Volumes of Activation for Electron Transfer in Low-Spin/Low-Spin Cationic Couples in Aqueous Solution

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Volumes of reaction $\Delta V_{Ag/AgCl}$ (vs Ag/AgCl/4.0 mol L^{-1} KCl) and of activation $\Delta V_{el}^{\ddagger}$ for the electrode reactions of the aqueous $Co(azacapten)^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Co(tacn)_2^{3+/2+}$ couples have been measured by high-pressure cyclic and AC voltammetry. For the low-spin/low-spin $Co(azacapten)^{3+/2+}$ couple, $\Delta V_{el}^{\ddagger} = -3.3 \pm 0.4$ cm^3 mol^{-1}, whereas high-pressure NMR measurements gave a volume of activation $\Delta V_{ex}^{\ddagger}$ for the self-exchange reaction of -6.5 ± 0.5 cm^3 mol^{-1}, in accordance with the "fifty-percent rule" (*J. Am. Chem. Soc.* **1997**, *119*, 7137) and with the prediction of an adaptation of the Marcus theory of intermolecular electron-transfer kinetics (*Can. J. Chem.* **1996**, *74*, 631). For the $Ru(en)_3^{3+/2+}$ self-exchange reaction, $\Delta V_{ex}^{\ddagger}$ was estimated indirectly as -15.1 ± 1.7 cm^3 mol^{-1} from the $Co(phen)_3^{3+}/Ru(en)_3^{2+}$ cross reaction ($\Delta V_{12}^{\ddagger} = -12.9 \pm 0.5$ cm^3 mol^{-1}), for which the rate constant k_{12} was consistent with the Marcus cross relation. For the $Fe(H_2O)_6^{3+}/Ru(en)_3^{2+}$ cross reaction ($\Delta V_{12}^{\ddagger} = -18.3 \pm 1.2$ cm^3 mol^{-1}), k_{12} was slower than predicted from the Marcus cross relation, and consequently the estimated $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ (-18.9 ± 2 cm^3 mol^{-1}) may be less reliable. For the $Ru(en)_3^{3+/2+}$ electrode reaction, $\Delta V_{el}^{\ddagger} = -7.5 \pm 0.4$ cm^3 mol^{-1}, again in accordance with the fifty-percent rule and, conversely, authenticating the estimated $\Delta V_{ex}^{\ddagger}$. The $\Delta V_{ex}^{\ddagger}$ estimates for $Ru(en)_3^{3+/2+}$, however, are some 10 cm^3 mol^{-1} more negative than can be accommodated by the adapted Marcus theory. For the low-spin/high-spin couple $Co(tacn)_2^{3+/2+}$, $\Delta V_{el}^{\ddagger}$ (-5.9 ± 0.9 cm^3 mol^{-1}) is intermediate between values expected for $Co^{III/II}$ clathrochelates and low-spin/high-spin tris(bidentate) chelates, although $\Delta V_{Ag/AgCl}$ places this couple within the latter group.

Introduction

For many outer-sphere self-exchange electron-transfer reactions of the type

$$ML_n^{(z+1)+} + ML_n^{z+} \rightarrow ML_n^{z+} + ML_n^{(z+1)+} \qquad (1)$$

in homogeneous aqueous solution, the volumes of activation $\Delta V_{ex}^{\ddagger}$ ($= -RT(\partial \ln k_{ex}/\partial P)_T$, where k_{ex} is the rate constant and P the pressure) can be accurately predicted from an extension of Marcus theory.[1,2] As may be expected, the predictions fail when the mechanism is not of the simple adiabatic outer-sphere type—for example, where alkali metal ions catalyze electron transfer between anions as with $Mo(CN)_8^{3-/4-}$,[3] where there is a coordination change as in $Co(EDTA)^-/Co(EDTAH)OH_2^-$,[4] or where there is incursion of an inner-sphere path as in the $Fe(aq)^{3+/2+}$ exchange.[5] Indeed, $\Delta V_{ex}^{\ddagger}$ may serve as a criterion of such mechanistic aberrations.

It is less obvious, however, why the predictions fail (giving $\Delta V_{ex}^{\ddagger}$ values some 10−15 cm^3 mol^{-1} more positive than by experiment) for the $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ couples, yet succeed for $Co(ttcn)_2^{3+/2+}$ and the clathrochelate (cage) complexes $Co(sep)^{3+/2+}$, $Co(diamsarH_2)^{5+/4+}$, and (less convincingly) $Co(diamsar)^{3+/2+}$ (Chart 1).[1,2,4−9]

For $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$, the Co^{III} complex is low-spin ($^1A_{1g}$) whereas the Co^{II} is high-spin ($^4T_{1g}$) in the respective ground states, and consequently spin-pairing must occur somewhere along the reaction coordinate. The spin multiplicity change implies either nonadiabatic electron transfer in a single step, or a two-step process in which a spin-pairing preequilibrium giving a Co^{II} doublet state precedes adiabatic electron transfer. In either case, $\Delta V_{ex}^{\ddagger}$ is expected to be about 10−15 cm^3 mol^{-1} more negative than for the low-spin/low-spin $Co(ttcn)_2^{3+/2+}$ exchange, for which $\Delta V_{ex}^{\ddagger}$ is accurately predicted by the theory.[7] In early papers from our laboratory[8,9] the nonadiabatic explanation was preferred, partly because the putative Co^{II} spin state change could not be observed for the relevant complexes and the associated energetics seemed to be prohibitive. However, subsequent observation of "normal" $\Delta V_{ex}^{\ddagger}$ values for low-spin/high-spin clathrochelate couples,[1] which are structurally similar to but slightly larger than $Co(en)_3^{3+/2+}$, rendered this interpretation untenable. Our current view is that the anomalously negative $\Delta V_{ex}^{\ddagger}$ values for $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ reflect structural reorganization of the Jahn−Teller type associated with the spin-state change in these chelate

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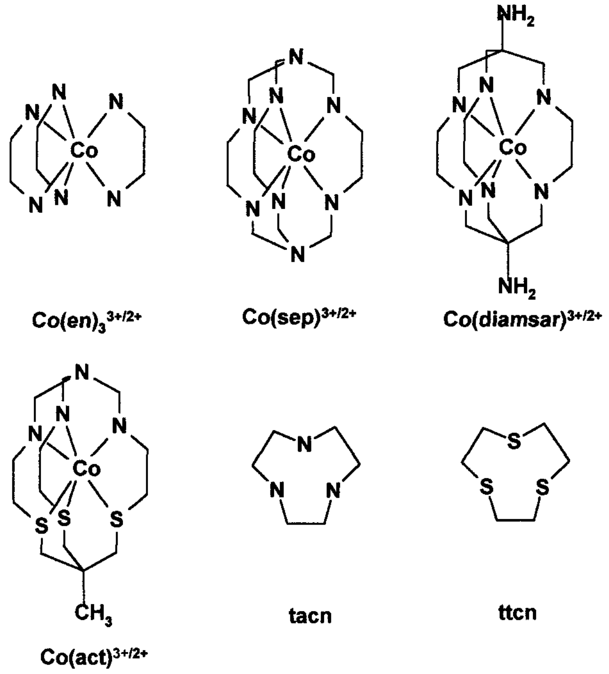
Chart 1



complexes—changes that are mechanically suppressed in the rigid clathrochelates. Beattie and Elsbernd[10] independently offered a similar interpretation. Binstead and Beattie's measurements[11] of a volume change of about -10 cm^3 mol^{-1} accompanying the observable rapid spin-pairing equilibrium in aqueous Co(terpy)$_2$$^{2+}$ [6] suggest that a similar value would indeed apply to Co(phen)$_3$$^{2+}$ and Co(en)$_3$$^{2+}$.

