4398 *Inorg. Chem.* **1985**, *24*, 4398-4402

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Outer-Sphere Electron-Transfer Reactions Involving the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ Couple. Determination of the $Rh_2^{0/+}$ Self-Exchange Rate Constant

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Received January 23, 1985

Kinetic and thermodynamic parameters have been measured for a series of outer-sphere electron-transfer reactions involving the acetate-bridged rhodium dimer complexes $Rh_2(O_2CCH_3)_4(OH_2)_2$ and $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ in aqueous perchlorate media. Nickel(II) and nickel(III) complexes containing polypyridine, hexaaza dioxime, and triaza and tetraaza macrocyclic ligands, along with tris(2,2′-bipyridine)ruthenium(II) and -(III), have been employed as cross-reactants. The cross-reaction rate constants are correlated in terms of the Marcus relationship, and a self-exchange rate constant of 1.5×10^5 M^{-1} s^{-1} is estimated for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple. The magnitude of this rate constant is consistent with small inner-sphere and moderate solvent reorganization barriers to electron exchange. This system, in which a weakly antibonding δ^* or π^* electron is exchanged, is compared with other metal complexes couples that involve the exchanges of π or σ^* electrons.

Introduction

The chemistry of dimeric rhodium(II) complexes,[1] especially those with bridging carboxylate ligands,[2] has received considerable attention during the last 20 years. In addition to possessing interesting structural and spectroscopic properties, these complexes are employed as catalytic reagents in several organic reactions[3] and have been investigated as potential antitumor agents.[4] Dirhodium(II) carboxylates, such as the acetate complex $Rh_2(O_2CCH_3)_4(OH_2)_2$, may undergo reversible, one-electron oxidations to form mixed-valence species in which the unpaired electron is completely delocalized between the two rhodium atoms. Electrochemical studies[5,6] on a series of $Rh_2(O_2CR)_4L_2^{0/+}$ couples have characterized the dependence of the redox potential on the nature of the bridging carboxylate RCO_2^- and the axial L groups. Chemical redox reactions of dirhodium carboxylates have, on the other hand, received considerably less attention.

Cannon and co-workers[7] recently reported the kinetics of the oxidation of $Rh_2(O_2CCH_3)_4(OH_2)_2$ by Ce(IV) and the reductions of $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ by $Fe(OH_2)_6^{2+}$ and VO^{2+} in acidic perchlorate and sulfate media. When the Marcus relationship was applied to the cross-reaction data a value of $10^{1.2\pm1.0}$ M^{-1} s^{-1} was determined for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ self-exchange rate constant. Their choices of Ce(IV) and VO^{2+} ions as cross-reactants for the estimation of such a parameter were somewhat inappropriate. The Ce^{4+}(aq) ion is extensively hydrolyzed even in 1.0 M $HClO_4$ and is complexed in sulfate media.[8] Electron exchange in the VO^{2+}/VO_2^+ couple is accompanied and complicated by proton transfer.[9] In addition the self-exchange rate constant used for the $Fe(OH_2)_6^{2+/3+}$ couple in their Marcus correlation was several orders of magnitude greater than the effective value derived from the majority of cross-reactions of Fe^{2+}(aq) or Fe^{3+}(aq).[10] The use of a smaller $Fe(OH_2)_6^{2+/3+}$ parameter would result in a proportionately larger self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple.

In an effort to arrive at a more definitive electron exchange rate constant for this important rhodium dimer couple, we have investigated the kinetics of a series of outer-sphere electron-transfer reactions involving $Rh_2(O_2CCH_3)_4(OH_2)_2$ and $Rh_2(O_2CCH_3)_4(OH_2)_2^+$. The cross-reactants employed in this study are well-characterized ruthenium and nickel complexes containing polydentate N-donor ligands. A modified Marcus relationship[11] has been used to correlate the cross-reaction data and provide a $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ self-exchange rate constant. The derived rate constant has been related, by means of a semiclassical model, to the magnitudes of the inner-sphere and solvent reorganization barriers to electron exchange. The $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple, in which a δ^* or π^* electron is exchanged, is compared to octahedral low-spin Ni(II)/Ni(III) and Co(II)/Co(III) couples, which involve exchange of a σ^* electron.

