{NH}_3)_5\text{Fum}](\text{PF}_6)_2$ (Fum = Fumarionitrile). Fumarionitrile (78 mg) was dissolved in degassed acetone (15 mL) in a 25-mL round-bottom flask equipped with an inlet tube at the bottom so that the gas could be continuously bubbled through the solution. The tube was connected by a ball and socket joint to the argon supply. To this solution was added 100 mg of the aquo complex $[\text{Ru}(\text{NH}_3)_5\text{O}(\text{H}_2)](\text{PF}_6)_2$, and the reaction was allowed to run for 2 h with a continuous stream of argon passing through the solution. Degassed ether was then added via a cannula to the acetone solution. A reddish brown precipitate formed immediately. The solid was collected by filtration in a glovebag under argon and stored in a vacuum desiccator. The Yield was 75%. Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5\text{C}_4\text{H}_2\text{N}_2](\text{PF}_6)_2$: C, 8.67; H, 3.07; N, 17.69. Found: C, 9.21; H, 3.49; N, 17.76.

$[\text{Ru}(\text{NH}_3)_5]_2\text{Fum}(\text{PF}_6)_4$. To 8 mg of fumarionitrile in acetone (15 mL) was added 110 mg of the aquo complex, and the reaction was allowed to proceed for 4 h. The yield of the red solid was 70%. Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5]_2\text{C}_4\text{H}_2\text{N}_2(\text{PF}_6)_4$: C, 4.66; H, 3.10; N, 16.30. Found: C, 5.10; H, 2.98; N, 16.80.

$[\text{Ru}(\text{NH}_3)_5\text{TCNE}](\text{PF}_6)_2$. To 128 mg of TCNE in acetone (15 mL) was added 100 mg of the aquo complex, and the reaction was allowed to proceed for 1 h. The yield of the blue-green solid was 69%. Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5\text{C}_6\text{N}_4](\text{PF}_6)_2$: C, 11.90; H, 2.49; N, 20.86. Found: C, 12.20; H, 2.60; N, 21.50.

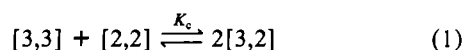
$[\text{Ru}(\text{NH}_3)_5]_4\text{TCNE}(\text{PF}_6)_8$. To 6.4 mg of TCNE in acetone (15 mL) was added 150 mg of the aquo complex, and the reaction was allowed to proceed for 10 min. The yield of the deep blue solid was 80%. Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5]_4\text{C}_6\text{N}_4(\text{PF}_6)_8$: C, 3.54; H, 2.95; N, 16.50. Found: C, 3.82; H, 3.22; N, 16.10.

Measurements. Ultraviolet-visible and near-infrared spectra were recorded on Cary 14 and Cary 118C recording spectrophotometers. Infrared spectra were recorded with a Perkin-Elmer 180 recording spectrophotometer. Electrochemical measurements were made by using a Bioanalytical Systems CV-1A voltammetry control unit, a Nicolet digital oscilloscope, and a Houston X-Y recorder. For integration, the oscilloscope was connected (Y-channel) to an Aim integrator that was interfaced with a Rockwell Aim 65-4K computer.

Results

Electrochemistry. The reduction potentials for the various Ru(III)-Ru(II) couples were measured in acetonitrile solution containing 0.1 M TBAH as supporting electrolyte. Values given in Table I are vs. the standard calomel electrode (SCE). All the cyclic voltammetry waves were reversible.

The potential difference, $[E_{1/2}(2) - E_{1/2}(1)]$, for the fumarionitrile dimer is 0.103 V corresponding to a value of 50 for the disproportionation constant, K_c . From the value of K_c and the equilibrium in eq 1, the equilibrium mixture was



found to be $\approx 80\%$ in the mixed-valence ion. The [3,2] ion was stable enough to permit the spectral measurements.

The cyclic voltammogram for the tetra-ruthenium TCNE ion displayed five well-separated waves in the region of -0.500

Table I. Reduction Potentials from Cyclic Voltammetry^a

couple ^b		$E_{1/2}, \text{V}^c$
	$[(\text{H}_3\text{N})_5\text{RuFum}]^{3+/2+}$	0.661 ± 0.005
(2) ^d	$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}^{6+/5+}$	0.762 ± 0.009
(1)	$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}^{5+/4+}$	0.659 ± 0.015
	$\text{TCNE}^{0/-}$	0.197 ± 0.010
	$\text{TCNE}^{-/2-}$	-0.799 ± 0.005
	$[(\text{H}_3\text{N})_5\text{RuTCNE}]^{3+/2+}$	0.399 ± 0.004
	$[(\text{H}_3\text{N})_5\text{RuTCNE}]^{2+/+}$	-0.096 ± 0.004
(4)	$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{12+/11+}$	0.899 ± 0.007
(3)	$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{11+/10+}$	0.753 ± 0.008
(2)	$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{10+/9+}$	0.456 ± 0.015
(1)	$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{9+/8+}$	0.280 ± 0.013
	$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{8+/7+}$	-0.299 ± 0.027

