which is commonly regarded as the strongest acid in HSO_3F.[24] If it is assumed that electrical conductance is predominantly caused by the acidium ion $H_2SO_3F^+$, the relative slopes represent an approximate order of acidity. While seemingly not quite as acidic as the HSO_3F–SbF_5–$3SO_3$ system, the HSO_3F–$Pt(SO_3F)_4$ system has some definite advantages, such as (a) chemical simplicity reflected in the ^{19}F NMR spectrum, (b) thermal stability, (c) absence of byproducts, such as free SO_3, capable of causing side reactions, and (d) a reasonable resistance toward reducing or oxidizing agents. The HSO_3F–$Au(SO_3F)_3$ system shares all these positive features, as well as the singular but obvious disadvantage, the rather high price of the respective metals, which may limit their extensive use.

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Registry No. $Pt(SO_3F)_4$, 36721-98-9; $Cs_2[Pt(SO_3F)_6]$, 90030-04-9; $(ClO_2)_2[Pt(SO_3F)_6]$, 90030-03-8; $Ba[Pt(SO_3F)_6]$, 71691-08-2; $(Br_3)_2[Pt(SO_3F)_6]$, 90046-22-3; $Cs[Pt(SO_3F)_5]$, 90030-05-0; Pt, 7440-06-4; $S_2O_6F_2$, 13709-32-5.

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Structural and Mechanistic Studies of Coordination Compounds. 39. Successful Application of the Marcus Theory in Predicting Rate Constants of Some Outer-Sphere Reductions of *trans*-Dihalogenotetraamineruthenium(III) Cations by Europium(II)

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The kinetics of the europium(II) reduction of *trans*-$[Ru(en)_2X_2]^+$ (en = ethane-1,2-diamine; X = Cl, Br, I) and *trans*-$[RuLCl_2]^+$ [L = 2,3,2-tet (3,7-diazanonane-1,9-diamine), cyclam (1,4,8,11-tetraazacyclotetradecane), [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane), teta or tetb (*C-meso*- or *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively)] has been studied at 25.0 °C in aqueous acidic solutions. From the Marcus cross-reaction relationship, self-exchange rate constants of some *trans*-$[RuLX_2]^{+/0}$ (X = Cl, Br) and $Eu_{aq}^{3+/2+}$ couples have been estimated. For the $Eu_{aq}^{3+/2+}$ couple, the estimated rate constants have been found to fall within the range of 2.3×10^{-4} to 1.7×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ at 25.0 °C and $\mu = 0.50$ mol dm^{-3}. The Marcus theory is found to be reasonably successful in predicting the rate constants for these cross-reactions.