Experimental Section

Materials. Dirhodium(II) tetraacetate (Aldrich) was used as received. Acidic perchlorate solutions of the pink $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ cation were prepared by either electrochemical oxidation at a platinum electrode or by oxidation using solid PbO_2, followed by filtration through a fine glass frit. The dimer concentrations were determined by measurements on a Perkin-Elmer 552 spectrophotometer: for $Rh_2(O_2CCH_3)_4(OH_2)_2$ λ_{max} = 585 nm (ϵ = 241 M^{-1} cm^{-1});[12] for $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ λ_{max} = 515 nm (ϵ = 308 M^{-1} cm^{-1}) and 758 nm (ϵ = 298 M^{-1} cm^{-1}).[13] Tris(2,2′-bipyridine)ruthenium(II) chloride was used as received (G.F. Smith). Tris(4,4′-dimethyl-2,2′-bipyridine)nickel(III) perchlorate was prepared as described previously.[14] The nickel macrocycle complexes $NiL(ClO_4)_2$, where L is 1,4,8,11-tetraazacyclotetradecane ([14]aneN_4), *meso-* and *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*meso-* and *rac*-Me_6[14]aneN_4), and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]dieneN_4), were synthesized by the addition of the ligand (Strem) to a solution of nickel acetate in methanol and crystallized with added $LiClO_4$.[15] The complexes $NiL(ClO_4)_2$, where L is 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_2[14]dieneN_4), and $NiL_2(NO_3)_2$, where L is 1,4,7-triazacyclononane ([9]aneN_3) were a gift from Professor A. McAuley. The complex $Ni(H_2ox)(ClO_4)_2$, where H_2ox = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, was prepared by a reported procedure.[16] $Ni(Me_6[14]dieneN_4)^{3+}$, $Ni(meso\text{-}Me_6[14]aneN_4)^{3+}$, and $Ru(bpy)_3^{3+}$ were generated in solution by the oxidation of the corresponding divalent complexes with solid PbO_2. Lithium perchlorate was prepared by the neutralization of $HClO_4$ with Li_2CO_3, followed by repeated recrystallizations from distilled water.

Kinetic Measurements. The kinetic measurements were made by using a TDI Model IIA stopped-flow apparatus (Cantech Scientific), with transmittance data collected by a TDI 1024C transient recorder and processed on an interfaced Sinclair ZX-81 microcomputer. All measurements were made under pseudo-first-order conditions, and plots of ln $(A_t - A_\infty)$ against time was linear for at least 3 half-lives. The reported first-order rate constants represent the average of six-eight replicate experiments. The oxidations of $Ru(bpy)_3^{2+}$ and $Ni(H_2ox)^{2+}$ were monitored at 454 and 500 nm, respectively, while the other reactions were followed between 380 and 400 nm. The reactions were studied in aqueous acidic perchlorate media with the ionic strength maintained at 0.10 or 1.00 M with $HClO_4/LiClO_4$ mixtures. Thermostating was

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0020-1669/85/1324-4398$01.50/0

Table I. Kinetic Parameters for the Redox Cross-Reactions Involving the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ Couple

reacn no.[n]	oxidant	reductant	$\ln K_{12}$	k_{12},[a] $M^{-1}\ s^{-1}$	k_{22},[b] $M^{-1}\ s^{-1}$	k_{11}^{calcd}, $M^{-1}\ s^{-1}$
1	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Ni([14]aneN_4)^{2+}$	10.1	1.59×10^6[c]	2×10^3[d]	5.6×10^4
2	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Ni([9]aneN_3)_2^{2+}$	10.9	5.0×10^6	6×10^3[e]	1.0×10^5
3	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Ni(Me_2[14]dieneN_4)^{2+}$	8.17	1.54×10^5[f]	6.0×10[g]	9.4×10^4
4	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Ni(H_2ox)^{2+}$	−0.39	1.60×10^4 (0.10)[h]	3×10^3[i]	9.9×10^4
5	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	Ni(*meso*-$Me_6[14]aneN_4)^{2+}$	−0.78	2.3×10^3	6.0×10[e]	1.2×10^5
6	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	Ni(*rac*-$Me_6[14]aneN_4)^{2+}$	−0.78	1.0×10^3	3.1×10[e]	4.4×10^4
7	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Ru(bpy)_3^{2+}$	−0.39	1.1×10^7 (0.10)	4.2×10^7 (0.10)	3.1×10^5
8	$Rh_2(O_2CCH_3)_4(OH_2)_2^+$	$Fe(OH_2)_6^{2+}$	17.6	1.07×10^5[k]	1×10^{-3}[l]	3.3×10^5
9	Ni(*meso*-$Me_6[14]aneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(OH_2)_2$	0.78	1.5×10^4	6.0×10[e]	1.0×10^6
10	Ni(*rac*-$Me_6[14]aneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(OH_2)_2$	0.78	8.7×10^3	3.1×10^3[e]	6.9×10^5
11	$Ru(bpy)_3^{3+}$	$Rh_2(O_2CCH_3)_4(OH_2)_2$	0.39	2.5×10^7 (0.10)	4.2×10^8[j]	3.4×10^5
12	$Ni(Me_6[14]dieneN_4)^{3+}$	$Rh_2(O_2CCH_3)_4(OH_2)_2$	3.89	1.64×10^3[m]	1[g]	4.1×10^4
13	$Ni(Me_2bpy)_3^{3+}$	$Rh_2(O_2CCH_3)_4(OH_2)_2$	14.0	1.2×10^7	1.5×10^3[h]	2.1×10^5

