Table V. Summary of Luminescence Decay Constants and the Corresponding Hydration Change

	k_{EuL}	Δk	Δn^b
	I. Binary Complexes		
malonate	6.61	2.19^a	2.3
succinate	7.33	1.47^a	1.5
glutarate	7.25	1.55^a	1.6
adipate	7.33	1.47^a	1.5
	II. Ternary Complexes		
malonate	2.92	2.08^c	2.2
succinate	3.55	1.45^c	1.5
glutarate	3.93	1.07^c	1.1
adipate	4.06	0.94^c	1.0

[a] The difference between the luminescence decay constant of aqueous europium (8.80 ms^{-1}) and the characteristic luminescence decay constant of the 1:1 complex. [b] Calculated from eq 1. [c] The difference between the luminescence decay constant of the EuNTA complex (5.00 ms^{-1}) and the characteristic luminescence decay constant of the 1:1:1 complex.

about 0.5 for solutions in D_2O containing about 70% of the 1:1 complexes or of the 1:1:1 complexes and this value is constant from one complex to another within the experimental error. These observations provide support for the validity of eq 1.

Among this group of dicarboxylic ligands, only malonate behaves strictly as a bidentate ligand in both the binary complexes and the ternary complexes ($\Delta n \simeq 2$). For the binary complexation succinate, glutarate, and adipate seem to give a mixture of mono- and bidentate ($\Delta n \simeq 1.5$) species. This is in agreement with the conclusions of ref 1, where it was shown that the stability constants of the lanthanide complexes with succinate, glutarate, and adipate reflect less stabilization than expected for bidentate complexation.

The value of k_{obs} for EuNTA gives a value of 4.5 for n_{H_2O}, indicating the displacement of four water molecules. For the ternary complexes, the succinate system seems to have a mixture of mono- and bidentate ($\Delta n \simeq 1.5$) species, while the complexation by glutarate and adipate would be best described as monodentate ($\Delta n \simeq 1$). This is in agreement with the conclusion proposed in ref 2 that the complexation goes from bidentate to monodentate in the ternary complexes as the length between the binding sites is increased from malonate to adipate.

We conclude that these europium luminescence lifetime measurements confirm the interpretation of the thermodynamic data for the same complexes and show the decrease in bidentate character as the alkyl chain length increases in the dicarboxylate ligands.

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Registry No. Malonate, 141-82-2; succinate, 56-14-4; glutarate, 110-94-1; adipate, 124-04-9.

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Electron-Exchange and Electron-Transfer Reactions Involving the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ Couple in Acetonitrile

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The kinetics of a series of outer-sphere electron-transfer reactions involving the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple ($E° = 1.16$ V vs NHE) with nickel tetraaza macrocycles and iron and ruthenium tris(polypyridine) complexes were investigated in acetonitrile at 25.0 °C and an ionic strength of 0.10 M. The application of the Marcus relationship to the cross-reaction kinetic data yields a self-exchange rate constant of $(3.0 \pm 1.7) \times 10^5$ M^{-1} s^{-1} for the dirhodium couple. The $Rh_2(O_2CCH_3)_4(CD_3CN)_2^{0/+}$ electron-exchange rate constant has been determined directly from ^1H NMR line-broadening experiments and at 25 °C is $(5.3 \pm 0.3) \times 10^4$ M^{-1} s^{-1} (independent of ionic strength) in acetonitrile. A small inner-sphere barrier, accompanying the transfer of a weakly antibonding π^* electron, accounts for the moderately large self-exchange rate constant, which is similar to the value for the $Rh_2(O_2CCH_3)_4(H_2O)_2^{0/+}$ couple in aqueous solution. The k_{11} value for the dirhodium couple is compared with self-exchange rate constants measured in acetonitrile for other couples of similar charge and size.

Introduction

The chemistry of carboxylate-bridged dirhodium(II) complexes has been extensively studied in the past two decades.[1,2] While the earlier investigations were concerned with the interesting structural and spectroscopic properties, more attention recently has been paid to the ligand-substitution and redox reactions in solution. The dirhodium(II) complexes may be chemically or electrochemically oxidized to the mixed-valence cation $Rh_2(O_2CR)_4L_2^+$ with the unpaired electron delocalized between the two rhodium atoms. The kinetics of a series of outer-sphere electron-transfer reactions involving $Rh_2(O_2CCH_3)_4(H_2O)_2$ and $Rh_2(O_2CCH_3)_4(H_2O)_2^+$ have been reported previously from this laboratory.[3,4] The relatively large self-exchange rate constant of $(1.5 \pm 1.1) \times 10^5$ M^{-1} s^{-1} determined for the $Rh_2(O_2CCH_3)_4(H_2O)_2^{0/+}$ couple from the application of the Marcus relation to the cross-reaction data is consistent with the exchange of a weakly antibonding Rh-Rh π^* electron. The self-exchange rate constant has recently been determined directly from ^1H NMR line-broadening experiments,[5] with the measured value of 2.9×10^5 M^{-1} s^{-1} found to be in excellent agreement with the Marcus calculations.