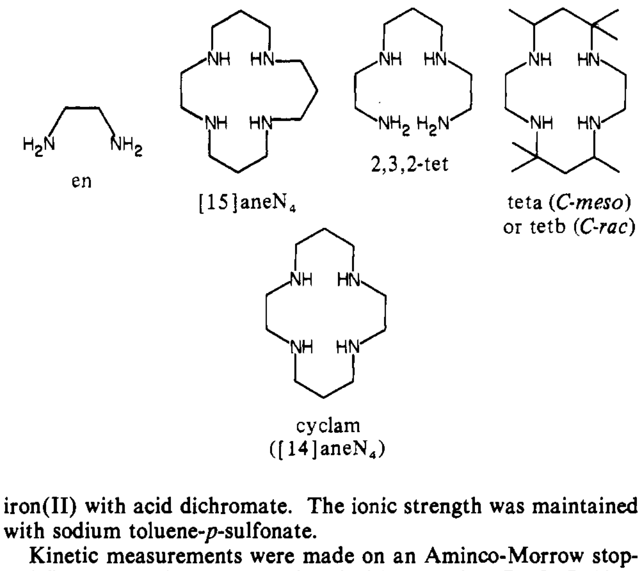
Introduction

As part of our program to examine the chemistry of ruthenium(III) amine complexes, we have reported the chromium(II) and vanadium(II) reductions of some *trans*-[Ru(tetraamine)$X_2]^+$ (X = Cl, Br, I) cations.[1,2] Two distinct pathways, inner-sphere by chromium(II) and outer-sphere by vanadium(II), were clearly demonstrated. We report here the europium(II) reduction of *trans*-$[Ru(en)_2X_2]^+$ (en = ethane-1,2-diamine; X = Cl, Br, I) and *trans*-$[RuLCl_2]^+$ [L = 2,3,2-tet (3,7-diazanonane-1,9-diamine), cyclam (1,4,8,11-tetraazacyclotetradecane), [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane), teta (*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), or tetb (*C-rac* isomer of teta)] (Chart I). The Marcus cross-reaction relationship[3] was employed to estimate the self-exchange rate constants of some *trans*-$[RuLX_2]^{+/0}$ and $Eu_{aq}^{3+/2+}$ couples.

Experimental Section

The complexes reported here were prepared according to published methods.[4,5] Europium(II) solutions were prepared from amalgamated zinc reduction of europium(III) carbonate (Alfa) in toluene-*p*-sulfonic acid under an atmosphere of argon. Europium(II) was analyzed by oxidizing with deoxygenated iron(III) and determining the reduced iron(II) with acid dichromate. The ionic strength was maintained with sodium toluene-*p*-sulfonate.

Chart I



Kinetic measurements were made on an Aminco-Morrow stopped-flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. Experimental details on data collection, temperature control, and data treatment have been described previously.[6] All operations were carried out under deoxygenated argon. Syringe techniques were used for the transfer of air-sensitive solutions.

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Table I. Second-Order Rate Constants, k_{Eu}, at 25.0 °C for Europium(II) Reductions of *trans*-$[RuLX_2]^+$ Complexes in 0.10 mol dm^{-3} Toluene-*p*-sulfonic Acid

L	X	μ^a/ mol dm^{-3}	$10^{-3}k_{Eu}{}^b$/ dm^3 mol^{-1} s^{-1}
$(en)_2$	Cl	0.50	7.1_0
		0.40	5.5_0
		0.30	4.0_0
		0.15	2.4_0
	Br	0.15	3.6_5
	I	0.15	5.1_5
2,3,2-tet	Cl	0.50	$10._0$
		0.40	7.8_0
		0.30	6.2_0
		0.15	3.5_0
cyclam	Cl	0.50	$11._5$
		0.40	$10._0$
		0.30	8.5_0
		0.15	5.8_5
$[15]aneN_4$	Cl	0.15	6.2_0
teta^c	Cl	0.60	$16._0$
		0.50	$14._5$
		0.40	$13._0$
		0.30	$11._0$
tetb^c	Cl	0.60	$15._0$
		0.50	$13._5$
		0.40	$11._5$
		0.30	9.9_0

[a] Ionic strength was maintained with sodium toluene-*p*-sulfonate. [b] Each entry was obtained from the slope of the appropriate linear plot of k_{obsd} vs. $[Eu_{aq}{}^{2+}]$ over at least five different $Eu_{aq}{}^{2+}$ concentrations by the method of least squares. [c] These two complexes are unstable in very dilute acids. Rate constants are independent of acid in the range 0.25–0.45 mol dm^{-3}.

Results

The reduction of halogenotetraamineruthenium(III) complexes was characterized by the gradual disappearance of the intense ligand-to-metal charge-transfer bands. The semilogarithmic pseudo-first-order rate plots were linear for at least 2 half-lives over the entire range of europium(II) concentrations (5.2×10^{-4} to 2.1×10^{-3} mol dm^{-3}). Although $Eu_{aq}{}^{2+}$ absorbs at 350 nm[7] ($\epsilon = 300$ dm^3 mol^{-1} cm^{-1}), the wavelength around which most of the kinetic runs were followed, its absorptivity is relatively very small and hence its contribution to the absorbance change for each run was negligible. For each kinetic run, the europium(II) concentration was always in considerable excess (>10-fold) over the ruthenium(III) complex to maintain the pseudo-first-order behavior. The pseudo-first-order rate constants, k_{obsd}, are independent of acid (0.050–0.45 mol dm^{-3}), ruthenium(III) (2.2×10^{-5} to 2.5×10^{-4} mol dm^{-3}), and additional chloride (0.1–0.3 mol dm^{-3}) concentrations, but they increase linearly with europium(II) concentrations. Second-order rate constants, k_{Eu}, were obtained from the slopes of the appropriate linear plots of k_{obsd} vs. $[Eu_{aq}{}^{2+}]$ over at least five different $Eu_{aq}{}^{2+}$ concentrations by the method of least squares.