[a] Ionic strength is 1.00 M unless otherwise indicated in parentheses. [b] k_{11} and k_{22} are the electron self-exchange rate constants for $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ and its cross-reaction partner, respectively. [c] $\Delta H^* = 0.9 \pm 0.5$ kcal mol^{-1}; $\Delta S^* = -27 \pm 2$ cal deg^{-1} mol^{-1}. [d] Reference 17. [e] Reference 18. [f] $\Delta H^* = 1.4 \pm 0.5$ kcal mol^{-1}; $\Delta S^* = -30 \pm 2$ cal deg^{-1} mol^{-1}. [g] Reference 19. [h] $\Delta H^* = 4.8 \pm 0.5$ kcal mol^{-1}; $\Delta S^* = -23 \pm 2$ cal deg^{-1} mol^{-1}. [i] Reference 20. [j] Young, R. L.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468. [k] Reference 7. [l] Reference 10. [m] $\Delta H^* = 13.2 \pm 2$ kcal mol^{-1}, $\Delta S^* = 0.6 \pm 2$ cal deg^{-1} mol^{-1}. [n] Numbering system for Figure 2.

maintained to ±0.05 °C over the temperature range of 1.0–35.0 °C by means of an external water bath.

Results

Tetrakis(μ-carboxylato)dirhodium(II) complexes, $Rh_2(O_2CR)_4L_2$, may undergo chemical or electrochemical one-electron oxidations to the corresponding mixed-valence cation while both their bridging and axially coordinated ligands are retained. The $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ ion is a moderately strong oxidant in aqueous media. Cyclic voltammetry experiments on $Rh_2(O_2CCH_3)_4(OH_2)_2$ were carried out in 0.10 and 1.00 M $HClO_4$ at potential scan rates of 50–200 mV s^{-1}. Quasi-reversible one-electron peak couples were observed with $E_{pa}-E_{pc} = 70$ mV and $i_{pa}/i_{pc} = 0.96 \pm 0.05$. Reduction potentials (vs. NHE) of 1.22 ± 0.01 V (1.00 M $HClO_4$) and 1.26 ± 0.01 V (0.10 M $HClO_4$) were found for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple. Reduction potentials have previously been measured for this couple in sulfate media,[13] $E° = 1.187$ V (1.0 M H_2SO_4) and 1.225 V (0.10 M H_2SO_4), and in chloride media,[5] E° = 1.26 V (0.10 M KCl). The slight medium effects are likely due to differences in the weak axial coordination by the electrolyte anions.

Kinetic Studies. The kinetic measurements of the oxidation of $Rh_2(O_2CCH_3)_4(OH_2)_2$ and the reduction of $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ by a series of outer-sphere cross-reactants were carried out in 0.10 or 1.00 M perchlorate media with the rhodium dimer present in excess.

$$\mathrm{Ox} + Rh_2(O_2CCH_3)_4(OH_2)_2 \underset{}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Red} + Rh_2(O_2CCH_3)_4(OH_2)_2^+ \quad (1)$$

The oxidation of Rh_2 by $Ni(Me_2bpy)_3^{3+}$ and $Ni(Me_6[14]dieneN_4)^{3+}$ follow the rate law

$$\frac{-d[\mathrm{Ox}]}{dt} = k_{12}[Rh_2][\mathrm{Ox}] \quad (2)$$

while the analogous first-order dependences on $[Rh_2^+]$ and [Red] were observed for the reductions of Rh_2^+ by $Ni([14]aneN_4)^{2+}$, $Ni([9]aneN_3)_2^{2+}$, and $Ni(Me_2[14]dieneN_4)^{2+}$. The observed pseudo-first-order rate constants for these reactions (and other in this study) are given in the supplementary material. The values of k_{12} and the corresponding activation parameters are summarized in Table I.

The nickel macrocycle complexes Ni(*meso*-$Me_6[14]aneN_4)^{3+/2+}$ and Ni(*rac*-$Me_6[14]aneN_4)^{3+/2+}$ have redox potentials ($E° = 1.24$ V[17]) that are very similar to that of the rhodium dimer couple.