In this paper we report the results of kinetic investigations of outer-sphere electron-transfer reactions involving the $Rh(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ complex couple in acetonitrile. While the majority of the kinetic studies of outer-sphere electron-transfer reactions between transition-metal complexes have been performed in aqueous solution, the use of nonaqueous media, notably acetonitrile, is receiving increasing attention.[6-9] The treatment of outer-sphere cross-reaction kinetic data according to the Marcus relationship is hampered by the limited number of self-exchange rate constants determined for metal complex couples in this solvent.

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The self-exchange rate constants of several Ni(II/III) tetraaza macrocycle couples have been estimated in this study from cross-reaction measurements. These species, along with iron and ruthenium tris(polypyridine) complexes have been employed in a determination of the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ exchange rate constant in acetonitrile. The self-exchange rate constant has also been measured directly by a study of the line broadening of the ^1H NMR signal of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ in the presence of the paramagnetic $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ cation. The rate constant is compared with the value for the diaqua adduct and with other metal complex couples of similar size and charge product. The relative electron-exchange rate constants are discussed in terms of the inner-sphere reorganization barriers and their relation to the electron configurations of the couples.

Experimental Section

Materials. Acetonitrile (BDH, Omnisolv) was used as received or washed with anhydrous sodium sulfate, filtered, and distilled from calcium hydride prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) and tetraethylammonium perchlorate were prepared by the metathesis of the corresponding bromide salt with perchloric acid. The precipitate was recrystallized from water and dried at 80 °C under reduced pressure. $Rh_2(O_2CCH_3)_4$ was used as received (Aldrich) or prepared by the method of Rempel et al.[10] The concentration of the $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ species in acetonitrile was determined spectrophotometrically at 553 nm ($\epsilon = 235$ M^{-1} cm^{-1}) and 437 nm ($\epsilon = 112$ M^{-1} cm^{-1}).[11] The cation $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ was prepared by electrochemical oxidation of the reduced species at platinum electrodes in acetonitrile (0 °C) using 0.10 M TBAP as the electrolyte. Concentrations of the dirhodium cation were determined spectrophotometrically at 797 nm ($\epsilon = 280$ M^{-1} cm^{-1}) and at 505 nm ($\epsilon = 260$ M^{-1} cm^{-1})[12] by using Perkin-Elmer 552 and Hewlett-Packard 8452A spectrometers. There was no spectroscopic evidence for the axial coordination of trace amounts of residual water in the acetonitrile solvent, and the rhodium complexes are regarded as bis(acetonitrile) adducts.

The nickel(II) complexes $[Ni([14]aneN_4)](ClO_4)_2$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane), $[Ni(Me_2[14]dieneN_4)](ClO_4)_2$ ($Me_2[14]dieneN_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclodeca-4,11-diene), $[Ni(Me_6[14]dieneN_4)](ClO_4)_2$ ($Me_6[14]dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $[Ni(rac\text{-}Me_6[14]aneN_4)](ClO_4)_2$, and $[Ni(meso\text{-}Me_6[14]aneN_4)](ClO_4)_2$ (*rac*- and *meso*-$Me_6[14]aneN_4$ = *rac*- and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by the addition of the appropriate ligand to nickel(II) perchlorate in methanol or ethanol.[13] The corresponding nickel(III) complexes were obtained in acetonitrile solution by electrochemical oxidation of the Ni(II) species as described above for the dirhodium complex. The ruthenium(II) and iron(II) tris(polypyridine) complexes were prepared as perchlorate or chloride salts by reported methods.[14] The iron(III) tris(polypyridine) complexes were prepared electrochemically in acetonitrile as described above.

Kinetic Studies. The kinetic measurements were made by using a TDI Model IIA stopped-flow apparatus and data-acquisition system (Cantech Scientific) interfaced to a Zenith ZF-151 microcomputer. Pseudo-first-order conditions of excess dirhodium tetraacetate concentrations were employed, and plots of ln ($A_\infty - A_t$) or ln ($A_t - A_\infty$) against time were linear for at least 3 half-lives. The first-order rate constants were determined from the average of four to six replicate experiments. The reactant solutions were prepared in dried acetonitrile containing 0.10 M (unless otherwise indicated) TBAP to maintain the ionic strength. The kinetic measurements were performed at 25.0 ± 0.1 °C, with thermostating provided by a circulating water bath.

