Table IV. Reactions of the Fluoroxysulfate Ion

reductant	k_2,[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(mol K)	ref
ClO_2^- [c]	2.4×10^4	$30._5$	−59	3
$Ru(bpy)_3^{2+}$ [d]	2.6×10^3	37	−55	*f*
Ag^+ [c]	2.0×10^3	$25._5$	−96	5
Pu^{3+} [c]	1.9×10^2	31	−98	7
Co^{2+} [e]	2.0×10^{-2}	64	−63	5

[a] For the rate law $-d[SO_4F^-]/dt = k_2[SO_4F^-][\text{reductant}]$, calculated at 25 °C from activation parameters. [b] From the temperature dependence between 0 and 25 °C. [c] At 1 M ionic strength. [d] At infinite dilution. [e] At 2 M ionic strength. [f] This work.

the rate-determining step, which could involve attack either on the ruthenium center or on the ligand. From the fact that $Ru(bpy)_3Cl_2$ and $Ru(bpy)_3(ClO_4)_2$ exhibit both the same stoichiometry and the same reaction rate, it would appear that low concentrations of chloride cannot compete with the initial rate-determining step, whatever it may be.

Comparing the reaction of $Ru(bpy)_3^{2+}$ with SO_4F^- with its reaction with other oxidants, we note that the one-electron oxidant cerium(IV) reacts more rapidly ($k_2 = 9 \times 10^3\ M^{-1}\ s^{-1}$ in sulfuric acid[9] and $>10^5\ M^{-1}\ s^{-1}$ in perchloric acid[10]), while the formally two-electron oxidant thallium(III) reacts considerably more slowly ($k_2 = 0.2\ M^{-1}\ s^{-1}$).[9] Both of these reactions are assumed to involve outer-sphere electron transfer, and the thallium oxidation is thought to proceed by a sequency of two one-electron steps. Unfortunately, for neither of these oxidants has the reaction stoichiometry been determined.

Table IV summarizes the kinetic information that is presently available regarding fluoroxysulfate reactions. These reactions span an impressive range of 10^6 in rates, with the $Ru(bpy)_3^{2+}$ reaction being among the fastest. It is not clear, however, just what factors are responsible for this large range, and it is evident that a great deal of further work will be required to clarify the situation.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; SO_4F^-, 73347-64-5.

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Luminescence Study of Complexation of Europium and Dicarboxylic Acids

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Luminescence lifetime measurements of Eu(III) have been used to study the hydration of Eu(III) when complexed by alkanedicarboxylate ligands. In its mono(malonate) complex, Eu(III) was found to have 2.3 fewer water molecules than the uncomplexed hydrated cation. In the formation of its 1:1 complexes with succinate, glutarate, and adipate, Eu(III) lost 1.5 molecules of water. When these dicarboxylate ligands reacted with the EuNTA complex to form the 1:1:1 ternary species, the malonate anion replaced 2.2, the succinate 1.5, and the glutarate and adipate 1.0 water molecules (all these values have ca. ±0.5 uncertainty). These data are discussed in terms of the effect on chelation of increased alkyl chain length.

Introduction

The thermodynamics of complexation of the lanthanides by dicarboxylate ligands (L = malonate, succinate, glutarate, or adipate) have been analyzed for insight into the nature of the complexes.[1] The data were consistent with bidentate chelation for all of the 1:1 complexes. However, it was pointed out that the values of the stability constants for the formation of the 1:1 complexes with succinate, glutarate, and adipate anions reflected less stabilization than expected from the basicity of the chelating ligands. In a subsequent paper,[2] the thermodynamics of the formation of ternary complexes of Gd(III) with nitrilotriacetic acid (NTA) and the same dicarboxylic acids were reported. Bidentate chelation was assigned to the malonate complexation, while the values for the succinate, glutarate, and adipate complexes were more consistent with monodentate structure of these dicarboxylate ligands in the ternary species.