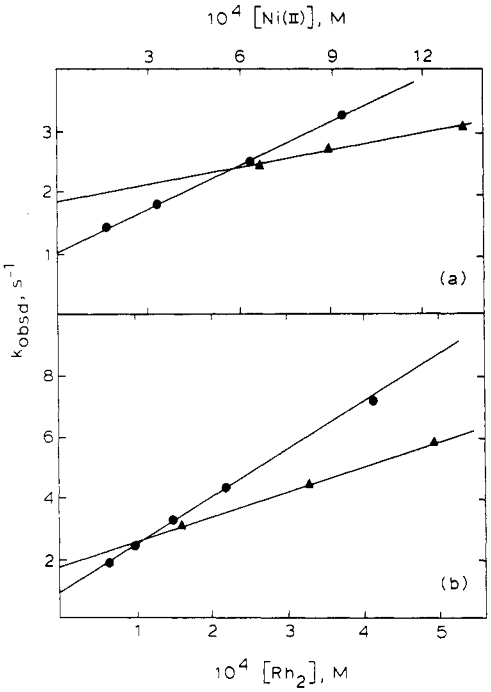

Figure 1. Dependences of the observed rate constants on the concentrations of (a) $[NiL^{2+}]$ and (b) $[Rh_2]$ for the reactions of $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ with Ni(*meso*-$Me_6[14]aneN_4)^{2+}$ (●) and Ni(*rac*-$Me_6[14]aneN_4)^{2+}$ (▲) in the presence of added reactants. In part a the added $[NiL^{2+}]$ are 1.65×10^{-4} and 6.88×10^{-5} M, and in part b the added $[Rh_2]$ are 1.34×10^{-3} and 5.02×10^{-4} M for Ni(*rac*-$Me_6[14]aneN_4)^{2+}$ and Ni(*meso*-$Me_6[14]aneN_4)^{2+}$, respectively.

The kinetics of both the forward and reverse processes represented by eq 3 were measured in 1.00 M $HClO_4$. Under pseudo-first-

$$Rh_2 + NiL^{3+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Rh_2^+ + NiL^{2+} \quad (3)$$

order conditions of excess Rh_2 and NiL^{2+} concentrations, the rate constant for the approach to equilibrium is given by eq 4. Plots

$$k_{obsd} = k_f[Rh_2] + k_r[NiL^{2+}] \quad (4)$$

of k_{obsd} against $[Rh_2]$ at constant $[NiL^{2+}]$ and of k_{obsd} against $[NiL^{2+}]$ at constant $[Rh_2]$ yielded values of k_f and k_r, respectively. Figure 1 shows these rate dependences for the oxidations of the $Ni(Me_6[14]aneN_4)^{2+}$ complexes by Rh_2^+ at 25 °C. Values of k_f and k_r derived from slope and intercept measurements were in good agreement with each other. The nickel(III) complexes

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produced in reaction 3 undergo subsequent decomposition reactions, believed to be an oxidation of the ligand.[21] These processes interfered only in the slowest reactions studied and were separated from the initial step by treating the system as two consecutive first-order reactions. Rate parameters for the forward and reverse reactions are included in Table I. The $Ru(bpy)_3^{2+/3+}$ couple also has a reduction potential similar to that of the $Rh_2^{0/+}$ couple in 0.10 M $HClO_4$. The kinetic studies of these very rapid cross-reactions were limited, however, to the range imposed by the stopped-flow technique. Pseudo-first-order rate constants were measured at 25 °C for several rhodium concentrations in the absence of added products. The experimental ratio of k_{12}/k_{21} (Table I) is in good agreement with the equilibrium constants K_{12} derived from the reduction potentials.

The octahedral $Ni(H_2ox)^{2+}$ ion is oxidized by $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ in a stoichiometric ratio of $Rh_2^+/Ni(II) = 1.98 \pm 0.05$ to yield a nickel(IV) complex, $Ni(ox)^{2+}$, stabilized by the deprotonation of the coordinated dioxime.

$$2Rh_2^+ + Ni(H_2ox)^{2+} \rightarrow 2Rh_2 + Ni(ox)^{2+} + 2H^+ \quad (5)$$

Previous investigations of the oxidation of $Ni(H_2ox)^{2+}$ by $Co^{3+}(aq)$[22] and tris(polypyridine) complexes of iron(III),[20] ruthenium(III),[14] and nickel(III)[14] suggest that the rate-determining step is the one-electron oxidation to the rather unstable $Ni(H_2ox)^{3+}$ species ($E° = 1.25$ V[22]). No reverse reaction in eq 5 is observed as the nickel(III) intermediate undergoes a rapid second one-electron oxidation to produce the stable Ni(IV) complex ($E° = 0.65$ V[22]).

$$Rh_2^+ + Ni(H_2ox)^{2+} \xrightarrow{k_{12}} Rh_2 + Ni(H_2ox)^{3+} \quad (6)$$

$$Rh_2^+ + Ni(H_2ox)^{3+} \xrightarrow{\text{fast}} Rh_2 + Ni(ox)^{2+} + 2H^+ \quad (7)$$

The kinetics of this system were measured in 0.05 M $HClO_4$ ($\mu = 0.10$ M, $LiClO_4$) and follow a rate law of the form

$$\frac{d[Ni(ox)^{2+}]}{dt} = \frac{-d[Rh_2^+]}{2dt} = k_{12}[Rh_2^+][Ni(H_2ox)^{2+}] \quad (8)$$

The addition of an excess of $Rh_2(O_2CCH_3)_4(OH_2)_2$ did not have any effect on k_{12}.