The accelerating effect of ionic strength on reaction rates is governed by eq 1, where A and B are two proportionality

$$\log k_{obsd} = A + B\mu^{1/2} \qquad (1)$$

constants. For the dichloro complexes, the values of B [$(en)_2$, 1.47; 2,3,2-tet, 1.42; cyclam, 0.93; teta, 0.71; tetb, 0.81] are much smaller than the expected value of 2.04 from the Brønsted–Debye–Hückel equation[8] for reactions of charge product two. It should be noted that the theoretical equation is derived for reactions in nearly ideal solutions. In the present investigation, reactions were carried out at relatively high ionic strength (μ = 0.15–0.60 mol dm^{-3}) and, therefore, it was reasonable to expect that the rate constants might lie in the tailing-off regions of the log k_{obsd} vs. ($\mu^{1/2}$) plots. Accordingly, the extrapolation of these plots to zero ionic strength does not yield the true rate constants at infinite dilution.

Table II. Second-Order Rate Constants at 25.0 °C for Chromium(II), Vanadium(II), and Europium(II) Reductions of *trans*-$[RuLX_2]^+$ Complexes in 0.10 mol dm^{-3} Toluene-*p*-sulfonic Acid

L	X	$10^{-1}k_{Cr}{}^a$/ dm^3 mol^{-1} s^{-1}	$10^{-3}k_V{}^a$/ dm^3 mol^{-1} s^{-1}	$10^{-3}k_{Eu}{}^b$/ dm^3 mol^{-1} s^{-1}
$(en)_2$	Cl	3.02	1.21	2.40 (7.10)
	Br	7.63	3.07	3.65 (~10.5)
	I	29.5	12.7	5.15 (~15.0)
2,3,2-tet	Cl	4.73	2.03	3.50 (10.0)
cyclam	Cl	6.46	3.48	5.85 (11.5)
$[15]aneN_4$	Cl	11.6	3.56	6.20 (~12.0)
teta^c	Cl	494	7.28	8.55 (14.5)
tetb^c	Cl	375	7.69	7.35 (13.5)

[a] Reference 2; at $\mu = 0.50$ mol dm^3. [b] At $\mu = 0.15$ mol dm^{-3}; data in parentheses at $\mu = 0.50$ mol dm^{-3} (see text). [c] In 0.20–0.45 mol dm^{-3} toluene-*p*-sulfonic acid.

All the rate data at 25.0 °C are summarized in Table I.

Discussion

Contrary to the chromium(II) and vanadium(II) reductions,[1,2] the mechanism for the europium(II) reduction of *trans*-$[RuLX_2]^+$ (X = halide) complexes is not immediately clear. Since $Eu_{aq}{}^{2+}$ and $Eu_{aq}{}^{3+}$ are substitutionally very reactive, both inner-sphere and outer-sphere mechanisms are feasible. The present observation that added chloride had no catalytic effect on rates might have been taken to indicate an inner-sphere mechanism.[7,9] This piece of evidence is rather indirect, and it is not particularly reliable on its own right in predicting mechanisms. A comparison of the rate data with those of the corresponding chromium(II) and vanadium(II) reactions (Table II[10]) appears useful in differentiating between the two mechanisms. The inner-sphere chromium(II) reductions are characterized by steric acceleration (*trans*-$[Ru(teta)Cl_2]^+$ and *trans*-$[Ru(tetb)Cl_2]^+$ are more reactive than *trans*-$[Ru(cyclam)Cl_2]^+$ by factors of 76.5 and 58.0, respectively) as well as a moderate ring-size effect (*trans*-$[Ru([15]aneN_4)Cl_2]^+$ is more reactive than *trans*-$[Ru(cyclam)Cl_2]^+$ by a factor of 1.8). However, steric and ring-size effects are relatively insignificant for both vanadium(II) and europium(II) reductions. It seems reasonable to assume that the europium(II) reduction proceeds via the same outer-sphere mechanism as the corresponding vanadium(II) reactions.