In an attempt to investigate more directly the presence of chelate structure in these complexes, we have studied the europium complexes by luminescence lifetime measurements. It has been shown that changes in the luminescence lifetime of Eu(III) upon complexation in solution are proportional to the number of water molecules in the coordination sphere of the complexed Eu(III) and are relatively unaffected by the interaction of Eu(III) with many ligands.[3]

Table I. Calibration Data for Eu(III) Solids with H_2O Hydration (k in ms^{-1})

anion (ref)	$n(H_2O)$[a]	k_{obs} this work	k_{obs} ref 3
dipicolinate (4)	0	0.73 ± 0.03	0.77
nicotinate (5)	2	2.40 ± 0.03	2.49
oxalate (6)	3	3.58 ± 0.07	3.55
thiodiacetate (7)	4	4.42 ± 0.08	5.35
sulfate	4	4.80 ± 0.01	4.79
chloride	6	8.25 ± 0.05	8.25
bromate (8)	9	8.83 ± 0.03	8.69

[a] Number of H_2O molecules in the primary coordination sphere of Eu(III).

Experimental Section

Reagents. A europium perchlorate stock solution was prepared by dissolving the oxide in perchloric acid and was standardized by complexometric titration with xylenol orange as the indicator.

The reagent grade malonic (Aldrich), succinic (J. T. Baker), glutaric (Aldrich), adipic (Mallinckrodt), and nitrilotriacetic (Aldrich) acids were used as received. The stock solutions were checked for purity and standardized by titration with standard base.

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Table II. Calibration Data for Eu(III) Solids with D_2O Hydration (k in ms^{-1})

anion	n_{D_2O}[a]	k
oxalate	3	0.62 ± 0.06
thiodiacetate	4	0.59 ± 0.10
sulfate	4	0.50 ± 0.10

[a] Number of D_2O molecules in the primary coordination sphere of Eu(III).

Working solutions were prepared by mixing various amounts of europium and ligand. All solutions had a final ionic strength of 0.1 M $NaClO_4$. The pH was adjusted with dilute sodium hydroxide: and measured with a combined pH electrode calibrated with buffer solutions ("BuffAR" pH 4.01 and "BuffAR" pH 7.00).

Crystalline europium compounds have been prepared according to the procedures used in ref 3. The references for each solid are listed in Table I. Europium chloride and europium sulfate were prepared by dissolving the oxide in hydrochloric acid and sulfuric acid, respectively, followed by recrystallization. Thiodiacetic acid (Aldrich), oxalic acid (Mallinckrodt), nicotinic acid (Matheson), and dipicolinic acid (Aldrich), all reagent grade, were used without further purification after titration to check the purity.

A few samples were prepared in the same way from D_2O solutions. D_2O (99.8 atom % D) was obtained from Aldrich and the D_2SO_4 (99.9 atom % D, used in the preparation of europium sulfate and europium oxalate) from Wilmad Glass Co. Europium sulfate was prepared directly by dissolving the oxide in D_2SO_4 followed by crystallization. For the other solids, the starting compounds (organic ligands and europium chloride) first were equilibrated with D_2O by successive evaporations and redissolutions in D_2O to eliminate as much H_2O as possible. The beakers containing the D_2O solutions were then placed in a desiccator with P_2O_5 to concentrate the solutions and induce crystallization. The values reported in the tables are the average of three to six measurements of the luminescence lifetimes. The error limits of k in the tables represent the standard deviations of these measurements. For most of the solids, the values listed are the average from measurement of two different samples.

Method

Europium was excited to the $^5L_6$ electronic level by a pulse laser beam at 395 nm. This resulted mainly in emission from the $^5D_0$ luminescent excited state to the ground ^7F manifold. The 395-nm pulsed laser beam was obtained with a pulsed (10-Hz) 532-nm output of a Quanta Ray DCR 2A Nd-YAG laser pumping Rhodamine 640 (Exciton Chemical) in methanolic solution in Quanta Ray PDL2 equipment. The beam from the dye laser was converted to 395 nm by frequency doubling and mixing with the 1064-nm fundamental in a Quanta Ray WEX-1 wavelength extender. The pulse energy was typically 3 mJ, and the pulse width was in the nanosecond range.