Discussion

The kinetic and thermodynamic parameters associated with the cross-reactions in this study involving $Rh_2(O_2CCH_3)_4(OH_2)_2$ and $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ are consistent with an outer-sphere mechanism of electron transfer. The axial aquo ligands on the rhodium dimers are labile, and inner-sphere reactions have been observed previously for the oxidation of Br^- by $Rh_2(O_2CCH_3)_4^+$ complexes.[24] The rates of mono adduct formation for the $Rh_2(O_2CCH_3)_4(OH_2)_2$ complex are 10^6–10^7 M^{-1} s^{-1},[25] while the aquo ligands are more strongly bound to the $Rh_2(O_2CCH_3)_4^+$ ion, with adduct formation rate constants of 10^3–10^4 M^{-1} s^{-1}.[24] For inert cross-reactants such as $Ru(bpy)_3^{2+}$, $Ni(Me_2bpy)_3^{3+}$, and $Ni([9]aneN_3)_2^{2+}$ an inner-sphere pathway may be ruled out, and for the others, including the nickel macrocycles, inner-sphere bridging is unlikely in the absence of potential bridging ligands, such as chloride ions. There was no spectroscopic evidence on the stopped-flow time scale for bridged intermediates in these reactions. The small ΔH^* (1–5 kcal mol^{-1}) and large negative ΔS^* (−20 to −30 cal deg^{-1} mol^{-1}) values observed for most of the cross reactions are common for rapid outer-sphere electron transfers.[26]

The electron self-exchange rate constant k_{11} for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple can be estimated from the cross-reaction data in this study by employing the Marcus cross-relations.[27] In terms of a recent modification of the theory,[11] the rate constant for a cross-reaction, k_{12}, is related to the rate constants for the component self-exchange reactions, k_{11} and k_{22}, and the equilibrium constant for the cross-reaction, K_{12}, by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (9)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \quad (10)$$

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

$$W_{ij} = \frac{z_iz_je^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}\mu^{1/2})} \quad (12)$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2\nu_n(\delta r)}{1000}\right]_{ii} \quad (13)$$

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 a_i and a_j, the radii of ions i and j), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, ν_n is the nuclear vibration frequency that destroys the activated complex configuration, and δr is the thickness of the reaction layer. The values of A_{ii} are in the range of (1–6) × 10^{12} M^{-1} s^{-1} depending on ν_n and σ_{ii} for a particular couple. Radii of 6.8 Å for the tris(polypyridine) complexes, 5.0 Å for the nickel macrocycles, and 4.8 Å for the rhodium dimer were used in evaluating σ.

The cross-reactants employed in this study are each well characterized in terms of their reduction potentials and electron self-exchange rate constants. The latter parameters have been measured directly or estimated from Marcus calculations on cross-reaction data. In the absence of a directly measured self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple, the best estimate of k_{11} would be provided by systems in which the cross-reactant is not substantially different from the rhodium dimer in size, geometry, and ligand type. In this respect the nickel macrocycles and the other complexes should act as suitable models.

The self-exchange rate constants for the rhodium dimer couple derived from eq 9 are presented in Table I. The values range from 4×10^4 to 1×10^6 M^{-1} s^{-1}. The spread in the values may in some instances reflect the uncertainties in the self-exchange rate constants of some of the cross-reactants,[28] but the agreement is considered to be good for a determination of this type. Figure 2 illustrates the adherance 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 near unity. The intercept value of 5.95 corresponds to 0.5 $\ln k_{11}$) and gives a self-exchange rate constant of 1.5×10^5 M^{-1} s^{-1} for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple. The points in Figure 2 that deviate the most from the line are for the cross-reactions with $Ni(\textit{rac}\text{-}Me_6[14]aneN_4)^{2+/3+}$ and $Ni(\textit{meso}\text{-}Me_6[14]aneN_4)^{2+/3+}$. For these systems the value of K_{12} (0.46) used in the correlations and derived from the respective reduction potentials differs somewhat from the K_{12} values (0.11–0.15) computed from the experimental k_r/k_f ratios (eq 3). The use of the latter values would bring the k_{11} rate constants into closer agreement but would not alter the average value. A similar self-exchange rate constant for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple has been derived from data of cross-reactions involving ascorbic acid and a series of substituted 1,2- and 1,4-benzendiols.[29]

Included in Table I and Figure 2 is the cross-reaction between $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ and $Fe(OH_2)_6^{2+}$, for which Cannon and

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(28) For example, k_{22} for $Ni(Me_6[14]dieneN_4)^{2+/3+}$ is reported[19] to be $10^{0\pm2}$ M^{-1} s^{-1}.