^a 0.1 M TBAH/ CH_3CN . ^b Fum = fumarionitrile; TCNE = tetracyanoethylene. ^c Values are vs. the SCE. ^d Values of 0.775 and 0.656 V were obtained for couples (2) and (1), respectively, by using the method of Richardson and Taube (Richardson, D. E.; Taube, H. *Inorg. Chem.* 1981, 20, 1278), and the couples were separated by a value of $\Delta E_{1/2}$ corresponding to $K_c = 62.5$.

to +1.300 V. The first wave at -0.299 V corresponds to the $\text{TCNE}^{0/-}$ couple. Unlike the value for fumarionitrile, the $\Delta E_{1/2}$ values are quite large, affording higher values for K_c indicating that TCNE is a better bridging group than Fum. Of particular interest is the difference between $E_{1/2}(3)$ and $E_{1/2}(2)$ ($\Delta E_{1/2} = 0.297$ V), which yields a value of $K_c = 10^5$. A two-electron oxidation at $E = 0.500$ V produced a solution that consisted almost entirely²³ of the doubly oxidized $[\text{Ru}(\text{NH}_3)_5]_4\text{TCNE}^{10+}$ ion. The 9+ and 11+ ions were found, respectively, to be $\approx 94\%$ and $\approx 88\%$ in their equilibrium mixtures.

Infrared Spectra. The infrared spectra of the complexes were taken, and all displayed the following general features: $\nu(\text{NH}_3)$ in the range $3100\text{--}3360$ cm^{-1} , $\delta(\text{NH}_3)$ (deg) between 1620 and 1632 cm^{-1} , $\delta(\text{NH}_3)$ (sym) from 1270 to 1320 cm^{-1} , and $\rho(\text{NH}_3)$ at $827\text{--}835$ cm^{-1} , which appears as a composite band.²⁵ The monoruthenium(II) complexes displayed the $\nu(\text{C}=\text{C})$ in the range $1570\text{--}1588$ cm^{-1} , which is infrared inactive in both the free and fully coordinated ligands.²⁶ The monoruthenium(II) fumarionitrile complex displayed two bands in the $\nu(\text{C}\equiv\text{N})$ region while the TCNE counterpart displayed three bands.²⁷ Also, when one nitrile is coordinated, the other nitrile(s) suffers a decrease, however small, in frequency.²⁸ The fumarionitrile dimer showed a strong band at 2165 cm^{-1} with a shoulder at 2207 cm^{-1} while the tetra-ruthenium(II) TCNE complex displayed a strong band at 2105 cm^{-1} and a shoulder at 2156 cm^{-1} . These results are summarized in Table II.

Ultraviolet-Visible Spectra. The spectra of the free ligands and complexes were taken in acetonitrile that was 0.1 M in TBAH. The most important feature displayed in the spectra of the complexes is the very intense ($\epsilon \sim 10^4$) band in the visible region with shoulder(s) on the high-energy side.²⁹ This band is assigned to a $d_{\pi}\text{--}\pi^*(\text{L})$ MLCT. This band is similar to those reported for $[(\text{H}_3\text{N})_5\text{Ru}(\text{py})]^{2+}$ ^{30,31} and pyridine

- (23) K_c values reported in this work were determined from the electrochemical (cyclic voltammetry) data for both the Fum and TCNE systems.
 (24) The 10+ ion was found to constitute 99% of the equilibrium mixture.
 (25) $\nu_3(\text{F}_6^-)$ for the PF_6^- anion appears as a strong band in the range $830\text{--}860$ cm^{-1} . Myfield, H. G., Jr.; Bull, W. E. *J. Chem. Soc. A* 1971, 2279.
 (26) The band is IR inactive in the free ligand, and its value for TCNE was obtained from the Raman spectrum.
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Table II. Vibrational Frequencies (cm^{-1}) and Assignments for Fumarionitrile, Tetracyanoethylene, and Their Pentaammineruthenium(II) Complexes^a