^1H NMR Kinetic Studies. The electron-self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(CD_3CN)_2^{0/+}$ couple was measured in CD_3CN (MSD Isotopes, 99.7% D) at 25.0 ± 0.5 °C from studies of the line broadening of the ^1H NMR spectrum in the presence of the paramagnetic Rh_2^+ cation. $Rh_2(O_2CCH_3)_4(CD_3CN)_2^+$ ((3-4 × 10^{-3} M) was generated in CD_3CN solution by the oxidation of the Rh_2 species using solid PbO_2 in the presence of 0.01 M anhydrous CF_3SO_3H. The filtered solutions were analyzed spectrophotometrically at 505 and 797 nm and showed negligible decay during the course of the NMR experiment. The ionic strength was adjusted as required between 0.005 and 0.10 M by using anhydrous $NaClO_4$ (G. F. Smith). The measurements were performed on a Bruker HX-60 instrument at 60 MHz using CD_3CN as a field lock.

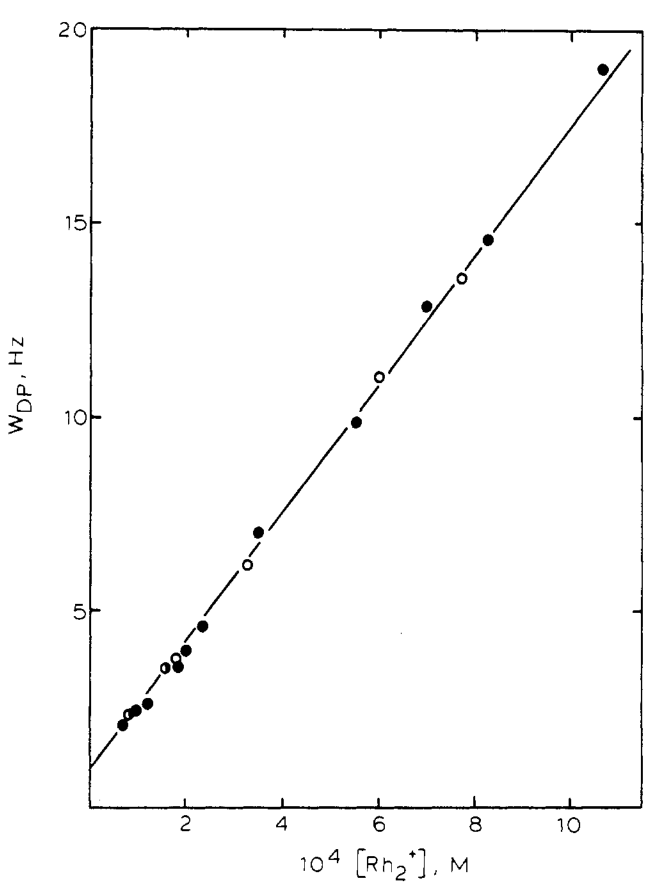

Figure 1. Plot of the observed $Rh_2(O_2CCH_3)_4(CD_3CN)_2$ ^1H NMR line width, W_{DP}, against the concentration of $Rh_2(O_2CCH_3)_4(CD_3CN)_2^+$ in CD_3CN (25 °C) at ionic strengths of ≈0.002 M (no added electrolyte) (●) and 0.10 M, using $NaClO_4$ (○) or TEAP (◐).

Cyclic Voltammetry. The cyclic voltammetric measurements were carried out in acetonitrile (0.10 M TBAP) with a BAS CV-1B cyclic voltammograph (Bioanalytical Systems) attached to a Houston Instruments 100 X-Y recorder. The working (Pt button) and auxiliary (Pt wire) electrodes in the sample solution were separated from the reference electrode (Ag/AgCl) by a glass frit. The ferrocinium/ferrocene couple ($FeCp_2^+/FeCp_2$, 0.400 V vs NHE) was used as an internal reference.[15]

Results

Electron-Exchange Kinetic Measurements. The electron-self-exchange rate constant, k_{11}, for $Rh_2(O_2CCH_3)_4(CD_3CN)_2^{0/+}$ (eq 1) was measured directly from ^1H NMR line-broadening experiments in CD_3CN at 25 °C.

$$Rh_2(O_2CCH_3)_4(CD_3CN)_2 + {}^*Rh_2(O_2CCH_3)_4(CD_3CN)_2^+ \xrightarrow{k_{11}} Rh_2(O_2CCH_4)_2(CD_3CN)_2^+ + {}^*Rh_2(O_2CCH_3)_4(CD_3CN)_2 \quad (1)$$