(29) Herbert, J. W.; Macartney, D. H., submitted for publication in *J. Chem. Soc., Dalton Trans.*

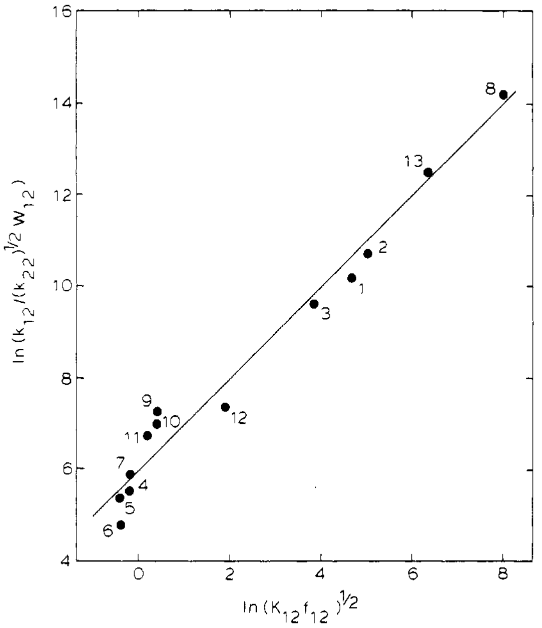

Figure 2. Marcus correlation of ln $(k_{12}/(k_{22})^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ for the cross-reactions involving the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple and the reactants as numbered in Table I. The intercept corresponds to 0.5(ln k_{11}), the self-exchange rate constant for the $Rh_2^{0/+}$ couple.

co-workers[7] reported a rate constant of 1.07×10^5 M^{-1} s^{-1}, measued in 1.0 M $HClO_4$. For the majority of outer-sphere cross-reactions involving the $Fe(OH_2)_6^{2+}$ ion it has been observed that the effective k_{22} value for the $Fe^{2+/3+}$ couple is several orders of magnitude smaller than the directly measured self-exchange rate constant, and Weaver[10] has suggested a value of 1×10^{-3} M^{-1} s^{-1} be used. The use of this lower effective k_{22} value yields a $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ self-exchange rate constant of $\sim 3 \times 10^5$ M^{-1} s^{-1}, consistent with the k_{11} values derived from the other cross-reactions in this study.

The value of k_{11} for the $Rh_2^{0/+}$ couple appears, therefore, to be about 4 orders of magnitude larger than previously reported. This rate constant is more consistent with the small reorganization barriers to electron exchange anticipated for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ system. Reasonable success in predicting the self-exchange rate constant for transition-metal complexes for their structural and vibrational properties has been achieved by using a semiclassical model for outer-sphere electron transfer.[30] In the formalism of this model the observed bimolecular rate constant k_{obsd} is expressed as the product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n, respectively:

$$k_{obsd} = K_A \nu_n \kappa_{el} \kappa_n \qquad (14)$$

For exchange reactions the nuclear factor contains both solvent and inner-sphere contributions

$$\kappa_n = \Gamma_n \exp[-(\Delta G^*_{out} + \Delta G^*_{in})/RT] \qquad (15)$$

where Γ_n is the inner-sphere nuclear tunneling factor. The ΔG^*_{out} term is associated with the change in solvent polarization upon electron exchange, and a value of 6.5 kcal mol^{-1} is calculated for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple.[31]

The inner-sphere reorganization energy ΔG^*_{in} is given by

$$\Delta G^*_{in} = \tfrac{1}{2}\sum f_i[(\Delta d_0)_i/2]^2 \qquad (16)$$

Table II. Rate Constants for the Electron-Exchange Reactions of d^7 Metal Complexes at 25.0 °C

couple	electronic configns	Δd_0, Å	k_{11}, M^{-1} s^{-1}
$Ni(bpy)_3^{2+/3+}$	$\pi^6\sigma^{*2}/\pi^6\sigma^{*1}$	0.12^a	$1.5 \times 10^{3\,b}$
$Ni([9]aneN_3)_2^{2+/3+}$	$\pi^6\sigma^{*2}/\pi^6\sigma^{*1}$	$\simeq 0.11^{c,d}$	$6 \times 10^{3\,e}$
$Co(terpy)_2^{2+/3+}$	$\pi^6\sigma^{*1}/\pi^6$	0.13^f	$3 \times 10^{3\,g}$
$Co(bpy)_3^{+/2+}$	$\pi^6\sigma^{*2}/\pi^5\sigma^{*2}$	-0.02^h	$\geq 10^{9\,h}$
$Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$	$\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}/$ $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$	$0.05^{i,j}$	$1.5 \times 10^{5\,k}$
$Rh(bpy)_3^{2+/3+}$	$\pi^6L\pi^{*1}/\pi^6$		$\geq 10^{9\,l}$