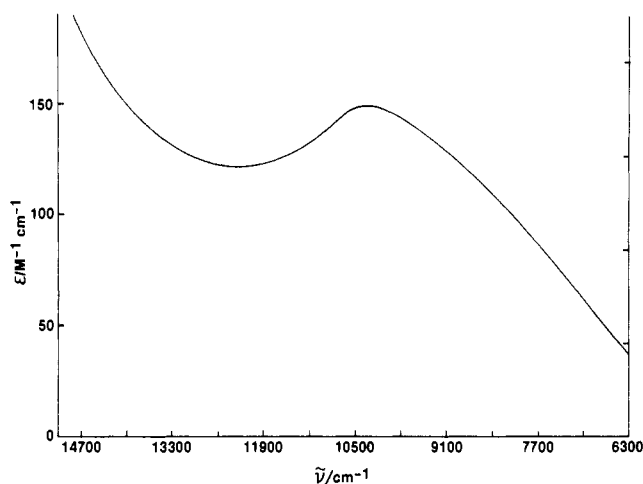
ligand or complex	$\nu(\text{N-H})$	$\nu(\text{C-H})$	$\nu(\text{CN})$	$\delta(\text{NH}_3, \text{deg})$	$\nu(\text{C}=\text{C})$	$\delta(\text{NH}_3, \text{sym})$	$\delta(\text{C-H})$	$\rho(\text{NH}_3), \nu(\text{PF}_6^-)$	$\rho(\text{CC}\equiv\text{N}), \nu(\text{PF}_6^-)$
Fum		3040 m ^b	2283 w, 2253 s, 2234 vs		1588 m	1270 s	960 s		542 m
$[(\text{H}_3\text{N})_5\text{RuFum}](\text{PF}_6)_2$	3334 br	3170 m	2228 w, 2182 s	1620 m	...	1275 m	933 w	830 vs ^c	553 s ^d
$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}(\text{PF}_6)_4$	3370-3220 br	3170 m	2207 sh, 2165 s	1620 m	830 vs ^c	557 s ^d
TCNE ^e			2260 s, 2225 s ^f		...				555 s
$[(\text{H}_3\text{N})_5\text{RuTCNE}](\text{PF}_6)_2$	3360-3210 br		2206 m, 2150 s, 2118 m	1632 m	1570 m	1320 m		835 vs ^c	556 s ^d
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_8$	3360-3295 br		2156 sh, 2105 s	1620 m	...	1290 m		827 vs ^c	550 s ^d

^a KBr pellet. ^b w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, br = broad. ^c Composite band (contains $\nu(\text{PF}_6^-)$ and $\rho(\text{NH}_3)$). ^d Contains $\nu(\text{PF}_6^-)$ and $\rho(\text{CC}\equiv\text{N})$. ^e TCNE is a D_{2h} point group; $\nu(\text{C}=\text{C})$ is at 1573 cm^{-1} in the Raman spectrum. ^f Rosenblum, M.; Fish, R. W.; Bennet, C. *J. Am. Chem. Soc.* **1964**, *86*, 5166.

Table III. UV-Visible Spectra for Fumarionitrile, Tetracyanoethylene, and Their Pentaammineruthenium(II) Complexes in Acetonitrile at 25°C

ligand or complex	$\lambda_{\text{max}}, \text{nm} (\log \epsilon)$
Fum	271 (4.47), 223 (4.29), 215 (4.46), 208 (4.47), 203 (4.49)
$[(\text{H}_3\text{N})_5\text{RuFum}](\text{PF}_6)_2$	466 (3.88), 352 (sh), 288 (sh), 254 (4.00)
$[(\text{H}_3\text{N})_5\text{RuFum}](\text{PF}_6)_3^a$	433 (3.46)
$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}(\text{PF}_6)_4$	500 (4.31), 338 (sh), 283 (sh), 248 (4.32)
$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}(\text{PF}_6)_5$	504 (4.05), 285 (sh), 256 (4.14)
$[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}(\text{PF}_6)_6^a$	463 (3.63)
TCNE	283 (sh), 268 (4.06), 259 (4.10), 254 (4.07), 217 (3.53), 202 (3.56)
$[(\text{H}_3\text{N})_5\text{RuTCNE}](\text{PF}_6)_2$	730 (3.88), 517 (3.15), 370 (sh), 280 (sh), 248 (4.20)
$[(\text{H}_3\text{N})_5\text{RuTCNE}](\text{PF}_6)_3$	697 (3.56), 510 (sh), 350 (sh), 285 (sh), 236 (3.88)
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_8$	775 (4.30), 530 (3.91), 385 (sh), 297 (4.20), 238 (4.30), 217 (3.41)
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_9$	783 (4.27), 560 (3.79), 335 (4.10), 288 (4.22), 259 (4.32)
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_{10}$	773 (4.34), 548 (3.79), 328 (4.17), 283 (4.23), 252 (4.36), 210 (3.72)
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_{11}$	848 (4.16), 700 (sh), 550 (sh), 472 (3.46), 335 (4.24), 300 (4.17), 262 (4.16), 212 (3.72)
$[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}(\text{PF}_6)_{12}$	853 (sh), 753 (4.01), 675 (sh), 453 (sh), 343 (4.30), 293 (4.16), 250 (4.32), 213 (3.91)

^a High-energy region is not recorded.