The sample was contained in a standard 1-cm fluorimetry cell within a dark box, and the experiments were conducted at room temperature. The light emitted by europium was collected at 90° by an optic cable after passing through a low-fluorescence filter (cutoff wavelength 520 nm) and detected by a Hamamatsu R955 photomultiplier tube. The whole emission wavelength range was observed. After amplification in a Lecroy 6103 amplifier, and signal was fed into a Lecroy TR 8828C transient recorder. The latter was connected to an IBM PC computer through a Lecroy 8901A GPIB interface for signal averaging with the program CATALYST (Lecroy).

Most of the luminescence decays observed in this work were single exponentials; semilogarithmic plots of the luminescence intensity versus time were made to obtain the luminescence decay constants. In a few cases, the observed signal was analyzed as a sum of two exponentials with a program written in this laboratory incorporating the simplex procedure.

Results

The luminescence from the solid samples were analyzed for the decay constant of the europium. These luminescence decay constants are listed in Table I for the crystals grown from H_2O and in Table II for the crystals grown from D_2O. We have also given in Table I the data reported in ref 3 for the same compounds. Values of k_{D_2O} higher than about 0.6 ms should be viewed with caution since they could result from H_2O contamination. In general, ligands are not as effective in causing nonradiative deexcitation of the excited state.[9-11]

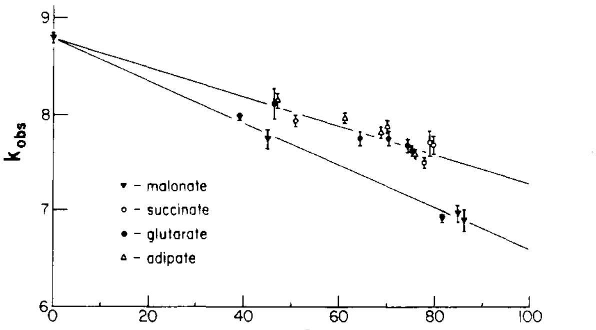

Figure 1. Variation of the decay constant (in ms^{-1}) as a function of the percent concentration of Eu(III) in the binary dicarboxylic acid complexes.

Table III. Luminescence Decay Constant of Eu(III) in Binary Complexes[a]

ligand concn, 10^3 M	pH	% Eu	% EuL	% EuL_2	k_{obs}, ms^{-1}
		a. Malonate			
0.7325	4.66	61.4	38.0	0.60	7.97 ± 0.02
0.7325	5.41	55.5	43.7	0.80	7.75 ± 0.10
1.465	5.39	23.5	71.2	5.30	6.91 ± 0.02
1.465	5.90	20.9	72.9	6.20	6.96 ± 0.07
1.465	6.15	20.2	73.3	6.50	6.89 ± 0.11
		b. Succinate			
1.465	5.19	48.9	51.1		7.94 ± 0.04
2.930	5.48	21.9	78.1		7.50 ± 0.03
4.395	5.06	20.6	79.4		7.70 ± 0.13
4.395	5.08	20.2	79.8		7.67 ± 0.10
		c. Glutarate			
1.472	5.29	53.5	46.5		8.11 ± 0.15
2.944	5.11	35.6	64.4		7.75 ± 0.08
4.416	4.92	29.6	70.4		7.75 ± 0.08
4.416	5.08	25.5	74.5		7.67 ± 0.07
4.416	5.12	24.7	75.3		7.63 ± 0.01
		d. Adipate			
1.466	5.49	53.1	46.9		8.15 ± 0.08
2.932	5.09	38.8	61.2		7.96 ± 0.03
4.398	4.97	31.1	68.9		7.81 ± 0.05
4.398	5.02	29.7	70.3		7.87 ± 0.06
4.398	5.28	24.0	76.0		7.58 ± 0.02

[a] [Eu(III)] = 0.001 46 M; I = 0.1 M $NaClO_4$, T = 25.0 °C.