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where f_i is a reduced force constant for the *i*th inner-sphere vibration defined in terms of the normal-mode force constants of the two oxidation states and Δd_0 is the corresponding difference in the equilibrium bond distances in the two oxidation states, with the summation over all the intramolecular vibrations. Structural data are available for both partners in the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple.[33,34] The larger changes in the equilibrium bond distances upon oxidation are found along the Rh–Rh axis, with the metal–metal bond decreasing by 0.069 Å and the Rh–O(water) bond by 0.088 Å. Each of the eight Rh–O(acetate) bond distances decreased by an average of only 0.025 Å. From reduced force constants estimated for the Rh–Rh and Rh–O intramolecular bonds[35] an inner-sphere reorganization energy of 1.2 kcal mol^{-1} is calculated. The nuclear factor κ_n for $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ is calculated (eq 15) to be 2.5×10^{-6}, by using $\Gamma_n = 1.1$. The nuclear tunneling factor is close to unity for an exchange occurring at room temperature and involving low-frequency vibrational modes.[11] The effective nuclear frequency ν_n is estimated to be 3×10^{12} s^{-1} for this couple[38] while K_A is calculated to be 0.6 M^{-1}. For an adiabatic electron exchange ($\kappa_{el} = 1$) between $Rh_2(O_2CCH_3)_4(OH_2)_2$ and $Rh_2(O_2CCH_3)_4(OH_2)_2^+$ the semiclassical model predicts a rate constant of $k_{11} = 4 \times 10^6$ M^{-1} s^{-1}, in reasonable agreement with the experimentally derived value of 1.5×10^5 M^{-1} s^{-1}. The discrepancy between the two exchange rate constants may be accommodated for by allowing the electronic factor in the semiclassical expression to be ~ 0.04. For the majority of electron exchange couples κ_{el} values range from 10^{-3} to 1.0,[11,39]

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(31) For the solvent reorganization energy in the ellipsoidal model[11,32] $\Delta G_{out}^* = [(22.5\, r^2 S(\lambda_0))/(l_a l_b^2)]$ in kcal mol^{-1} where $S(\lambda_0)$ is a shape factor and $2l_a$ and $2l_b$ are the lengths of the major and minor axes, respectively. For $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$; $2l_a$, $2l_b$, and r are estimated to be 19.2, 10.0, and 9.6 Å, respectively, and $S(\lambda_0)$ is estimated to be 0.75.

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(35) Stretching frequencies (force constants) of 155 cm^{-1} (67 N m^{-1}) for Rh–Rh and 342 cm^{-1} (170 N m^{-1}) for Rh–O(acetate) have been reported for $Rh_2(O_2CCH_3)_4(OH_2)_2$.[36a] A Rh–O stretching frequency of 330 cm^{-1} has been observed for the $Rh_2(O_2CCH_3)_4^+$ ion,[36b] while the Rh–Rh frequency has not been reported. The Rh–O(water) stretching vibrations have not been observed for the complexes in either oxidation state. Reduced force constants, f_i, of 100, 170, and 140 N m^{-1} were estimated for Rh–Rh, Rh–O(acetate), and Rh–O(water), respectively, from correlations[37] of bond lengths and force constants for M–M and M–O bonds in other complexes of second-row transition elements.

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(38) $\nu_n = [(\nu_{out}^2\Delta G^*_{out} + \nu_{in}^2\Delta G^*_{in}/(\Delta G^*_{out} + \Delta G^*_{in})]^{1/2}$ where $\nu_{out} = 9 \times 10^{11}$ s^{-1} and ν_{in} is estimated to be 8×10^{12} s^{-1} for $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$.

(39) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

with the lower values applying to exchanges that are formally spin forbidden (e.g. Co(II)/Co(III) couples) and the upper values associated with the adiabatic exchanges in couples such as $Ru(bpy)_3^{2+/3+}$. A value of $\kappa_{el} = 0.04$ for the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ exchange is therefore not unreasonable as this couple is intermediate between Ru(II)/(III) and Co(II)/Co(III) systems in several respects, including reorganization barriers and the orbital origin of the exchanged electron.

In the $Rh_2(O_2CCH_3)_4(OH_2)_2^{0/+}$ couple the electron to be exchanged is believed to reside in either a δ^* or π^* orbital.[6a,40–42] The bond distance changes accompanying this δ^* or π^* electron exchange are consistent with a change in the population of a weakly antibonding orbital and are intermediate between those observed for couples in which a nonbonding π electron is exchanged and those in which an antibonding σ^* electron is exchanged. This trend may be illustrated by the consideration of several metal complex couples in which one partner has a d^7 configuration, as set out in Table II. It can be seen from the first three entries that the exchange of a σ^* electron in either a d^6/d^7 or a d^7/d^8 couple proceeds at a moderate rate, 10^3–10^4 M^{-1} s^{-1}, and involves considerable change in metal–ligand bond distances. In the case of $Co(bpy)_3^{+/2+}$, on the other hand, a high-spin Co(II) electronic configuration results in the exchange of a nonbonding π electron. A negligible inner-sphere reorganization barrier allows for an exchange rate constant of $\geq 10^9$ M^{-1} s^{-1}. Similar structural and exchange parameters are found for the low-spin d^5/d^6 tris(polypyridine) complexes of iron, ruthenium, and osmium.[30] The only other rhodium couple for which self-exchange data have been measured is $Rh(bpy)_3^{2+/3+}$ (Table II). Although this d^6/d^7 couple should be analagous to $Co(terpy)_2^{2+/3+}$, the electron exchange, at $\geq 10^9$ M^{-1} s^{-1}, is much more rapid. It has been suggested that the metal σ^* and ligand π^* orbitals are very close in energy such that $Rh^{II}(bpy)_3^{2+}$ may exist as or be in equilibrium with $[Rh^{III}(bpy)_2(bpy^-)]^{2+}$, allowing for a low-energy electron exchange via L π^* orbitals.