If this interpretation is correct and there are no complications, one can anticipate the following: (a) $\Delta V_{ex}^{\ddagger}$ for low-spin/low-spin clathrochelate Co$^{III/II}$ couple Co(act)$^{3+/2+}$ [6,12] should be about the same as for its low-spin/high spin analogues (-8 ± 2 cm^3 mol^{-1})—that is, it should conform to our Marcus-based theoretical predictions;[1,2] (b) $\Delta V_{ex}^{\ddagger}$ for the low-spin/high-spin Co(tacn)$_2$$^{3+/2+}$ couple, in which the ligand system is more rigid than for Co(phen)$_3$$^{3+/2+}$ or Co(en)$_3$$^{3+/2+}$ but less rigid than for the clathrochelates, should lie between the corresponding values (-6 and -16 cm^3 mol^{-1});[13] and (c) $\Delta V_{ex}^{\ddagger}$ for the low-spin/low-spin Ru(en)$_3$$^{3+/2+}$ exchange should be close to the theoretical -6 cm^3 mol^{-1} rather than the -16 cm^3 mol^{-1} [13] found for the Co(en)$_3$$^{3+/2+}$ analogue.

In this article, we describe experimental tests of predictions (a)−(c). An effort was also made to measure $\Delta V_{ex}^{\ddagger}$ for a further low-spin/low-spin Co system, the Co(diars)$_3$$^{3+/2+}$ couple,[6,14,15] primarily with triflate as the anion. Unfortunately, salts of the Co^{II} complex proved to be insufficiently soluble in water, acetone, or chloroform to allow detection of any Co$^{III/II}$ exchange in these solvents by NMR line broadening or electrochemical methods. Furthermore, although Co(diars)$_3$$^{2+}$ salts are quite easy to make and handle, oxidation to Co^{III} in solution appeared to result in loss of one of the diars ligands.[16]

For the Co(act)$^{3+/2+}$ couple, self-exchange is 10^3-fold faster[12] than for comparable low-spin/high-spin Co clathrochelates, and so $\Delta V_{ex}^{\ddagger}$ was measurable by high-pressure ^{1}H NMR line broadening. We also report measurements of the rate constant k_{el} and the corresponding volume of activation $\Delta V_{el}^{\ddagger}$ for Co(act)$^{3+/2+}$ at an electrode surface. We have shown[17−19] that, for 13 transition metal complex couples of various charge-types in aqueous solution,

$$\Delta V_{el}^{\ddagger} = \Delta V_{ex}^{\ddagger}/2 \tag{2}$$

with surprising accuracy; we call this relationship the "fifty-percent rule". It has a theoretical basis in work by Marcus;[20] in essence, reaction 1 in homogeneous solution requires that the M−L bond lengths and surrounding solvent of *both* $ML_n^{(z+1)+}$ and ML_n^{z+} be reorganized to a common intermediate configuration before electron transfer can occur, but for the corresponding electron transfer at an electrode only *one* complex ion and its surroundings have to be reorganized to the intermediate configuration. The Co(act)$^{3+/2+}$ couple presented a further opportunity to test eq 2.

Conversely, eq 2 was used to estimate $\Delta V_{ex}^{\ddagger}$ from measurements of $\Delta V_{el}^{\ddagger}$ for the Co(tacn)$_2$$^{3+/2+}$ and Ru(en)$_3$$^{3+/2+}$ couples. For Co(tacn)$_2$$^{3+/2+}$, self-exchange is too slow ($k_{ex}^{298} = 0.135$ L mol^{-1} s^{-1} in 0.1 mol L^{-1} NaCl, from the Marcus cross-relation)[21] for measurement by NMR line broadening yet too rapid for conventional sampling techniques at high pressures, and methods based on optical isomerism[1,7,9] are inapplicable. For Ru(en)$_3$$^{3+/2+}$, k_{ex} can be obtained from ^{13}C NMR,[22] but the necessary ^{1}H−^{13}C decoupling could not be implemented with our high-pressure NMR probe.[23] The electrochemically estimated values of $\Delta V_{ex}^{\ddagger}$ were just as predicted for the Co couples but unexpectedly strongly negative for Ru(en)$_3$$^{3+/2+}$. Accordingly, an attempt was made to confirm $\Delta V_{ex}^{\ddagger}$ for the latter by an independent method involving the Marcus cross-relation.[24]

Experimental Section

Materials. Distilled water, the solvent for all these studies, was further purified by passage through a Barnstead NANOpure train. [Fe(H$_2$O)$_6$](ClO$_4$)$_3$·3.5H$_2$O (Aldrich) and analytical-quality reagents were used as received.

[Co(act)](ClO$_4$)$_3$·2H$_2$O, [Co(act)](CF$_3$SO$_3$)$_3$·3H$_2$O, [Co(phen)$_3$](ClO$_4$)$_3$·2H$_2$O, and [Co(tacn)$_2$]Cl$_3$·1.5H$_2$O were made by literature methods and checked for purity by CHN microanalysis and the UV−visible and ^{1}H NMR spectra.[9,12,25−27][**Warning!** *Perchlorate salts of Co^{III} complexes containing organic ligands are potentially explosive.*] Cyclic voltammetry (CV) showed single, completely reversible waves for both Co(act)$^{3+/2+}$ and Co(tacn)$_2$$^{3+/2+}$.