Except in the case of the thiodiacetate complex, where a small but significant difference is observed, the present results are in very good agreement with the previously reported data.[3] This indicates that the correlation between n_{H_2O} and $k_{H_2O} - k_{D_2O}$ of ref 3 is valid under our experimental conditions. The value from this study for the thiodiacetate solid fits the correlation better than that in ref 3. Table II shows that k_{D_2O} is almost constant for all the complexes studied in the solid state, as it is for solutions.[3] A consequence of such invariance of k_{D_2O} is that the correlation between n_{H_2O} and $k_{H_2O} - k_{D_2O}$ is paralleled by an equally valid one between n_{H_2O} and k_{H_2O} (Figure 1). Omitting the value for europium chloride, we derived for our experimental conditions

$$n_{H_2O} = 1.05k_{H_2O} - 0.70 \qquad (1)$$

If there is no contribution from the ligand to the deexcitation of the luminescent excited state, the hydration of europium in various complexes can thus be obtained directly from the value of k_{H_2O}. This simplified procedure should give results consistent with those obtained by the previously proposed procedure[3] within the inherent uncertainty of the luminescence method of about ±0.5 water molecule. The k value for uncomplexed $Eu^{III}(aq)$ in $Eu(ClO_4)_3$

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Table IV. Luminescence Decay Constant of Eu(III) in Ternary Complexes[a]

ligand concn., 10^3 M	pH	% Eu	% EuL	k_{obs}, ms^{-1}
		a. Malonate		
1.465	5.38	74.9	25.1	4.37 ± 0.03
2.930	5.08	65.9	34.1	4.16 ± 0.07
5.860	5.12	46.8	53.2	3.76 ± 0.02
5.860	5.52	37.0	63.0	3.49 ± 0.07
11.72	5.24	26.3	73.7	3.40 ± 0.05
		b. Succinate		
2.930	5.20	82.1	17.9	4.84 ± 0.06
5.860	5.11	71.9	28.1	4.67 ± 0.04
11.72	5.19	52.7	47.3	4.45 ± 0.08
11.72	5.48	45.0	55.0	4.27 ± 0.02
		c. Glutarate		
2.944	5.35	77.3	22.7	4.83 ± 0.10
5.888	5.12	67.4	32.6	4.75 ± 0.12
11.78	5.17	48.7	51.3	4.39 ± 0.03
11.78	5.30	45.7	54.3	4.50 ± 0.03
11.78	5.46	43.0	57.0	4.43 ± 0.02
		d. Adipate		
2.932	5.13	77.1	22.9	4.82 ± 0.01
5.864	5.07	63.7	36.3	4.75 ± 0.06
11.73	5.18	42.8	57.2	4.50 ± 0.04
11.73	5.35	39.2	60.8	4.46 ± 0.04
11.73	5.64	35.0	65.0	4.38 ± 0.04

[a] Conditions as in footnote *a* of Table III.

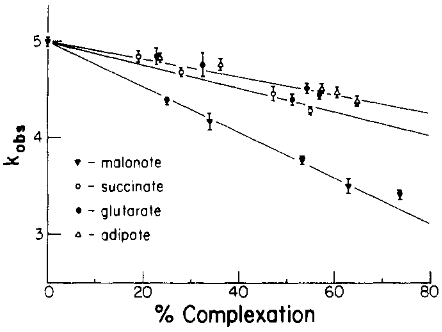

Figure 2. Variation of the decay constants (in ms^{-1}) as a function of the percent concentration of Eu(III) in the ternary complexes of NTA plus dicarboxylic acids.

solution was measured to be 8.80 ± 0.05 ms^{-1}.

For the study of the binary complexes of europium with the dicarboxylic ligands, solutions of varying ratios of europium perchlorate and ligand were prepared. In the case of the mixed complexes Eu(NTA)L, various amounts of the dicarboxylic ligands were added to a solution in which europium perchlorate and NTA were in 1:1 ratio. The results of measurement of the europium luminescence decay constant are reported in Table III for the binary complexes and in Table IV for the mixed complexes. The percentages of complexation were calculated by using the stability constants for solutions of the same ionic strength. For the binary complexes, the stability constants (β_1 and β_2) for malonate were taken from ref 12, and for succinate, glutarate, and adipate the constants for samarium complexation from ref 1 have been used. For the mixed complexes Eu(NTA)L, the stability constants reported for gadolinium in ref 2 were used (it was assumed that the NTA complexation was 100% under our conditions).