The ^1H NMR spectrum of the $Rh_2(O_2CCH_3)_4(CD_3CN)_2$ complex consists of a single resonance for the acetate protons at 1.79 ppm with a line width of 1.2 Hz. For the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ cation the ^1H signal is shifted 1060 Hz upfield to −15.9 ppm, with a line width of 38 Hz. Successive additions of the paramagnetic Rh_2^+ cation ((0.6–10.3) × 10^{-4} M) resulted in a linear increase in the line width of the diamagnetic signal ((4–5) × 10^{-3} M). For a system in the

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Table I. Rate Constants for Electron-Transfer Cross-Reactions Involving Nickel Tetraaza Macrocycles in Acetonitrile at 25.0 °C

oxidant	reductant	$E°$, V	I, M	k_{12}, $M^{-1}\ s^{-1}$	$k_{11}(CH_3CN)$,[a] $M^{-1}\ s^{-1}$	$k_{11}(H_2O)$,[b] $M^{-1}\ s^{-1}$
$Ni(Me_6[14]dieneN_4)^{3+}$	$Ru(bpy)_3^{2+}$	0.07	0.10	1.68×10^4	1.1	6
$Ni(rac\text{-}Me_6[14]aneN_4)^{3+}$	$Ru(bpy)_3^{2+}$	−0.02	0.10	8.78×10^3	9.7	31
$Ni(meso\text{-}Me_6[14]aneN_4)^{3+}$	$Ru(bpy)_3^{2+}$	−0.02	0.10	1.22×10^4	19	60
$Fe(5,6\text{-}Me_2phen)_3^{3+}$	$Ni([14]aneN_4)^{2+}$	0.02	0.052	2.28×10^5	1.1×10^3	2.0×10^3
$Fe(5,6\text{-}Me_2phen)_3^{3+}$	$Ni(Me_2[14]dieneN_4)^{2+}$	0.01	0.052	2.55×10^5	2.0×10^3	3.0×10^3

[a] Calculated by using self-exchange data from ref 6; $k_{22} = 1.7 \times 10^7\ M^{-1}\ s^{-1}$ for $Ru(bpy)_3^{2+/3+}$ and $2.0 \times 10^7\ M^{-1}\ s^{-1}$ for $Fe(5,6\text{-}Me_2phen)_3^{2+/3+}$. [b] Data from ref 28–30.

slow-exchange domain, $k_{11}[Rh_2^+] \ll 2\pi(\delta\nu)$, the electron-exchange rate constant may be determined from the relationship between the extent of the line broadening and the concentration of the paramagnetic species.[16] In eq 2 W_D is the line width (full width

$$k_{11}[Rh_2^+] = \pi(W_{DP} - W_D) \tag{2}$$

at half-maximum) of the diamagnetic signal and W_{DP} is the line width of the signal in the presence of the paramagnetic species. From the slope of a plot of W_{DP} against the concentration of the paramagnetic $Rh_2(O_2CCH_3)_4(CD_3CN)_2^+$ cation (Figure 1), the exchange rate constant was found to be $(5.3 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C and an ionic strength of ≈0.002 M (no added electrolyte). The ionic strength was adjusted between ≈0.002 M and 0.10 M by using anhydrous $NaClO_4$, and the line widths at $[Rh_2^+] = 1.9 \times 10^{-4}$ M were the same, within experimental error (3.7 ± 0.2 Hz) at several ionic strengths in this range. At an ionic strength of 0.10 M the plot of W_{DP} against $[Rh_2^+]$ yielded a self-exchange rate constant of $(5.4 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$. Two points are also included in Figure 1 at an ionic strength of 0.10 M using TEAP (the methyl peaks of TEAP interfere with the broadening signal at higher $[Rh_2^+]$), and these fall on the same slope as the other data.

Electron-Transfer Kinetic Studies. The $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ ion is a moderately strong oxidant in acetonitrile. The reduction potential of 1.16 V vs NHE (0.10 M TBAP) measured by cyclic voltammetry is in good agreement with the previously reported value of 0.75 V vs $FeCp_2^+/FeCp_2$.[12] The kinetics of the outer-sphere oxidation of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ and the reduction of $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ by a series of nickel tetraaza macrocycles and ruthenium tris(polypyridine) complexes were investigated at 25.0 °C in acetonitrile containing 0.10 M TBAP.

$$Rh_2(O_2CCH_3)_4(CH_3CN)_2 + Ox \overset{k_{12}}{\rightleftharpoons} Rh_2(O_2CCH_3)_4(CH_3CN)_2^+ + Red \tag{3}$$

For the reactions involving the nickel tetraaza macrocycles, the reductant was present in a pseudo-first-order excess, and the process was followed by monitoring the changes in the Ni(III) absorbances in the 350–400-nm range. The reactions involving the iron and ruthenium tris(polypyridine) complexes were followed by monitoring the absorbance changes at the maximum of the Fe(II) or Ru(II) species, with the dirhodium complex present in a pseudo-first-order excess. Plots of k_{obs} against reductant concentration were linear. The second-order rate constants for these reactions are presented in Table I.