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[13] Theory[2] predicts that $|\Delta V_{ex}^{\ddagger}|$ should decrease somewhat with increasing pressure, but, over the usual 0−200 MPa range, curvature of ln k_{ex} vs P plots is only discernible outside experimental uncertainty when $|\Delta V_{ex}^{\ddagger}|$ is large, as for Co(en)$_3$$^{3+/2+}$. In effect, the values of $\Delta V_{ex}^{\ddagger}$ quoted in this paper are averaged over the 0−200 MPa range, that is, they are correct at 100 MPa.
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$[Ru(en)_3]Cl_3$ was made from $RuCl_3$ (Aldrich) via $[Ru(en)_3][ZnCl_4]$ under Ar using Schlenk techniques.[28] $[Ru(en)_3](CF_3SO_3)_2$ and $[Ru(en)_3](CF_3SO_3)_3$ were made from the chloride salts by metathesis with $Pb(CF_3SO_3)_2$, and shown to be pure by CHN microanalysis and by UV/visible spectrophotometry of their aqueous solutions (maxima at 372 and 302 nm, molar absorbances $\epsilon = 361$ and 1020 L mol^{-1} cm^{-1}, respectively, for $Ru(en)_3^{2+}$, and at 310 nm with $\epsilon = 360$ L mol^{-1} cm^{-1} for $Ru(en)_3^{3+}$).[28] In particular, $Ru(en)_3^{3+}$ solutions were scrutinized for absence of the oxidation product $Ru(en)_2(HN{=}CH{-}CH{=}NH)^{2+}$ (absorbance maximum at 448 nm, $\epsilon = 6900$ L mol^{-1} cm^{-1}).[29]

NMR Line Broadening Measurements. All NMR spectra were obtained with a Bruker AMX2-300 spectrometer, the temperature readout of which was calibrated against the temperature dependence of the peak separation of either methanol (below 298 K) or ethylene glycol (80% in DMSO-d_6, above 298 K). High-pressure NMR measurements were made using the static probe previously described,[23] the internal temperature of which was monitored with a calibrated platinum resistance sensor. Persistent magnetic field inhomogeneities led to rather broad "natural" ^{1}H line widths (60 Hz), but line widths obtained with chemical exchange were at least twice as large, and rate constants obtained in the pressure assembly, extrapolated to atmospheric pressure, agreed well with those obtained with spinning samples in the Bruker probe at the same temperature.

The ^{59}Co NMR spectrum of $Co(act)^{3+}$ showed a single resonance at 4450 ppm (relative to $K_3[Co(CN)_6]$ at 0 ppm and $[Co(en)_3]Cl_3$ at 7130 ppm), but the signal was too broad (half-width 1400 Hz at 300 K in the Bruker probehead) for kinetic line-broadening measurements, for which the ^{1}H resonance near 1.4 ppm was used. Solutions of purple $Co(act)^{2+}$ in D_2O were made by reducing argon-purged solutions of red $Co(act)^{3+}$ triflate or perchlorate with zinc amalgam for 1 h immediately prior to use, and $Co(act)^{3+/2+}$ reaction mixtures were made by adding the requisite weighed amounts of the solid $Co(act)^{3+}$ salt to aliquots of the Co^{II} solution under Ar in capped 5 mm NMR tubes (for ambient pressure studies) or a 10 mm tube fitted with a Teflon piston sealed with rubber O-rings (for high-pressure studies).

The $Ru(en)_3^{3+/2+}$ self-exchange rate at ambient pressure was measured in Ar-purged CF_3SO_3H/D_2O at various temperatures and variable ionic strength (KCl) by observing the broadening of the ^{1}H-decoupled ^{13}C resonance at 45.4 ppm.[11] The natural line width of this peak in the Bruker probe (4.0 Hz) was independent of temperature, 280−320 K. Lack of a decoupling system for the high-pressure probe precluded measurement of $\Delta V_{ex}^‡$ for $Ru(en)_3^{3+/2+}$ by this method.

Stopped-Flow Kinetics. The rates of oxidation of $[Ru(en)_3](ZnCl_4)_2$ (in 0.02 mol L^{-1} CF_3COOH) by $[Fe(H_2O)_6](ClO_4)_3$ (in 0.2 mol L^{-1} $HClO_4$) or $[Co(phen)_3](ClO_4)_3$ (in water saturated with free phen) were followed spectrophotometrically at the oxidant absorbance maxima (240 nm[30] and 265 nm, respectively) using a Hi-Tech HPSF-56 high-pressure stopped-flow system thermostated to ±0.1 °C. The Ru^{II} complex was unaffected by $HClO_4$ on the time scale of the stopped-flow experiments. Oxygen was removed from all solutions by purging with Ar. The $Ru(en)_3^{2+}$ solutions were kept for 1 h over Zn amalgam in an Ar atmosphere prior to use, and a small pellet of Zn amalgam was added to the syringe barrel containing the Ru^{II} solution to obviate any oxidation to Ru^{III} by contaminants prior to mixing within the stopped-flow apparatus. Concentrations of $Ru(en)_3^{2+}$ in the reactant solution were measured spectrophotometrically and were in large excess over the oxidant to ensure pseudo-first-order kinetics.

Electrochemical Measurements. Cyclic (CV) and alternating-current (ACV) voltammograms were obtained at 25.0 ± 0.1 °C over the pressure range 0−200 MPa as described previously,[17−19] using Pt wire counter electrodes and a Ag/AgCl/4.0 mol L^{-1} KCl reference electrode. A glassy carbon disk (∅ 2 mm) working electrode was used for voltammetry with $[Co(act)](CF_3SO_3)_3$ and $[Ru(en)_3][ZnCl_4]$, and a Pt wire electrode for $[Co(tacn)_2]Cl_3$. The supporting electrolyte was KCl in all cases. For experiments using $[Ru^{II}(en)_3]ZnCl_4$, acidification with HTFA[6] (0.02 mol L^{-1}) was necessary, and the presence of a small amount of Zn amalgam helpful, to suppress the oxidation of $Ru(en)_3^{2+}$ to interfering byproducts; the purity of the $Ru(en)_3^{2+}$ solution was nevertheless checked spectrophotometrically before and after each experiment. These problems did not arise with the use of $[Ru^{III}(en)_3]Cl_3$.

Results

In experiments at variable pressure, only those data sets in which the measurements at low pressure before and after the pressure cycle agreed (within the experimental uncertainty) were accepted.

$Co(act)^{3+/2+}$ Self-Exchange. It was confirmed that the $Co(act)^{3+/2+}$ self-exchange rate lies in the "slow" NMR region and is first-order with respect to both reactants.[12] Thus, the rate constant k_{ex} is given by

$$k_{ex} = \pi(W_{1/2} - W_0)/[Co(act)^{2+}] \tag{3}$$

where $W_{1/2}$ and W_0 are respectively the ^{1}H NMR peak widths at half-height of the $Co(act)^{3+}$ resonance in the presence and in absence of $Co(act)^{2+}$. Line broadening measurements over the range 278−340 K on solutions containing 0.01 mol L^{-1} $[Co(act)](ClO_4)_3$ and 0.0023 mol L^{-1} $[Co(act)](ClO_4)_2$ in D_2O gave $\Delta H^‡ = 23.4 \pm 1.2$ kJ mol^{-1}, $\Delta S^‡ = -93 \pm 4$ J K^{-1} mol^{-1}, and $k_{ex}^{298} = 6.9 \times 10^3$ L mol^{-1} s^{-1}, in reasonable agreement with literature values.[12] NMR line broadening measurements at high pressure with 0.022 mol L^{-1} $[Co(act)](ClO_4)_3$ and 0.079 mol L^{-1} $[Co(act)](ClO_4)_2$ in D_2O at 298.2 K showed that ln k_{ex} is a linear function of pressure from 0 to 200 MPa (Supporting Information, Table S1):

$$\ln k_{ex}{}^{P} = \ln k_{ex}{}^{0} - P\Delta V_{ex}{}^{‡}/RT \tag{4}$$

giving $\Delta V_{ex}^‡ = -6.5 \pm 0.5$ cm^3 mol^{-1} and $k_{ex}^0 = 7.3 \times 10^3$ L mol^{-1} s^{-1} for these conditions.