Figure 1. Intervalence-transfer band for $[(\text{H}_3\text{N})_5\text{Ru-Fum-Ru}(\text{NH}_3)_5]^{5+}$ in CH_3CN .

complexes of Ir(III),³² which were assigned to metal-to-ligand charge transfers. The spectra also display shoulders in the range 400–300 nm that are not present in the spectra of the free ligands. These shoulders are likely to be LF (d-d) transitions since pentaammineruthenium(II) and -(III) do exhibit absorptions of considerable intensities in this region.²⁸ Bands in the UV region are assigned to $\pi-\pi^*$ (ligand band) transitions since both Fum and TCNE possess bands in this region, and their positions and intensities are slightly perturbed by coordination. Data are shown in Table III.

Near-Infrared Spectra. The spectrum of $[(\text{H}_3\text{N})_5\text{Ru}]_2\text{Fum}^{5+}$ displayed a band at 975 nm ($\epsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$), which is not present in the spectra of the fully oxidized or fully reduced ions. As shown in Figure 1, the band appears as a shoulder on the tail of the intense MLCT band. The energy of this band showed a dependence on the dielectric

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Table IV. Near-Infrared Spectral Data for the $[(H_3N)_5Ru-Fum-Ru(NH_3)_5]^{5+}$ Ion in Various Solvents^a

solvent ^d	$1/n^2 - 1/D_s$ ^b	E_{op} , $cm^{-1} \times 10^3$	χ_o , kcal mol ⁻¹ ^c	
			calcd	obsd
acetonitrile	0.626	10.26	27.69	24.59
ethanol	0.499	9.97	26.26	23.33
acetone	0.493	10.00	25.95	23.05
DMF	0.462	9.57	24.32	21.60
Me ₂ SO	0.435	9.35	22.90	20.33
benzonitrile	0.388	8.70	20.42	18.14

^a Measurements were made at 25 °C. ^b n is the refractive index, and D_s is the dielectric constant. ^c Calculation was made with use of the dielectric continuum model. ^d DMF = dimethylformamide; Me₂SO = dimethyl sulfoxide.

properties¹⁴ of the solvent. The energy, E_{op} , has a contribution from both the inner- and outer-sphere reorganizational terms, χ_i and χ_o , as shown in

$$E_{op} = \chi_i + \chi_o \quad (2a)$$

and

$$E_{op} = \chi_i + e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d} \right) \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \quad (2b)$$

where r_1 and r_2 are the molecular radii of the two sites, d is the distance between the two centers, n is the index of refraction for the solvent, D_s is its dielectric constant, and e is the electronic charge. A plot of E_{op} vs. $(1/n^2 - 1/D_s)$ produced a straight line whose intercept is χ_i and slope is $e^2(1/2r_1 + 1/2r_2 - 1/d)$, from which χ_o can be evaluated. The plot is shown in Figure 2, and the results are shown in Table IV.

Discussion

The mixed-valence ion $[(H_3N)_5Ru]_2Fum^{5+}$ shows the properties expected for a class II¹³ weakly coupled system. The cyclic voltammogram of this ion shows two reversible waves in the potential region of -0.5 to +1.5 V corresponding to stepwise oxidation of the reduced form of the ion in two discrete one-electron steps. The potential difference, $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$, listed in Table I for the two steps is 0.103 V, which corresponds to a comproportionation constant of $K_c = 55$. Although considerably above the statistical value of 4, it is in the range expected for a weakly coupled system.

Further evidence for coupling between the metal centers in the [2,3] ion is the fact that the ion displays an intervalence-transfer (IT) band at 975 nm. According to Hush,¹⁴ the IT transition is the result of a light-induced electron transfer from the Ru(II) center to Ru(III) to give the ion in a vibrationally excited state.