The luminescence decay constant is plotted as a function of the percentage of complexation in Figures 1 and 2. In the case of the binary complex EuL with malonate, the percentage of complexation was defined as % EuL + 2(% EuL_2), which assumes that twice as much water is released from the first coordination sphere of europium in the 1:2 complex as in the 1:1 complex (see below). Since % EuL_2 is always small, this is not a critical assumption.

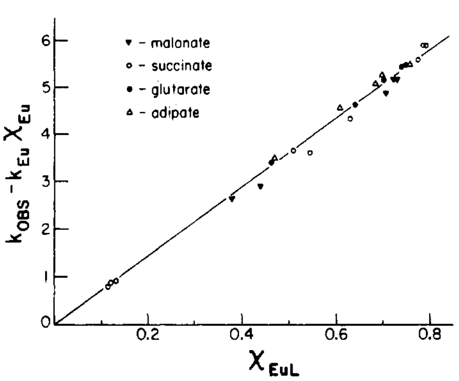

Figure 3. Plot of $k_{obs} - k_{Eu}\chi_{Eu}$ vs χ_{EuL} for the binary complexes of Eu(III) and dicarboxylic acids (L).

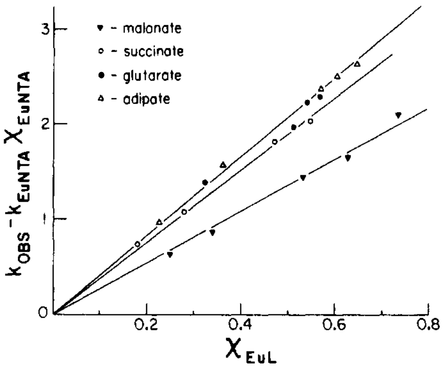

Figure 4. Plot of $k_{obs} - k_{EuNTA}\chi_{EuNTA}$ vs $\chi_{Eu(NTA)L}$ for the ternary complexes of Eu(III), NTA, and dicarboxylic acids (L).

Discussion

For our experimental conditions, the luminescence decay of all the solutions was a simple exponential, indicating that the observed luminescence decay constant, k_{obs}, is a weighted average of the characteristic luminescence decay constants k of all the europium species in solution. Thus, for the binary complexes

$$k_{obs} = k_{Eu}\chi_{Eu} + k_{EuL}\chi_{EuL} + k_{EuL_2}\chi_{EuL_2} \tag{2}$$

and for the mixed complexes

$$k_{obs} = k_{EuNTA}\chi_{EuNTA} + k_{Eu(NTA)L}\chi_{Eu(NTA)L} \tag{3}$$

where χ_i is the mole fraction of the particular Eu(III) species. As described above, for malonate complexation, the percentage of complexation was calculated as % EuL + 2(% EuL_2).

Figures 1 and 2 show that the behavior of malonate is different from the behavior of the other ligands. Furthermore, while succinate, glutarate, and adipate behave similarly in the binary complexation, some difference appears between these three ligands in the decay from the mixed complexes. A more quantitative insight may be gained by deriving the characteristic decay constant of the complexed species. In the case of the binary complex with malonate, a plot of $(k_{obs} - k_{Eu}\chi_{Eu})/\chi_{EuL_2}$ vs χ_{EuL}/χ_{EuL_2} gives a straight line, the slope of which is k_{EuL}.[13] In all the other cases, a plot of $k_{obs} - k_{Eu}\chi_{Eu}$ vs χ_{EuL} gives a straight line with a slope of k_{EuL} (Figures 3 and 4). The results are summarized in Table V. Included in that table is the difference of hydration between aqueous europium and the 1:1 complex (for the binary complexes) or the difference of hydration between the EuNTA complex and the Eu(NTA)L complexes as calculated with eq 1.

This equation assumes that the ligands do not quench europium luminescence within the uncertainties of our experiments. Under our experimental conditions, the luminescence decay constant was

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(13) The *y* intercept of such a plot should be the characteristic luminescence decay constant of the 1:2 complex k_{EuL_2}. However, the uncertainty in that value is too large to allow further consideration.

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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