Oxidation Kinetics of $Ru(en)_3^{2+}$. Proton-decoupled ^{13}C NMR line broadening measurements in a commercial probe over the range 280−322 K on solutions containing 0.25 mol L^{-1} $[Ru(en)_3](CF_3SO_3)_2$, 0.0017 mol L^{-1} $[Ru(en)_3](CF_3SO_3)_3$, and 0.032 mol L^{-1} CF_3SO_3H in D_2O gave $\Delta H_{ex}^‡ = 25.3 \pm 1.2$ kJ mol^{-1}, $\Delta S_{ex}^‡ = -76 \pm 3$ J K^{-1} mol^{-1}, and $k_{ex}^{298} = 2.4 \times 10^4$ L mol^{-1} s^{-1} for the $Ru(en)_3^{3+/2+}$ exchange, in good agreement with the data of Beattie and Smolenaers after allowance for concentration dependence.[22] In KCl media (0−0.73 mol L^{-1}) at 280 K, k_{ex} increased with the ionic strength I (0.015−0.88 mol L^{-1}) according to the Brønsted−Bjerrum−Christiansen equation

$$\ln k_{ex} = \ln k_{ex}{}^{I=0} + 2(z_1 z_2 A I^{1/2})/(1 + BaI^{1/2}) \tag{5}$$

in which z_1 and z_2 are the charge numbers of the Ru complexes, A (= 1.093 L$^{1/2}$ mol$^{-1/2}$) and B (= 3.26 L$^{1/2}$ mol$^{-1/2}$ nm^{-1}) are the Debye−Hückel constants for 280 K, and a is an empirical parameter, ostensibly the anion−cation close approach distance. The best fit of the data (Supporting Information, Figure S1) corresponded to $k_{ex}^{I=0} = (1.55 \pm 0.09) \times 10^4$ L mol^{-1} s^{-1} and $a = 0.88 \pm 0.03$ nm. No particular physical significance is attached to these parameters; the essential point is that rate constants for the $Ru(en)_3^{3+/2+}$ exchange reaction are concentration dependent and some 20-fold larger in chloride media than in comparable triflate solutions.

As noted above, however, we were unable to obtain ^{1}H-decoupled ^{13}C spectra with our high-pressure probe, and an estimate of $\Delta V_{ex}^‡$ for the $Ru(en)_3^{3+/2+}$ self-exchange reaction

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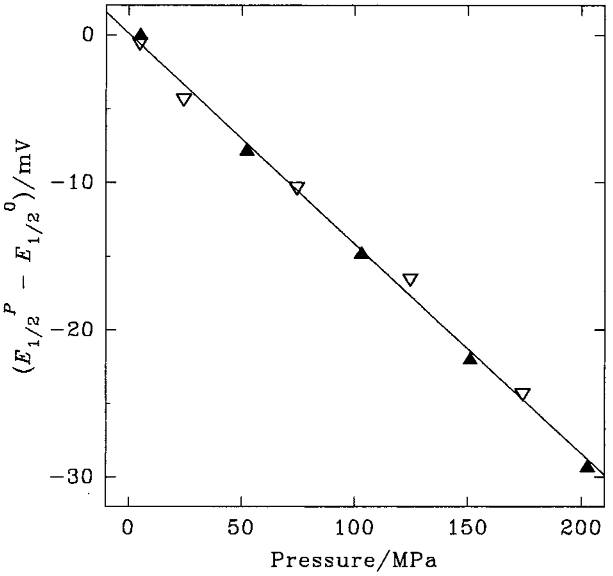

Figure 1. Pressure dependence of the half-wave potential $E_{1/2}$ for Co(act)$^{3+/2+}$ from CV measurements on 0.63 mmol L^{-1} [Co(act)](CF$_3$SO$_3$)$_3$ in 0.1 mol L^{-1} KNO$_3$ at a gold wire electrode (∅ 0.5 mm) relative to Ag/Ag$^+$ (0.01 mol L^{-1} AgNO$_3$/0.1 mol L^{-1} KNO$_3$); (▲) increasing pressure; (▽) decreasing pressure.

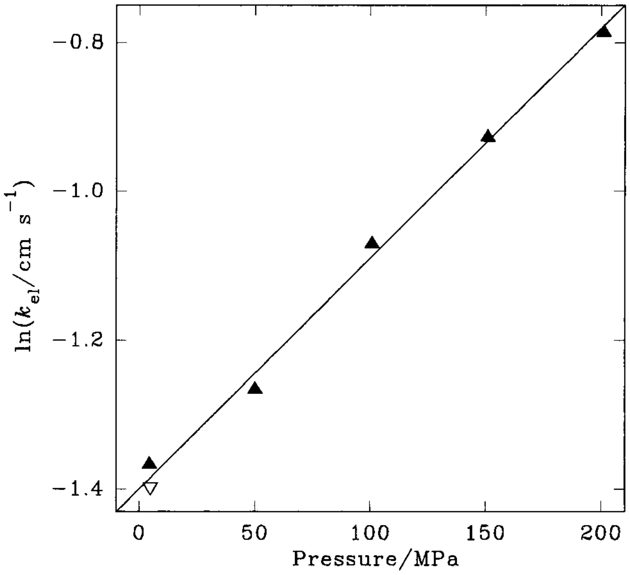

Figure 2. Pressure dependence of the Ru(en)$_3^{3+/2+}$ electrode reaction rate constant k_{el} from ACV measurements on 1.21 mmol L^{-1} [Ru(en)$_3$]Cl$_3$ in 0.40 mol L^{-1} NaTFA/0.001 mol L^{-1} HTFA; (▲) increasing pressure; (▽) decreasing pressure.

was obtained from measurements of the pressure dependences of the rate constants k_{12} for the oxidations of Ru(en)$_3^{2+}$ by Fe(H$_2$O)$_6^{3+}$ and Co(phen)$_3^{3+}$.