The bandwidth at half-height, $\Delta\bar{\nu}_{1/2}$, is given by Hush¹⁴ as $\Delta\bar{\nu}_{1/2} = (2310\bar{\nu}_{op})^{1/2}$ in cm^{-1} . The calculated value for the bandwidth is 4867 cm^{-1} while the experimental one is 5040 cm^{-1} . For weakly coupled systems,¹³ the experimental value is, in fact, a little larger than calculated.

Hush's theory¹⁴ predicts that for a weakly coupled system the IT band energy would show linear dependence on the dielectric properties of the solvent. The slope and intercept of the line in Figure 2 are 16.35×10^3 and 2.00×10^3 cm^{-1} , respectively.

From eq 2b, a calculated value of 18.41×10^3 cm^{-1} was obtained (by using $r_1 = r_2 = 3.8$ Å and $d = 10.1$ Å). The calculation was found to be sensitive to the values of both r and d , and if a value of $r = 4.1$ Å instead of 3.8 Å were used, both the calculated and the experimental values would be the same. Accordingly, in CH₃CN, the outer-sphere reorganizational term, χ_o evaluated from the slope in Figure 2, has a

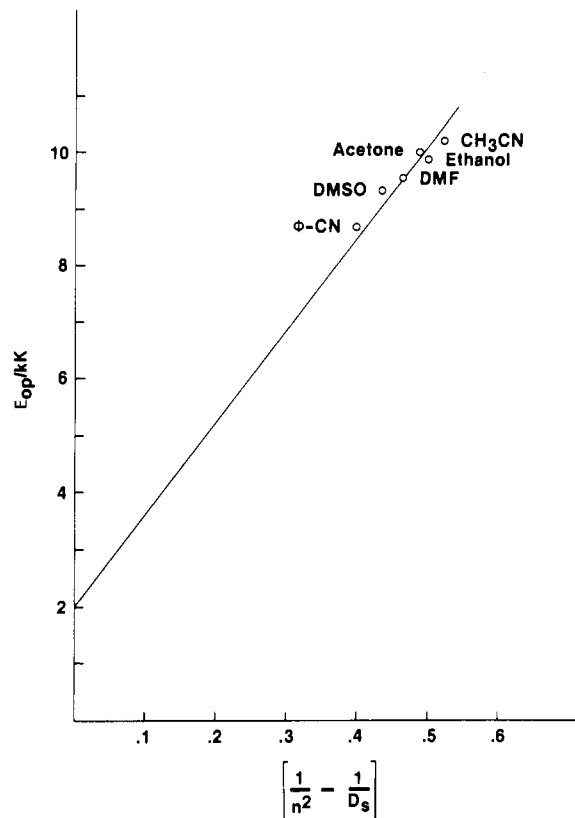


Figure 2. Plot of E_{op} vs. $(1/n^2 - 1/D_s)$ for $[(H_3N)_5Ru-Fum-Ru(NH_3)_5]^{5+}$ in various solvents.

value of 24.59 kcal mol⁻¹ and is in a fair agreement with the calculated value of 27.69 kcal mol⁻¹ in the same solvent.

Due to lack of structural information for Ru(II) and Ru(III) Fum complexes as well as known force constant values for $\bar{\nu}(Ru-NC)$, it was not possible to obtain a calculated value for χ_i for comparison with the value of the intercept in Figure 2.³³

The extent of electronic delocalization in the ground state, α^2 , can be calculated¹³ from the band oscillator strength, its energy in $cm^{-1} \times 10^3$, and the distance d , in Å, separating the two metal centers, estimated for $[(H_3N)_5Ru-Fum-Ru(NH_3)_5]^{5+}$ to be 10.1 Å.

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

A value of 3×10^{-4} for α^2 is in the range expected for electron trapped or weak coupling.³⁴ This value, compared with 1.7×10^{-3} reported for the μ -4,4'-bipyridyl system,³⁵ which is known to belong to class II, indicates essentially localized valence.^{13,14} The oscillator strength, f , for the IT band has a value of 3.5×10^{-3} , the dipole moment $D = 0.177$ Å, the transition dipole moment $|M| = 8.5 \times 10^{-11}$ e Å, and the mixing coefficient $a = 1.75 \times 10^{-2}$. These values support the conclusion that $[(H_3N)_5Ru]_2Fum^{5+}$ is a class II ion.

In the case of $[(H_3N)_5Ru]_4TCNE^{n+}$ ($n = 9-11$) ions, the IT bands were not observable in the expected spectral region (ca. 1000 nm) even though large values of K_c were found. However, careful examination of the spectra in Figure 3 gives a possible explanation as to why these bands were difficult to

(33) $\chi_i = (4n/2)[f_1f_2/(f_1 + f_2)](\Delta r)^2$, where n is the number of M-L bonds/metal center, f_1 and f_2 are force constants for $\nu(M^{II}-L)$ and $\nu(M^{III}-L)$, respectively, and Δr is the difference between M^{II}-L and M^{III}-L bond lengths.