The kinetics of the reaction of $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ with $Ni(Me_6[14]dieneN_4)^{3+}$ were investigated as a function of ionic strength. The cross-reaction rate constant decreased slightly with increasing ionic strength (TBAP) from 0.001 M ($k_{12} = 2.51 \times 10^4\ M^{-1}\ s^{-1}$) to 0.10 M ($k_{12} = 1.63 \times 10^4\ M^{-1}\ s^{-1}$). The rate constant for the reduction of $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ by $Ni([14]aneN_4)^{2+}$ increased between $I = 0.001$ M ($k_{12} = 4.7 \times 10^4\ M^{-1}\ s^{-1}$) and 0.10 M ($k_{12} = 7.3 \times 10^5\ M^{-1}\ s^{-1}$).

Reactions of Nickel Tetraaza Macrocycles. The self-exchange rate constants of the $Ni([14]aneN_4)^{2+/3+}$ ($E° = 0.99$ V vs NHE), $Ni(Me_2[14]dieneN_4)^{2+/3+}$ ($E° = 1.00$ V), $Ni(rac\text{-}Me_6[14]aneN_4)^{2+/3+}$ ($E° = 1.24$ V), $Ni(meso\text{-}Me_6[14]aneN_4)^{2+/3+}$ ($E° = 1.24$ V), and $Ni(Me_6[14]dieneN_4)^{2+/3+}$ ($E° = 1.33$ V) couples were determined from the kinetic data for cross-reactions with iron and ruthenium tris(polypyridine) complexes[6] in acetonitrile at 25.0 °C (Table I).

$$Ni([14]N_4)^{2+} + ML_3^{3+} \rightleftharpoons Ni([14]N_4)^{3+} + ML_3^{2+} \tag{4}$$

The reactions were followed by monitoring the changes in absorbance at the wavelength maxima of the Fe(II) and Ru(II) species and were carried out with a pseudo-first-order excess of the nickel complex ($(1\text{–}5) \times 10^{-4}$ M) over the metal tris(polypyridine) complex ($(6\text{–}8) \times 10^{-6}$ M). For the reactions of $Ru(bpy)_3^{2+}$ with the Ni(III) tetraaza macrocycles the ionic strength of the solution was maintained at 0.10 M with the addition of TBAP. For the cross-reactions of $Ni([14]aneN_4)^{2+}$ and $Ni(Me_2[14]dieneN_4)^{2+}$ with $Fe(5,6\text{-}Me_2phen)_3^{3+}$, the rate was too rapid to be measured accurately at this ionic strength, and therefore a lower range (0.010–0.052 M TBAP) was employed. An increase in the rate constant with ionic strength was also observed in these reactions.

Discussion

The electron-self-exchange rate constant measured directly for the $Rh_2(O_2CCH_3)_4(CD_3CN)_2^{0/+}$ couple in acetonitrile, $5.3 \times 10^4\ M^{-1}\ s^{-1}$, is somewhat smaller than the corresponding value of $2.9 \times 10^5\ M^{-1}\ s^{-1}$ determined by ^1H NMR line-broadening experiments for the diaqua adduct couple, $Rh_2(O_2CCH_3)_4(D_2O)_2^{0/+}$,[5] in aqueous solution. Decreases in electron-transfer rate constants on going from aqueous to acetonitrile media have been observed previously for systems such as the $Co(bpy)_3^{3+}/Co(terpy)_2^{2+}$ reaction (9.9 $M^{-1}\ s^{-1}$ in H_2O and 1.0 $M^{-1}\ s^{-1}$ in CH_3CN; $I = 0.0027$ M)[17] and were related to the greater solvent reorganization barrier in acetonitrile. The $Rh_2^{0/+}$ exchange rate constant was found to be independent of ionic strength over the range 0.002–0.10 M. The self-exchange rate constant of the $FeCp_2^{0/+}$ (Cp^- = cyclopentadienyl anion) couple has been found to decrease with an increase in the ionic strength ($NaClO_4$) in acetonitrile. This dependence was attributed to a slightly greater reactivity of the free $FeCp_2^+$ ion ($k = 5.2 \times 10^6\ M^{-1}\ s^{-1}$) over the $FeCp_2^+,ClO_4^-$ ($k = 3.0 \times 10^6\ M^{-1}\ s^{-1}$) ion pair.