For the oxidation of Ru(en)$_3^{2+}$ by Fe(H$_2$O)$_6^{3+}$, it was confirmed spectrophotometrically[31] that less than 2% of the Fe^{III}(aq) was present as Fe(H$_2$O)$_5$OH^{2+} in the reaction media on mixing, and that the reaction rate was accurately first-order in [Ru(en)$_3^{2+}$]. Measurements over the range 7−30 °C (Supporting Information, Table S2) gave a linear Eyring plot with $\Delta H_{12}^{\ddagger} = 14.6 \pm 0.7$ kJ mol^{-1}, $\Delta S_{12}^{\ddagger} = -103 \pm 3$ J K^{-1} mol^{-1}, and $k_{12}^{298} = 7.5 \times 10^4$ L mol^{-1} s^{-1} at $I = 0.11$ mol L^{-1} (0.1 mol L^{-1} HClO$_4$, 0.01 mol L^{-1} CF$_3$COOH), in reasonable agreement with the results of Meyer and Taube.[30] Three independent runs in the same medium with variable pressure (0−200 MPa; Supporting Information, Table S3) gave linear plots of ln k_{12} vs P, with $\Delta V_{12}^{\ddagger} = -17.0 \pm 0.4$ (5.0 °C, 6 points), -18.2 ± 0.5 cm^3 mol^{-1} (7.0 °C, 13 points), and -19.6 ± 1.0 cm^3 mol^{-1} (7.0 °C, 10 points); if $\Delta V_{12}^{\ddagger}$ is not significantly temperature dependent, the average value (-18.3 ± 1.2 cm^3 mol^{-1}) may be taken as definitive for $I = 0.11$ mol L^{-1}.

For the oxidation of Ru(en)$_3^{2+}$ with Co(phen)$_3^{3+}$, the reaction rate was accurately first-order with respect to each reactant (Supporting Information, Table S4), and the linear Eyring plot gave $\Delta H_{12}^{\ddagger} = 29.3 \pm 2.6$ kJ mol^{-1}, $\Delta S_{12}^{\ddagger} = -73 \pm 8$ J K^{-1} mol^{-1}, and $k_{12}^{298} = 7.0 \times 10^3$ L mol^{-1} s^{-1} at $I = 0.006$ mol L^{-1} (0.005 mol L^{-1} HClO$_4$). The pressure dependence of ln k_{12} was linear, 0−190 MPa, giving $\Delta V_{12}^{\ddagger} = -12.9 \pm 0.5$ cm^3 mol^{-1} (25.0 °C, $I = 0.0057$ mol L^{-1}; Supporting Information, Table S5).

High-Pressure Electrochemistry. All measurements were made at 25.0 °C. The half-wave potentials $E_{1/2}$ and electrode reaction rate constants k_{el} were obtained from CVs and ACVs as described elsewhere.[17−19] Representative plots showing the pressure dependences of $E_{1/2}$ (for Co(act)$^{3+/2+}$) and ln k_{el} (for Ru(en)$_3^{3+/2+}$) are given in Figures 1 and 2, respectively. Further results are given in the Supporting Information (Tables S6 and S7). The electrochemical results are summarized in Tables 1 and 2. To verify that cell reaction volumes were not significantly dependent on electrode dimensions, CV measurements were made on solutions of 1 mmol L^{-1} [Co(act)](CF$_3$SO$_3$)$_3$ in 0.1 mol L^{-1} KNO$_3$ using a Ag/Ag$^+$(0.01 mol L^{-1} AgNO$_3$ in 0.1 mol L^{-1} KNO$_3$) electrode for maximum electrical stability and either a gold ultramicroelectrode (12.7 mm diameter) or a gold wire (2 mm long, 0.5 mm diameter) as the working electrode. These gave cell reaction volumes of 15.0 ± 0.6 and 13.8 ± 0.3 cm^3 mol^{-1}, respectively; thus, conventional electrodes give better precision in variable-pressure studies and were adopted for all further work. Conversion of the weighted mean to the Ag/AgCl/KCl (4 mol L^{-1}) reference scale[32,33] gave $\Delta V_{Ag/AgCl} = 17.1 \pm 0.6$ cm^3 mol^{-1}. For kinetic studies on 0.6 mmol L^{-1} [Co(act)](CF$_3$SO$_3$)$_3$ in 0.1 mol L^{-1} KCl using ACV, electron-transfer rates were too high at Au or Pt surfaces but measurable at a glassy carbon disk.

Table 1. Pressure Dependence of Half-Wave Potentials from Cyclic Voltammetry

couple, electrode	medium (mol L^{-1})	$E_{1/2}{}^{a}$ (mV)	α	$\Delta V_{Ag/AgCl}{}^{a}$ (cm^3 mol^{-1})
Co(act)$^{3+/2+}$, Au^b	KNO$_3$, 0.10	−45	0.50	17.1 ± 0.7
Co(sep)$^{3+/2+}$, Pt^c	KCl, 0.50	−290	0.42	15.8 ± 0.5
Co(diamsar)$^{3+/2+}$, Au^c	NaClO$_4$, 0.1	−410	0.27	17.4 ± 0.5
Co(diamsarH$_2$)$^{5+/4+}$, Au^c	(H,Na)ClO$_4$, 0.13	−35	0.41	19.5 ± 0.8
Co(tacn)$_2^{3+/2+}$, Pt^b	KCl, 0.50	−590	0.45	25.7 ± 0.5
Co(ttcn)$_2^{3+/2+}$, Pt^c	NaClO$_4$, 0.1	+230	0.50	24.4 ± 1.0
Co(phen)$_3^{3+/2+}$, Pt^c	NaCl, 0.1	+330	0.50	27.3 ± 1.1
Co(phen)$_3^{3+/2+}$, Pt^d	KNO$_3$, 0.1			24.3 ± 1.1
Co(en)$_3^{3+/2+}$, Pt^c	KCl, 0.5	−290	0.42	26.7 ± 0.7
Ru(en)$_3^{3+/2+}$, C$_{gl}{}^b$	KCl, 0.40^e	10	0.50	13.2 ± 1.0
Ru(en)$_3^{3+/2+}$, Hg(Au)^d	KNO$_3$, 0.1			16.9 ± 0.6

[a] Relative to Ag/AgCl/4.0 mol L^{-1} KCl, ± 5 mV, in neutral solution except as noted. [b] This work. [c] Reference 18. [d] Reference 34; corrected to Ag/AgCl standard. [e] 0.01 mol L^{-1} HTFA present.