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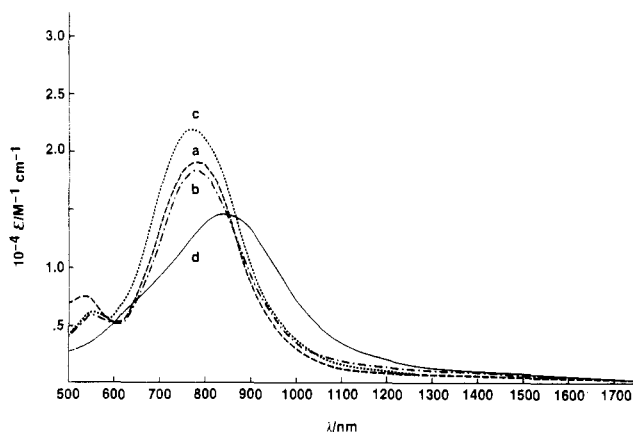


Figure 3. Visible-near-infrared spectra for $[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{n+}$ at 25 °C in CH_3CN : (a) $n = 8$; (b) $n = 9$; (c) $n = 10$; (d) $n = 11$.

observe. As shown in Figure 3, the spectra are dominated by the very intense $d_x-\pi^*(\text{L})$ charge-transfer band near the 800-nm region that is tailing into the entire near-IR region. If the TCNE system were considered to be a weakly coupled system similar to that of Fum, then one would expect the IT band(s) to appear in the neighborhood of 1000 nm with ϵ in the range of $(1-2) \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$. In Figure 3, the red side of the 800-nm band has an $\epsilon = (4-5) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in this region and would evidently mask the weak IT band(s). On this basis, the 800-nm band would not be considered an IT band for the following reasons: (a) The band is narrow ($\Delta\bar{\nu}_{1/2} = 3.3 \times 10^3 \text{ cm}^{-1}$) compared with usual IT bands ($4-8 \times 10^3 \text{ cm}^{-1}$). (b) The band has an $\epsilon \approx 20\,000 \text{ M}^{-1} \text{ cm}^{-1}$, which is too large for such a weak IT transition. Furthermore, this band is present in the spectrum of the $[(\text{H}_3\text{N})_5\text{Ru}]\text{TCNE}^{2+}$ ion, which does not possess an IT band.

However, a much more likely alternative reason for not observing IT bands is offered below. The spectra of $[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{12+}$ ions possess strong bands in the 800-nm region (see Table III), which are assigned to LMCT transitions. Since the metal centers (any two centers attending the IT transition) are separated by large distances,³⁶ they (Ru^{II} and Ru^{III}) interact through higher order perturbations utilizing nonorthogonal LMCT and MLCT states.³⁷ Now, since both MLCT and LMCT transitions required low energy (800-nm region), the interaction between $\text{Ru}(\text{II})$ and $\text{Ru}(\text{III})$ must be strong. According to Hush,³⁸ for a delocalized system, the separation between the excited and ground states increases as the extent of coupling increases and consequently an IT band(s) in the 800-nm region is not unusual. The band appears quite narrow, which is usual for a delocalized system. Of course the band envelope includes the MLCT and LMCT as well. The above argument is supported by the large values for the K_c 's.

It was shown^{5,39} that the $d_x-\pi^*(\text{L})$ MLCT transition ($\text{L} = \text{pyrazine}$) in the [2,2] ion is affected by the remote metal ion. This remote metal ion stabilizes the charge-transfer excited state ($\text{Ru} \rightarrow \text{L}$),⁵ and the band is red shifted. As shown in Table III, this red shift in going from nonmetallic to poly-metallic ions was observed in both the Fum and TCNE systems.

The above mentioned stabilization of the charge-transfer excited state is coupled with an increase in the extent of $d_x-\pi^*$ back-donation. This is manifested in the value of ϵ , which

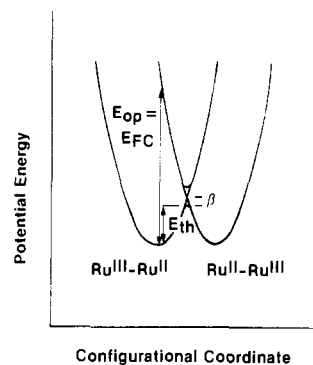


Figure 4. Potential energy as a function of nuclear configuration for a symmetrical binuclear ion such as $[(\text{H}_3\text{N})_5\text{Ru}-\text{Fum}-\text{Ru}(\text{NH}_3)_5]^{5+}$.

increases by a factor of ~ 2.5 in going from mononuclear to bi- or tetranuclear ions. When one ruthenium center is oxidized to form the mixed-valence ion, the value of ϵ is always higher than its value in the mononuclear ion. This, again, is due to the effect of the remote positive $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ group, which makes the bridging ligand more acidic and hence increases the $d_x-\pi^*$ back-bonding.