In addition to a direct measurement of the self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple, this value may also be determined from an application of the Marcus relations[18] to outer-sphere cross-reaction kinetic data or estimated by using structural and vibrational data in a semiclassical model calculation. While the axially coordinated solvent molecules on the nickel(II) and dirhodium(II) complexes are quite labile,[19,20] the substitution inertness of their cross-reactants and the lack of potential bridging ligands in this study ensure that the electron-transfer reactions proceed by an outer-sphere mechanism.

The cross-reaction kinetic data from this study may be correlated in terms of the Marcus equation,[18] which relates the rate constant for a cross-reaction k_{12} to the rate constant for the component self-exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross reaction K_{12} by[21]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{5}$$

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where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \qquad (6)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (7)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s \sigma_{ij}(1 + \beta\sigma_{ij} I^{1/2})} \qquad (8)$$

In the above expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of the radii of the ions), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, and $A_{ii} = (4\pi N\sigma_{ii}^2\nu_n(\delta r)/1000)$, where δr is the thickness of the reaction shell (≈0.8 Å[21]). The values of A_{ii} are in the range (1–6) × 10^{12} M^{-1} s^{-1}, depending on the nuclear frequency ν_n and σ_{ii} for a particular couple. Radii of 5.5 Å for the rhodium dimer, 5–7 Å for the nickel macrocycles, and 7–8 Å for the iron and ruthenium tris(polypyridine) complexes were used in calculating σ.

It has become evident, from several recent kinetic investigations of electron-exchange[6,7,22] and electron-transfer[23-25] reactions of metal complexes in acetonitrile, that ion pairing plays a major role in the rates of outer-sphere processes and their dependences on ionic strength in this medium. The ion-pair association constants for a number of metal complex cations with anions such as ClO_4^-, PF_6^-, and BF_4^- have been determined from conductivity and kinetic measurements in CH_3CN. At an ionic strength of 0.10 M, ion pairing of the ClO_4^- ion with the cationic metal complexes used in this study is expected to be extensive. Conductivity measurements by Braga and Wahl[24] on FeL_3^{2+},ClO_4^- and CoL_3^{3+},ClO_4^- (L = 2,2′-bipyridine or the 4,4′-dimethyl or 4,4′-diphenyl derivatives) ion pairs indicate K_{IP} values for the $M(bpy)_3^{2+}$ ions are <100 M^{-1}, whereas the association constants for the $M(bpy)_3^{3+}$ ions are in the range 170–900 M^{-1}. While ion-pair association constants in acetonitrile have not been measured for the Ni(II) and Ni(III) tetraaza macrocycles used in this study, a value of 190 M^{-1} has recently been determined for the (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) perchlorate ion pair.[26] In nitrobenzene, a much larger value of K_{IP} for $Ni([14]aneN_4)^{2+}$ (11 000 M^{-1})[27] than for $Ni((N\text{-}Me)_4\text{-}[14]aneN_4)^{2+}$ (1190 M^{-1})[26] has been attributed to hydrogen bonding of ClO_4^- to the NH protons on the former complex. The nickel macrocycle complexes in this study, therefore, likely form very strong ion pairs or perhaps ion triplets, in the case of Ni(III), with perchlorate in acetonitrile.

The observed decrease in the rate constant with increasing ionic strength for the reduction of $Ni(Me_6[14]aneN_4)^{3+}$ by $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ indicates that the ion-paired oxidant species are less reactive than the free complex. A similar dependence has been reported for the oxidations of ferrocene by cobalt(III) clathrochelates in acetonitrile. The independence of the self-exchange rate constant for the $Rh_2^{0/+}$ couple on ionic strength suggests that the ion-pair association constant for $Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$ with ClO_4^- is small (<10 M^{-1}) and/or there is no difference in the reactivities of the free and ion-paired species. In the absence of definitive ion-pair association constants and specific rate constants for the free and ion-pair pathways of the cross-reactions, the work terms (charges z_i and z_j) in eq. 8 are calculated on the basis of ion-paired reactants for the nickel macrocycles and the metal(III) tris(polypyridine) complexes. In the majority of cross-reactions in this study the work terms in eq 7 tend to cancel each other out such that W_{12} is not significantly different from unity.