For the Co(tacn)$_2^{3+/2+}$ couple, satisfactory CV and ACV results were obtained at a Pt wire electrode despite the closeness of $E_{1/2}$ to the H$_2$ evolution potential. For the Ru(en)$_3^{3+/2+}$ couple,

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Table 2. Diffusion Coefficients, Electrode Reaction Rate Constants at Ambient Pressure, and Volumes of Activation in Water at 25.0 °C

couple, electrode	medium[a] ($\mathrm{mol\ L^{-1}}$)	D ($10^{-6}\ \mathrm{cm^2\ s^{-1}}$)	$k_{el}{}^0$ ($\mathrm{cm\ s^{-1}}$)	$\Delta V_{el}{}^{\ddagger}$ ($\mathrm{cm^3\ mol^{-1}}$)	$\Delta V_{ex}{}^{\ddagger}$ ($\mathrm{cm^3\ mol^{-1}}$)
$\mathrm{Co(act)^{3+/2+}}$, $\mathrm{C_{gl}}$	KCl, 0.28	6.48	0.32 ± 0.06	−3.3 ± 0.4[b]	−6.5 ± 0.5[b]
$\mathrm{Co(sep)^{3+/2+}}$, Pt	KCl, 0.5	6.57	0.091 ± 0.001	−3.0 ± 0.4[c]	−6.4 ± 0.2[d]
$\mathrm{Co(diamsar)^{3+/2+}}$, Au	$\mathrm{NaClO_4}$, 0.1	5.85	0.0162 ± 0.0007	−3.5 ± 0.2[c]	−10.5 ± 0.6[e]
$\mathrm{Co(diamsarH_2)^{5+/4+}}$, Au	$\mathrm{(H,Na)ClO_4}$, 0.13	5.21	0.010 ± 0.001	−3.8 ± 0.3[c]	−9.4 ± 0.9[e]
$\mathrm{Co(tacn)_2{}^{3+/2+}}$, Pt	KCl, 0.50	5.85	0.075 ± 0.008	−5.9 ± 0.9[b]	−
$\mathrm{Co(ttcn)_2{}^{3+/2+}}$, Pt	$\mathrm{NaClO_4}$, 0.1	5.69	0.27 ± 0.02	−2.8 ± 0.7[c]	−4.8 ± 0.2[d]
$\mathrm{Co(phen)_3{}^{3+/2+}}$, Pt	NaCl, 0.1	5.96	0.108 ± 0.002	−9.1 ± 0.4[c]	−17.6 ± 0.7[f]
$\mathrm{Co(en)_3{}^{3+/2+}}$, Pt	KCl, 0.5	6.17	0.036 ± 0.001	−8.3 ± 0.5[c]	−15.5 ± 0.8[g]
$\mathrm{Ru(en)_3{}^{3+/2+}}$, $\mathrm{C_{gl}}$	KCl, 0.40[h]	6.23	0.34 ± 0.06	−7.4 ± 0.4[b]	−15.1 ± 1.7[b,i]
	NaTFA, 0.40[j]	6.23	0.25 ± 0.03	−7.6 ± 0.3[b]	

[a] For electrode processes only; see references for conditions for $\Delta V_{ex}{}^{\ddagger}$. [b] This work. [c] Reference 18. [d] Reference 7. [e] Reference 1. [f] Reference 9; $\mathrm{Cl^-}$ medium. [g] Reference 8. [h] 0.01 $\mathrm{mol\ L^{-1}}$ HTFA present. [i] From the $\mathrm{Ru(en)_3{}^{2+}/Co(phen)_3{}^{3+}}$ cross reaction; 0.1 $\mathrm{mol\ L^{-1}\ HClO_4}$. [j] 0.001 $\mathrm{mol\ L^{-1}}$ HTFA present.

Table 3. Average Metal−Ligand Bond Lengths[a]

couple	bond	bond length/pm	bond	bond length/pm
$\mathrm{Co(en)_3{}^{3+/2+}}$	$\mathrm{Co^{III}{-}N}$	196	$\mathrm{Co^{II}{-}N}$	216[b]
$\mathrm{Co(tacn)_2{}^{3+/2+}}$	$\mathrm{Co^{III}{-}N}$	198	$\mathrm{Co^{II}{-}N}$	216
$\mathrm{Co(phen)_3{}^{3+/2+}}$	$\mathrm{Co^{III}{-}N}$	194	$\mathrm{Co^{II}{-}N}$	213
$\mathrm{Co(sep)^{3+/2+}}$	$\mathrm{Co^{III}{-}N}$	199[c]	$\mathrm{Co^{II}{-}N}$	216[c]
$\mathrm{Co(act)^{3+/2+}}$	$\mathrm{Co^{III}{-}N}$	201	$\mathrm{Co^{II}{-}N}$	207
	$\mathrm{Co^{III}{-}S}$	223	$\mathrm{Co^{II}{-}S}$	213
$\mathrm{Co(ttcn)_2{}^{3+/2+}}$	$\mathrm{Co^{III}{-}S}$	225	$\mathrm{Co^{II}{-}S}$	232
$\mathrm{Ru(en)_3{}^{3+/2+}}$	$\mathrm{Ru^{III}{-}N}$	211	$\mathrm{Ru^{II}{-}N}$	213

[a] Data from refs 12, 27, and 36−39. [b] By analogy with $\mathrm{Co(NH_3)_6{}^{2+}}$. [c] Co−N bond lengths in other $\mathrm{Co{-}N_6}$ clathrochelates are closely similar to these values.[36]

the use of trifluoroacetate ($\mathrm{TFA^-}$) as a nonoxidizing supporting anion led to apparent poisoning of Pt electrodes, but, with the precautions noted above, reliable CV and ACV data were obtained with glassy carbon electrodes. Values of $\Delta V_{Ag/AgCl}$ obtained with $\mathrm{[Ru^{II}(en)_3]ZnCl_4}$ (13.2 ± 1.0, 13.3 ± 0.9 $\mathrm{cm^3\ mol^{-1}}$) were in excellent agreement with those obtained with $\mathrm{[Ru^{III}(en)_3]Cl_3}$ (14.0 ± 1.1, 12.4 ± 0.8 $\mathrm{cm^3\ mol^{-1}}$), all in 0.5 $\mathrm{mol\ L^{-1}}$ KCl; Tregloan and co-workers[34] report 16.9 ± 0.6 $\mathrm{cm^3\ mol^{-1}}$ (after correction to the Ag/AgCl standard) for the $\mathrm{Ru(en)_3{}^{3+/2+}}$ couple in 0.1 $\mathrm{mol\ L^{-1}\ KNO_3}$.

Discussion

Volumes of Reaction. The cell reaction volumes $\Delta V_{Ag/AgCl}$ listed in Table 1 fall roughly[35] into three groups: the Co clathrochelates, for which $\Delta V_{Ag/AgCl} = 17 \pm 2\ \mathrm{cm^3\ mol^{-1}}$, the "open" Co chelates with $\Delta V_{Ag/AgCl} = 26 \pm 2\ \mathrm{cm^3\ mol^{-1}}$, and $\mathrm{Ru(en)_3{}^{3+/2+}}$ for which $\Delta V_{Ag/AgCl}$ may be somewhat medium-dependent but in any event is the smallest of those listed. The factors that influence cell reaction volumes have been discussed in detail elsewhere.[33,34] We note here simply that the excess of almost 10 $\mathrm{cm^3\ mol^{-1}}$ in $\Delta V_{Ag/AgCl}$ in the Co open chelates over the clathrochelates cannot be attributed to Co−ligand bond length effects, since the difference Δd in Co−N bond lengths on going from $\mathrm{Co^{III}}$ to $\mathrm{Co^{II}}$ (Table 3) is about the same in all cases. Furthermore, $\mathrm{Co(ttcn)_2{}^{3+/2+}}$ and $\mathrm{Co(act)^{3+/2+}}$ are typical members of their respective structural groups, despite being low-spin/low-spin couples whereas the other members are all low-spin/high-spin. Thus, it would appear that $\mathrm{Co^{III/II}}$ cell reaction volumes are influenced (made less positive) by loss of torsional flexibility, as in the clathrochelates, but not by the ground-state spin multiplicities of the Co complexes. Significantly, the strain energy in Co clathrochelates originates largely in the torsional deformations imposed by the rigid ligand structures.[12]