With the availability of two related sets of outer-sphere rate data, it is possible to test the applicability of the Marcus cross-reaction relationship[3] for these ruthenium(III) reduction reactions. According to Endicott and Taube,[11] the work terms for the reactions of amine complexes are small and the simplified Marcus' relation for adiabatic electron-transfer reactions is given by

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (2)$$

where k_{12} is the observed rate constant of the redox reaction, k_{11} and k_{22} are the self-exchange rate constants for the com-

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(10) For teta and tetb complexes, the rate constants at μ = 0.15 mol dm^{-3} were obtained by extrapolation of rate data in Table I. The rate constants for *trans*-$[Ru(en)_2X_2]^+$ (X = Br, I) and *trans*-$[Ru([15]aneN_4)Cl_2]^+$ were only followed at μ = 0.15 mol dm^{-3}. For a more direct comparison with rate data of k_{Cr} and k_V, their rate constants at μ = 0.50 mol dm^{-3} were estimated from eq 1 with the assumption that they had the same B values as *trans*-$[Ru(en)_2Cl_2]^+$ and *trans*-$[Ru(cyclam)Cl_2]^+$, respectively.

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Table III. Estimates of the *trans*-$[RuLX_2]^{+/0}$ (k_{22}) and $Eu_{aq}^{3+/2+}$ (k_{11}^{Eu}) Self-Exchange Rate Constants at 25.0 °C and $\mu = 0.50$ mol dm^{-3} from the Marcus Cross-Reaction Relationship[a]

trans-$[RuLX_2]^+ + Y_{aq}^{2+} \rightleftharpoons$ *trans*-$[RuLX_2] + Y_{aq}^{3+}$

		$Y_{aq}^{2+} = V_{aq}^{2+}$			$Y_{aq}^{2+} = Eu_{aq}^{2+}$		
L	X	K_{12}^V	f^V	k_{22}/ dm^3 mol^{-1} s^{-1}	K_{12}^{Eu}	f^{Eu}	k_{11}^{Eu}/ dm^3 mol^{-1} s^{-1}
$(en)_2$	Cl	1.35×10	0.96	1.9×10^7	1.25×10^4	0.69	1.7×10^{-3}
	Br	3.75×10	0.92	4.6×10^7	3.40×10^4	0.62	6.4×10^{-4}
2,3,2-tet	Cl	2.95×10	0.93	2.5×10^7	2.70×10^4	0.64	1.3×10^{-3}
cyclam	Cl	7.60×10	0.89	3.0×10^7	6.75×10^4	0.58	6.2×10^{-4}
$[15]aneN_4$	Cl	1.30×10^2	0.86	1.9×10^7	1.15×10^5	0.55	6.5×10^{-4}
teta	Cl	2.15×10^2	0.83	4.9×10^7	1.95×10^5	0.52	2.3×10^{-4}

[a] See Discussion for explanation; values of reduction potentials not available for *trans*-$[Ru(en)_2I_2]^+$ and *trans*-$[Ru(tetb)Cl_2]^+$.

ponent couples (here subscript "1" will refer to the reducing agent and subscript "2" to the ruthenium(III) complex), K_{12} is the equilibrium constant for the reaction and

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)} \qquad (3)$$

(Z is the collision frequency for the uncharged species, which is usually taken[7,11,12] to be 1×10^{11} dm^3 mol^{-1} s^{-1}).