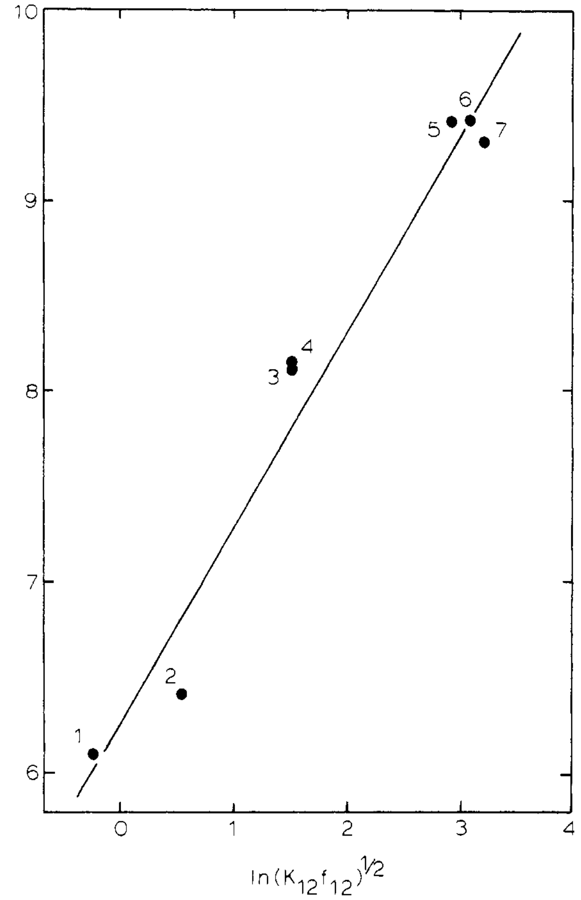

Figure 2. Plot of ln $(k_{12}/(k_{22})^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ for the cross-reactions of the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple in acetonitrile at 25.0 °C with (1) $Ru(4,4'\text{-}Ph_2bpy)_3^{2+}$, (2) $Fe(5\text{-}Cl\text{-}phen)_3^{3+}$, (3) Ni(*rac*-$Me_6[14]aneN_4)^{3+}$, (4) Ni(*meso*-$Me_6[14]aneN_4)^{3+}$, (5) $Ni(Me_2\text{-}[14]dieneN_4)^{2+}$, (6) $Ni([14]aneN_4)^{2+}$, and (7) $Ni(Me_6[14]dieneN_4)^{3+}$.

The self-exchange rate constants of the nickel tetraaza macrocycle complexes used in the cross-reactions with the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple were determined by an application of the Marcus relationship to the kinetic data (Table I) from reactions with iron or ruthenium tris(polypyridine) complexes. The self-exchange rate constants of these species have previously been measured directly in acetonitrile at ionic strengths (perchlorate electrolyte) comparable to the conditions used in the cross-reactions.[6] The Ni(II)/Ni(III) exchange rate constants reported here (Table I) are very similar to the values determined in aqueous solution.[28-30] The self-exchange rate constants for the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple, derived from the cross-reaction data, are presented in Table II. The values range from 1.2 × 10^5 to 5.3 × 10^5 M^{-1} s^{-1}, with a geometric mean of (3.0 ± 1.7) × 10^5 M^{-1} s^{-1}. The agreement may be considered to be good for a determination of this type, with the spread in values likely reflecting the uncertainties in the reduction potentials and self-exchange rate constants of the cross-reactants and the assumptions made for ion pairing. Figure 2 illustrates the adherence of the cross-reaction data to the Marcus relationship, as the plot of ln $(k_{12}/(k_{22})^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ results in a line with a slope of 1.03 ± 0.09, very close to the theoretical value of unity. The k_{11} value of (3.0 ± 1.7) × 10^5 M^{-1} s^{-1} is in reasonable

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Table II. Kinetic Parameters for Electron-Transfer Cross-Reactions Involving the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ Couple in Acetonitrile at 25.0 °C

oxidant	reductant	$E°$, V	k_{12},[a] $M^{-1}\,s^{-1}$	k_{22},[b] $M^{-1}\,s^{-1}$	$10^{-5}k_{11}^{calc}$, $M^{-1}\,s^{-1}$
$Ni(Me_6[14]dieneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(CH_3CN)_2$	0.17	1.63×10^4	1.1	1.8
Ni(*rac*-$Me_6[14]aneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(CH_3CN)_2$	0.08	1.50×10^4	9.7	5.0
Ni(*meso*-$Me_6[14]aneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(CH_3CN)_2$	0.08	2.18×10^4	1.9×10	5.3
$Fe(5\text{-}Cl\text{-}phen)_3^{3+}$	$Rh_2(O_2CCH_3)_4(CH_3CN)_2$	0.03	3.3×10^6	1.5×10^7	1.2
$Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$	$Ru(4,4'\text{-}Ph_2bpy)_3^{2+}$	−0.01	2.0×10^6	1.9×10^7	2.7
$Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$	$Ni([14]aneN_4)^{2+}$	0.17	7.3×10^5	1.1×10^3	3.0
$Rh_2(O_2CCH_3)_4(CH_3CN)_2^+$	$Ni(Me_2[14]dieneN_4)^{2+}$	0.16	8.1×10^5	2.0×10^3	4.3