Volumes of Activation. For $\mathrm{Co(act)^{3+/2+}}$, $\Delta V_{ex}{}^{\ddagger}$ (Table 2) is just as predicted from an extension of Marcus theory[2] for a low-spin/low-spin $\mathrm{Co^{III/II}}$ couple with complex-ion radii 450−500 pm. For $\mathrm{Co(tacn)_2{}^{3+/2+}}$, $\Delta V_{ex}{}^{\ddagger}$ could not be determined directly, but $\Delta V_{el}{}^{\ddagger}$ is midway between the corresponding values for $\mathrm{Co^{III/II}}$ clathrochelates and bidentate chelates (Table 2), as might be expected since the bis(tacn) ligand environment is intermediate between the two groups in terms of flexibility.

Thus far, the theoretical expectations listed above are vindicated, but, for the $\mathrm{Ru(en)_3{}^{3+/2+}}$ self-exchange reaction, indirect determinations of $\Delta V_{ex}{}^{\ddagger}$ by three independent methods gave highly anomalous yet self-consistent results. Two estimates of $\Delta V_{ex}{}^{\ddagger}$ for $\mathrm{Ru(en)_3{}^{3+/2+}}$ were obtained from $\Delta V_{12}{}^{\ddagger}$ for the cross reactions of $\mathrm{Ru(en)_3{}^{2+}}$ with $\mathrm{Fe(H_2O)_6{}^{3+}}$ and $\mathrm{Co(phen)_3{}^{3+}}$. In these cases, the cross reactions are symmetrical with respect to the charges on the reactants, so we have[24]

$$\Delta V_{12}{}^{\ddagger} = 0.5(\Delta V_{11}{}^{\ddagger} + \Delta V_{22}{}^{\ddagger} + \Delta V_{12}) + C \tag{6}$$

$$C = [X\Delta V_{12} \ln K_{12} - 2(\ln K_{12})^2(\Delta V_{11}{}^{\ddagger} + \Delta V_{22}{}^{\ddagger} - \Delta V_{11}{}^{\mathrm{coul}} - \Delta V_{22}{}^{\mathrm{coul}})]/X^2 \tag{7}$$

$$X = 4[\ln(k_{11}k_{22}/Z_{11}Z_{22}) + (w_{11} + w_{22})/RT] \tag{8}$$

In eqs 6−8, the subscript 11 refers to k_{ex} and $\Delta V_{ex}{}^{\ddagger}$ for the $\mathrm{Ru(en)_3{}^{3+/2+}}$ self-exchange reaction, 22 to k_{ex} and $\Delta V_{ex}{}^{\ddagger}$ for either $\mathrm{Fe(H_2O)_6{}^{3+/2+}}$ or $\mathrm{Co(phen)_3{}^{3+/2+}}$, and 12 to the kinetic parameters for the corresponding "cross" reactions. For a cross reaction, the equilibrium constant K_{12} and the associated volume of reaction ΔV_{12} are obtainable from $\Delta E_{1/2} = E_{1/2(11)} - E_{1/2(22)}$ and $\Delta V_{12} = \Delta V_{Ag/AgCl(11)} - \Delta V_{Ag/AgCl(22)}$, respectively. The symbols w and $\Delta V_{ii}{}^{\mathrm{coul}}$ refer to the Coulombic work required to bring the reactants together. Z_{ij} are frequency factors associated with the expression of k_{ij} in terms of a free energy of activation $\Delta G_{ij}*$

$$k_{ij} = Z_{ij} \exp(-\Delta G_{ij}*/RT) \tag{9}$$

as in the simplest version of Marcus theory,[40] and may taken

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to be 1×10^{11} L mol^{-1} s^{-1}. We have demonstrated elsewhere[24] that eq 6−8 are accurate for moderate values of $\Delta E_{1/2}$.

Solution of eqs 6−8 for $\Delta V_{11}^{\ddagger}$ is complicated by the inevitable differences in temperature, pressure, and reaction media necessary to determine the kinetic parameters for the various self-exchange and cross reactions experimentally. For the reaction of $Ru(en)_3^{2+}$ with $Fe(H_2O)_6^{3+}$, $\Delta V_{12}^{\ddagger}$ was measured at 5−7 °C and $I = 0.11$ mol L^{-1}, $\Delta V_{22}^{\ddagger}$ ($= -11.1 \pm 0.4$ cm^3 mol^{-1}) at 2 °C and $I = 0.5$ mol L^{-1},[4] and the other parameters at 25 °C. Experience, however, suggests that volumes of activation are not strongly dependent on temperature or ionic strength.[24] The standard potential change and volume of reaction must be derived from $\Delta V_{Ag/AgCl}$ and $E_{1/2}$ data obtained in the same medium, preferably one that is consistent with those of the kinetic measurements. For this reason, the data of Tregloan and co-workers[34] for $I = 0.10$ mol L^{-1} ($\Delta E_{1/2} = 534$ mV, $\Delta V_{12} = -14.3 \pm 1.5$ cm^3 mol^{-1}) were used, for compatibility with our stopped-flow measurements. For the $Ru(en)_3^{3+/2+}$ self-exchange, k_{11} for $I = 0.10$ mol L^{-1} at 25 °C can be estimated to be 1.0×10^4 L mol^{-1} s^{-1}.[22] The Coulombic work factors were calculated assuming radii of 420 and 340 pm for $Ru(en)_3^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively, leading to $C = 2.7 - 0.0605\Delta V_{11}^{\ddagger}$, so that, from eq 6, $\Delta V_{11}^{\ddagger} = -11.2 - 2C = -18.9$ cm^3 mol^{-1}. Propagation of experimental errors suggests a standard deviation of ± 1.4 cm^3 mol^{-1} in this value, but the actual uncertainty is likely to be at least ± 2 cm^3 mol^{-1} because of the assumptions made and the neglect of possible temperature, pressure, and ionic strength effects. Furthermore, the value of k_{12} estimated from the Marcus cross relation[40]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{10}$$

$$\ln f = (\ln K_{12})^2/X \tag{11}$$

for the oxidation of $Ru(en)_3^{2+}$ by $Fe(H_2O)_6^{3+}$ using these data is 5.7×10^5 L mol^{-1} s^{-1} at 25 °C, whereas our measured value is 7.5×10^4 L mol^{-1} s^{-1}. We have noted previously[24] that eqs 6−8 and 10−11 tend to break down when $\Delta E_{1/2}$ is relatively large.