K_{12} values were calculated from the known reduction potentials of V_{aq}^{3+} (−0.255 V),[12,13] Eu_{aq}^{3+} (−0.386 V),[13] and the ruthenium(III) complexes.[14] From the vanadium(II) reactions, trial values of k_{22} at $\mu = 0.50$ mol dm^{-3} were calculated from eq 2 by using the known k_{11}^V value,[15] with the values of f^V and k_{22} being iterated until satisfactory agreement between successive values was reached. the calculated k_{22} values were then used for the calculation of k_{11}^{Eu} from eq 2 for the europium(II) reactions, again with the values of k_{11}^{Eu} and f^{Eu} being iterated. All the calculated data are collected in Table III.

The results of this exercise show that the calculated k_{11}^{Eu} values fall within the narrow range 2.3×10^{-4} to 1.7×10^{-3} dm^3 mol^{-1} s^{-1} at 25.0 °C and $\mu = 0.50$ mol dm^{-3}. This is in reasonable agreement with the values estimated by other workers.[12,16] This exercise provides kinetic evidence for the assignment of an outer-sphere mechanism for the europium(II) and vanadium(II) reductions of *trans*-$[RuLX_2]^+$ (X = halide) complexes, and it also serves to demonstrate that the simplified Marcus theory is reasonably successful in predicting outer-sphere electron-transfer rate constants of these ruthenium(III) reactions. However, it should be noted that eq 2 and 3 are derived on the assumptions of strict adiabaticity and complete cancellation of work terms in the self-exchange and cross-reactions.[12] These assumptions may not be met, and, hence, the application of the simplified Marcus relation should, in general, be used with care and reservations.[12,17]

As far as we are aware, no self-exchange rate data for any halogenoamineruthenium(III/II) couples have ever been reported. In fact, most ruthenium(II) acido–amine complexes are substitutionally very reactive,[18] and this makes the direct studies of their isotopic exchange reactions rather difficult, if not impossible. The Marcus theory appears to provide the most convenient method for the estimation of these self-exchange rate constants. As shown in Table III, these rate constants are much larger than that of $Ru(NH_3)_6^{3+/2+}$ (4.3×10^3 dm^3 mol^{-1} s^{-1})[19] but are similar to those of pyridine-containing ruthenium(III/II) couples [$Ru(NH_3)_5py^{3+/2+}$, 4.7×10^5;[20] $Ru(NH_3)_4(bpy)^{3+/2+}$, 7.7×10^5;[21] $Ru(NH_3)_2(bpy)_2^{3+/2+}$, 8.4×10^7;[21] $Ru(bpy)_3^{3+/2+}$, 4.2×10^8 dm^3 mol^{-1} s^{-1};[22] py = pyridine, bpy = 2,2′-bipyridine]. It appears that the presence of π bonding, whether ligand-to-metal π bonding leading to the stabilization of the ruthenium(III) state in halogeno complexes or metal-to-ligand back-bonding leading to the stabilization of the ruthenium(II) state in pyridine complexes,[12] will mobilize the metal π electrons and provide an efficient pathway for the self-exchange reactions of ruthenium(III/II) couples. Alternatively, the relatively fast self-exchange rate constants for the dichloro complexes in the present investigation may be the consequence of charge effect, i.e. $[RuL_4Cl_2]^{+/0}$ as against $[Ru(NH_3)_6]^{3+/2+}$. More work is in progress to examine the self-exchange reactions of these halogenotetraamineruthenium(III/II) couples.

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Registry No. Eu, 7440-53-1; *trans*-$[Ru(en)_2Cl_2]^+$, 45839-20-1; *trans*-$[Ru(en)_2Br_2]^+$, 73238-27-4; *trans*-$[Ru(en)_2I_2]^+$, 87655-42-3; *trans*-$[Ru(2,3,2\text{-}tet)Cl_2]^+$, 78477-92-6; *trans*-$[Ru(cyclam)Cl_2]^+$, 66652-53-7; *trans*-$[Ru([15]aneN_4)Cl_2]^+$, 76721-66-9; *trans*-$[Ru(teta)Cl_2]^+$, 76740-65-3; *trans*-$[Ru(tetb)Cl_2]^+$, 76705-21-0.

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