Sutton and Taube⁴⁰ have recently discussed the factors involved in the stabilization of weakly coupled binuclear systems based on ruthenium amines. These include electrostatic interaction, an inherent electronic instability of the [2,2] state, and stabilization of the [3,2] state by the inductive effect of the 3+ charge. The resonance contribution, ΔG_R , was found to be usually less than 10% for a series of bipyridyl-bridged complexes while the electrostatic contribution, ΔG_E , calculated from an ellipsoidal model was about 25% of the total ΔG . The remainder was attributed to the other two factors. Certainly in the tetranuclear TCNE system, ΔG_R makes an important contribution to the stability of the mixed-valence ions while ΔG_E would be insignificant. The other two factors could also make important contributions to stability of the 9+, 10+, and 11+ ions. Thus, the inherent electronic instability the [2,2,2,2] ion should be considerably greater than that of the [2,2] ion, and the inductive effects of the 3+ charges might be expected to be greater in the tetranuclear ion.

The mixed-valence ion $[(\text{H}_3\text{N})_5\text{Ru}]_4\text{TCNE}^{10+}$ ($K_c = 10^5$) was more stable than either the 9+ ($K_c = 10^3$) or 11+ ($K_c = 300$) ions. The reason for the increased stability of the 10+ is not known, but it seems reasonable that the inductive effects are at a maximum in the species containing two $\text{Ru}(\text{II})$'s and two $\text{Ru}(\text{III})$'s. The increased interaction in the 10+ ion is reflected in the value of $\epsilon = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

According to Hush,¹⁴ the energy of the IT transition for a symmetrical ion such as $[(\text{H}_3\text{N})_5\text{Ru}-\text{L}-\text{Ru}(\text{NH}_3)_5]^{5+}$ ($\text{L} = \text{bifunctional}, \pi\text{-acceptor}$) is equal to the Franck-Condon barrier to the electron transfer, E_{Fc} , as shown in eq 5 and

$$E_{\text{op}} = E_{\text{Fc}} \quad (5)$$

Figure 4. It can be seen that the energy, E_{op} , is related to the thermal energy for electron transfer, E_{th}

$$E_{\text{th}} = \frac{E_{\text{op}}}{4} - \beta = \frac{E_{\text{Fc}}}{4} - \beta \quad \beta \approx \alpha E_{\text{op}} \quad (6)$$

where β is the delocalization or resonance energy, and its value for the fumaronitrile dimer is 0.022 V. The calculated thermal energy for electron transfer, E_{th} , is 6.82 kcal mol⁻¹ at 25 °C in CH_3CN . The first-order rate constant for the intramolecular electron exchange, k_{et} , is $\approx 10^8 \text{ s}^{-1}$.⁴¹

(36) Geminal Ru-Ru = 8.1 Å, cis Ru-Ru = 6.0 Å, and trans Ru-Ru = 10.1 Å.

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(41) $k_{\text{et}} = k_{\text{B}}T/h \exp(-E_{\text{th}}/RT)$; k_{B} is Boltzmann's constant and h is Planck's constant.

Conclusion

The evidence indicates the diruthenium fumarionitrile mixed-valence ion belongs to class II. The evidence includes the calculated value of α^2 , the IT bandwidth $\Delta\bar{\nu}_{1/2}$, and the solvent dependence of E_{op} . On the other hand, the spectral and electrochemical properties of the tetraruthenium TCNE mixed-valence species suggest this system is strongly delocalized. Of the three mixed-valence ions (9+, 10+, 11+), the doubly oxidized 10+ species was the most stable.