[a] Ionic strength is 0.10 M (TBAP), except 0.05 M for the oxidation by $Fe(5\text{-}Cl\text{-}phen)_3^{3+}$. [b] Self-exchange rate constants of Ni(II)/Ni(III) cross-reactants determined in this study (k_{11} values in Table I); values for $ML_3^{2+/3+}$ extrapolated from data in ref 6.

agreement with the directly measured electron-exchange rate constant. The former value is slightly larger, likely a result of the ion pairing occurring in the cross-reactions, a feature that is absent in the direct-exchange process. The self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple is comparable to the value of $(1.5 \pm 1.1) \times 10^5$ $M^{-1}\,s^{-1}$ derived for the $Rh_2(O_2CCH_3)_4(H_2O)_2^{0/+}$ couple from a series of cross-reactions with similar inorganic complexes[3] and substituted 1,2- and 1,4-benzenediols[4] and to a directly measured value of 2.9×10^5 $M^{-1}\,s^{-1}$.[5]

Reasonable success has been achieved in predicting the self-exchange rate constants for transition-metal-complex couples from their structural and vibrational parameters by using classical or semiclassical models for outer-sphere electron transfer.[31] The electronic configuration of the $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ complex (and other O- and N-donor bisadducts) is considered to be $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, and electron exchange in the Rh_2/Rh_2^+ couple would involve a weakly antibonding Rh–Rh π^* orbital.[32,33] While structural[34] and vibrational[11] data are only available for the reduced bis(acetonitrile) adduct, the parameters for the $Rh_2(O_2CCH_3)_4(H_2O)_2^{0/+}$ couple[35,36] would likely provide a good estimate of the inner-sphere reorganizational barrier (≈1.6 kcal mol^{-1}) of the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple. The main differences in the values of k_{11} between the two couples should arise from ν_n and ΔG_{out}^*, which have dependences on the properties of the solvent. Each of these terms would therefore lead to the prediction of a slightly larger value of k_{11} for the acetonitrile adduct than for the aqua adduct, whereas a similar k_{11} value for the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple is observed.

The relative magnitudes of the self-exchange rate constants for a series of related metal complexes, such as $M(H_2O)_6^{2+/3+}$ or $M(bpy)_3^{2+/3+}$, may be predicted on the basis of the symmetry of orbitals ($d\pi$ or $d\sigma^*$) involved in the electron exchange[31] by comparing the electronic configurations of the respective partners. The value of the electron-self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(CH_3CN)_2^{0/+}$ couple may be compared with the k_{11} values (determined in acetonitrile) for several other couples that have a similar radius and charge product. For the $M(CpMe_5)_2^{0/+}$ couples ($CpMe_5^-$ = pentamethylcyclopentadienyl), the self-exchange rate constants, k_{11}, at 25 °C are 3.8×10^7 $M^{-1}\,s^{-1}$ for M = Fe[8] and 4.3×10^8 $M^{-1}\,s^{-1}$ for M = Co.[38] The rapid exchange rate constants for these couples ($\sigma \approx 10$ Å) are consistent with a negligible inner-sphere reorganization barrier ($\Delta d_0 = 0.035$ Å,[39] $\Delta G_{in}^* < 0.35$ kcal mol^{-1}) accompanying the exchange of a nonbonding metal-centered electron. For the low-spin d^6/d^5 $Ru(hfac)_3^{0/+}$ ($hfac^-$ = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) couple, $k_{11} = 5.0 \times 10^6$ $M^{-1}\,s^{-1}$ at 25 °C ($\sigma \approx 10$ Å).[40] The exchange of the electron in this couple involves a nonbonding $d\pi$ orbital, and a relatively small inner-sphere reorganization barrier ($\Delta G_{in}^* = 3.9$ kcal mol^{-1}) has been calculated.[41] The exchange of an antibonding $d\sigma^*$ electron, however, as in the low-spin d^7/d^6 $Co((dmg)_3(BF)_2)^{0/+}$ ($(dmg)_3(BF)_2$ is 1,8-bis(fluoroboro)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexamethylbicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaene) couple ($\sigma \approx 11$ Å), requires more substantial inner-sphere reorganization ($\Delta d_0 = 0.08$ Å),[42] and a smaller exchange rate constant is observed; $k_{11} = 65 \pm 20$ $M^{-1}\,s^{-1}$ at 25.0 °C.[23] Direct measurements of the electron-exchange rate constants of other $Rh_2(O_2CR)_4S_2^{0/+}$ couples in various solvents (S), using NMR line-broadening methods, are in progress to investigate the solvent reorganizational barrier in more detail.

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