The replacement of H_2O by other ligands in the axial positions in $Rh_2(O_2CR)_4L_2$ has a much larger effect on the Rh–Rh bond length than does a change in the nature of the bridging carboxylate group.[2] Variations in the σ-donor ability of L are also predicted to affect the differences in Rh–Rh and Rh–L bond distances upon oxidation to the corresponding cations. It is suggested that the oxidation of a rhodium dimer with axial triphenylphosphine ligands (which involves the removal of a σ electron[6,41]) will yield a cation with shorter Rh–P bonds but a longer Rh–Rh bond, in contrast to rhodium dimers with O-donor ligands.[41] Electron-transfer reactions involving a series of rhodium carboxylate dimers with P-donor ligands are currently under investigation to determine how changes in L affect the electron exchange parameters.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this research in the form of an operating grant to D.H.M. and a graduate scholarship to J.W.H. This research was also facilitated by a grant from the Advisory Research Committee of Queen's University. We thank Dr. J. A. Page for assistance in electrochemical measurements and Dr. A. McAuley for the gift of two nickel complexes.

Supplementary Material Available: Tables of kinetic data (4 pages). Ordering information is given on any current masthead page.

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Characterization of Pentakis(dithiocarbamato)dicobalt(III) Complexes, $[Co_2(RR'dtc)_5]^+$, and Related Complexes in Dichloromethane Using Electrochemical and Cobalt-59 NMR Techniques

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Received November 12, 1984

Controversy has arisen as to whether $[Co(RR'dtc)_3]^+$ or $[Co_2(RR'dtc)_5]^+$ is the product of oxidation of $Co(RR'dtc)_3$. In this work electrochemical and ^{59}Co NMR techniques have been used to examine the chemistry and redox properties of cobalt dithiocarbamate complexes in dichloromethane solution in an endeavor to rationalize literature data. Electrochemical measurements at platinum electrodes show that the species $Co(RR'dtc)_3$, $[Co(RR'dtc)_3]^+$, $[Co_2(RR'dtc)_5]^+$, and also $[Co_2(RR'dtc)_5]^{2+}$ may exist under appropriate conditions. On oxidation of $Co(RR'dtc)_3$, $[Co(RR'dtc)_3]^+$ is formed as either a stable intermediate (RR'dtc = c-Hx_2dtc) or a transient intermediate (RR'dtc = pyrrdtc). $[Co_2(RR'dtc)_5]^+$ is produced from this species via an internal redox reaction at a rate that is extremely sensitive to substituent effects. The rate of transformation of $[Co(RR'dtc)_3]^+$ to $[Co_2(RR'dtc)_5]^+$ is concentration-dependent, implying the formation of a dimeric intermediate such as $[Co_2(RR'dtc)_6]^{2+}$. Reaction of $[CoL_3]^+$ and $[CoL'_3]^+$ (L and L' are different dithiocarbamate ligands) produces a mixture of $[Co_2L_5]^+$, $[Co_2L_3L'_2]^+$, $[Co_2L_2L'_3]^+$, and $[Co_2L'_5]^+$, which is again consistent with the formation of dimeric intermediates. $[Co_2(RR'dtc)_5]^{2+}$ can be identified by electrochemical oxidation of $[Co_2(RR'dtc)_5]^+$ at low temperature, but it is unstable – generating $[Co(RR'dtc)_3]^+$ (R = R' = c-Hx) at ambient temperature under conditions of cyclic voltammetry. $Co_2(RR'dtc)_5$ produced by reduction of $[Co_2(RR'dtc)_5]^+$ has no inherent stability and very rapidly converts to $Co(RR'dtc)_3$ and $Co(RR'dtc)_2$. $[Co_2(RR'dtc)_5]^+$ itself decomposes slowly in dichloromethane to $Co(RR'dtc)_3$ as demonstrated by ^{59}Co NMR and electrochemical measurements. Cobalt-59 NMR demonstrates that in solution $[Co_2(RR'dtc)_5]^+$ has two nonequivalent cobalt centers, in accordance with a previously published crystal structure. The formally cobalt(IV) complexes are generated at very positive potentials and are far more reactive than similar high-oxidation-state dithiocarbamates of other metals. Electrochemical data in acetone are qualitatively similar to those in dichloromethane.

Introduction

Tris(dithiocarbamato)cobalt(III) complexes, $Co(RR'dtc)_3$, have been extensively studied.[3–6] A related and also formally cobalt(III) compound, pentakis(diethyldithiocarbamato)dicobalt(III) tetrafluoroborate, $[Co_2(Et_2dtc)_5]BF_4$, has been made from Co-

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