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Registry No. [(H₃N)₅RuFum](PF₆)₂, 85748-65-8; [(H₃N)₅RuFum](PF₆)₃, 85748-67-0; [(H₃N)₅Ru]₂Fum(PF₆)₄, 85748-69-2; [(H₃N)₅Ru]₂Fum(PF₆)₅, 85748-71-6; [(H₃N)₅Ru]₂Fum(PF₆)₆, 85748-73-8; [(H₃N)₅RuTCNE](PF₆)₂, 85748-75-0; [(H₃N)₅RuTCNE](PF₆)₃, 85748-77-2; [(H₃N)₅Ru]₄TCNE(PF₆)₈, 85748-79-4; [(H₃N)₅Ru]₄TCNE(PF₆)₉, 85748-81-8; [(H₃N)₅Ru]₄TCNE(PF₆)₁₀, 85748-83-0; [(H₃N)₅Ru]₄TCNE(PF₆)₁₁, 85748-85-2; [(H₃N)₅Ru]₄TCNE(PF₆)₁₂, 85748-87-4; [Ru(NH₃)₅OH₂](PF₆)₂, 34843-18-0.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305

Autoxidation of Binuclear Ruthenium(II) Ammines

DAVID M. STANBURY, DENNIS GASWICK, GILBERT M. BROWN, and HENRY TAUBE*

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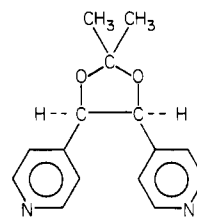
The reduction of oxygen to hydrogen peroxide by a series of binuclear ruthenium(II) amines has been studied in acidic aqueous solution. The complex [(Ru(NH₃)₅)₂L]⁴⁺, where L = BPDO = *meso*-4,5-bis(4-pyridyl)-2,2-dimethyl-1,3-dioxolane, was studied in greatest detail. BPDO has a geometry such as to force the two ruthenium centers into close proximity. The kinetics of the autoxidation of the BPDO binuclear complex, as measured by the decay of the charge-transfer band characteristic of ruthenium(II) pyridyl type complexes, showed biphasic behavior. The first phase corresponds to the pseudo-first-order reaction of the fully reduced complex, while the second phase corresponds to the reaction of the mixed-valence species. Inhibition of the second phase by Ru(III) at higher pH is taken as evidence that the mechanism involves outer-sphere electron transfer to form free superoxide. Subsequent protonation of superoxide and reduction to hydrogen peroxide complete the reaction. By comparison of the rates and expected steric and electrostatic effects, it is argued that the mechanism of the first phase likewise has a rate-limiting step involving outer-sphere generation of superoxide.

Introduction

A major kinetic barrier in the reactions of small molecules is that they often proceed through unstable free-radical intermediates. Two-electron transfers have been well documented for certain inner-sphere reactions of mononuclear complexes,¹ and the chemistry of platinum amines provides some especially interesting examples.² There is growing interest in binuclear species as providing a means of bypassing the unstable intermediates that attend a one-electron change, and the validity of this approach has been convincingly demonstrated for the reactions with O₂ of certain cofacial cobalt-containing porphyrins.³ These reagents undoubtedly react with O₂ by inner-sphere mechanisms. Whether there can be cooperation between two centers when reaction occurs by an outer-sphere mechanism is more problematical, but the possibility that cooperativity of this kind might be documented provided the incentive for the work to be described.

Our continuing interest in binuclear ruthenium amines⁴ suggested them as a logical starting point in the search for multielectron reactions. The choice of oxygen as the redox partner was dictated by a certain familiarity with its chemistry,^{5,6} its known participation in two-electron reactions,^{1b} and

its relevance to the development of an efficient oxygen electrode. Our first goal was to delineate the behavior of a system in which two weakly interacting metal centers are held in a geometry such that oxygen could interact with both centers simultaneously. The bifunctional ligand BPDO⁷ served this purpose.



BPDO

When each nitrogen carries a pentaammineruthenium unit, the metal centers are separated by ~ 7 Å.

When the rates of reaction of the binuclear complexes are compared with the mononuclear ones based on the same ligands, rate accelerations for the reducing agents presented in the binuclear mode compared to mononuclear are observed. Though these rate enhancements are not large, any unambiguous evidence of cooperativity ascribable to concerted attack by the two centers would be significant and would encourage us to try to enhance the effects. We therefore considered it important to analyze the results critically. Our conclusion is that the rate enhancements we observe do not arise from the kind of cooperativity we were searching for. Nevertheless, we

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- (7) Abbreviations: BPDO = *meso*-4,5-bis(4-pyridyl)-2,2-dimethyl-1,3-dioxolane, BPA = 1,2-bis(4-pyridyl)ethane, BPED = *meso*-1,2-bis(4-pyridyl)ethane-1,2-diol, TFA = trifluoroacetate, DMF = dimethylformamide, TFMS = trifluoromethanesulfonate. Units: wavelength, nm; ϵ , M⁻¹ cm⁻¹ (subscript on ϵ specifies wavelength).