For the reaction of $Ru(en)_3^{2+}$ with $Co(phen)_3^{3+}$ at 25 °C, $\Delta V_{22}^{\ddagger}$ is -17.6 ± 0.7 cm^3 mol^{-1} and $k_{22} = 6.7$ L mol^{-1} s^{-1} in chloride media ($I = 0.1$ mol L^{-1}),[8] ΔV_{12} from Tregloan et al.[34] is $+7.4 \pm 1.2$ cm^3 mol^{-1} with $\Delta E_{1/2} = 186$ mV ($I = 0.1$ mol L^{-1}, KNO_3), and $\Delta V_{12}^{\ddagger}$ is -12.9 ± 0.5 cm^3 mol^{-1} ($I = 0.006$ mol L^{-1}, this work). If the effective radius of $Co(phen)_3^{z+}$ ions is ∼700 pm,[41] these data give $C = -0.35 - 0.00664\Delta V_{11}^{\ddagger}$, and hence, from eq 6, $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+} = \Delta V_{11}^{\ddagger} = -15.1 \pm 1.7$ cm^3 mol^{-1} at 25 °C, $I \sim 0.1$ mol L^{-1}. In this case, the Marcus cross relation works well because $\Delta E_{1/2}$ is not large (eqs 10 and 11 predict $k_{12} = 7.8 \times 10^3$ L mol^{-1} s^{-1}, cf. 7.0×10^3 L mol^{-1} s^{-1} observed), and all measurements were at 25 °C, so that this value of $\Delta V_{ex}^{\ddagger}$ may be accepted with greater confidence.

A third estimate of $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ was obtained by application of the fifty-percent rule to $\Delta V_{el}^{\ddagger}$, giving -15.0 ± 0.7 cm^3 mol^{-1} at 25 °C, $I \sim 0.4$ mol L^{-1}, in excellent agreement with that derived from the oxidation of $Ru(en)_3^{2+}$ by $Co(phen)_3^{3+}$ and consistent (given the experimental uncertainties and the reservations noted above) with the value of -18.9 cm^3 mol^{-1} estimated from the $Ru(en)_3^{2+}/Fe(H_2O)_6^{3+}$ reaction. Certainly, $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ is not more positive than -15 ± 1 cm^3 mol^{-1}. This contrasts sharply with the value of -6.3 cm^3 mol^{-1} predicted for 25 °C and $I \sim 0.1$ mol L^{-1} in the manner described elsewhere.[2]

On the other hand, the experimental $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ is similar to those for $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ (Table 2), and it is tempting to conclude that $\Delta V_{ex}^{\ddagger}$ reflects properties of the tris(en) or -(phen) ligand systems rather than those of the central metal atoms. This is untenable, however, because $\Delta V_{ex}^{\ddagger}$ for the low-spin/low-spin $Fe(phen)_3^{3+/2+}$ exchange in aqueous media is -2.2 cm^3 mol^{-1},[42] in agreement with theoretical predictions but greatly different from that for low-spin/high-spin $Co(phen)_3^{3+/2+}$ (Table 2). Furthermore, the strongly negative $\Delta V_{ex}^{\ddagger}$ values for $Co(en)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ are satisfactorily explained[1,2,10] on the basis of an initial spin pairing step involving the Co^{II} partner, whereas $Ru(en)_3^{2+}$ is already low-spin in the ground state—any spin-state change at Ru in the activation process would result in an *increase* in spin multiplicity, with a corresponding *positive* contribution to $\Delta V_{ex}^{\ddagger}$.

An alternative possibility is that the anomalous strongly negative values of $\Delta V_{ex}^{\ddagger}$ for $Co(en)_3^{3+/2+}$, $Co(phen)_3^{3+/2+}$, and $Ru(en)_3^{3+/2+}$ reflect a counterion effect of some kind, since we have shown in this study and a previous one[9] that k_{ex} for the latter two self-exchange reactions is unusually sensitive to the nature of the anion. Against this interpretation, however, is the observation[9] that $\Delta V_{ex}^{\ddagger}$ determined directly for $Co(phen)_3^{3+/2+}$ was essentially the same for both Cl^- and NO_3^- media. Unfortunately, similar direct determinations of $\Delta V_{ex}^{\ddagger}$ for the $Ru(en)_3^{3+/2+}$ couple in various media are not presently practicable.

In fact, the unexpectedly strongly negative $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ appears to be just one more instance of anomalous behavior specific to $Ru^{III}-N$ complexes. For example, reaction volumes for intramolecular $Ru^{III} \rightarrow Fe^{II}$ electron transfer in complexes of the type $(NH_3)_4(L)Ru^{III}$(cytochrome c^{II}) involve a strongly positive contribution associated with the NH_3 ligands that has been attributed to loss of specific solvation when Ru^{III} is reduced.[32] Similarly, Meyer and co-workers[43] have argued that extensive H-bonding to solvent by the $-Ru^{III}(NH_3)_5$ group in $[(bpy)_2ClOs^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ [6] mixes solvent character into $d_p(Ru^{III})$, so decreasing electronic coupling to Os^{II} across the pz bridge. Likewise, Curtis et al.[44] attribute trends in the optically induced intramolecular electron-transfer rates in bridged $Ru^{III}-Ru^{II}$ complexes to redox-dependent H-bonding to solvent at $Ru-NH_3$ functions. If these arguments can be extended to *inter*molecular electron transfer of Ru−en rather than $Ru-NH_3$ complexes, then the anomalous strongly negative $\Delta V_{ex}^{\ddagger}$ for $Ru(en)_3^{3+/2+}$ in water may be tentatively explained in terms of a pressure-induced enhancement of solvation at the Ru^{II} center, bringing the Ru^{II} partner closer to a common Franck−Condon configuration prior to electron transfer.

To close on a less speculative note, we remark that the $\Delta V_{ex}^{\ddagger}$ value determined for $Ru(en)_3^{3+/2+}$ from the cross relation with $Co(phen)_3^{3+/2+}$, and that measured directly for $Co(act)^{3+/2+}$, are accurately twice the corresponding $\Delta V_{el}^{\ddagger}$ values (Table 2), so providing further examples of adherence to the fifty-percent rule[17−19] (eq 2). To date, no significant exceptions to the fifty-percent rule have been found, although the measured $\Delta V_{ex}^{\ddagger}$ for the $Co(diamsar)^{3+/2+}$ and $Co(diamsarH_2)^{5+/4+}$ couples are 2−3

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cm^3 mol^{-1} more negative than the rule predicts; of all the couples studied, however, the transfer coefficient deviated farthest from 0.5 ($\alpha = 0.27$ and 0.41, respectively), and $\Delta V_{\mathrm{Ag/AgCl}}$ was least precisely reproducible, for these two.[18]

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Supporting Information Available: Tables S1−S7 and Figure S1, as specified in the foregoing text. This material is available free of charge via the Internet at http://pubs.acs.org.

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