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Article

Highly Localized Charges Control Electrostriction: Reaction Volumes for the Reduction of Mononuclear and Bridged Ruthenium Complexes

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Changes in electrostriction caused by the reduction of metal centers in monomeric Ru and bridged Ru/Fe complexes reported in this work are highly localized in a polar solvent such as water. In mononuclear complexes, such as $[(\text{edta-H})\text{Ru}^{\text{III}}(\text{H}_2\text{O})]$, where the pendant carboxylate is protonated or not depending on pH, the charge that determines electrostricted solvent behavior is defined within distances encompassed by the first coordination sphere of the redox center ($\Delta V_{\text{complex}} = 1.4 \pm 0.6$ cm^3 mol^{-1} (pH 4) or 0.9 ± 0.6 cm^3 mol^{-1} (pH 1.1)). Furthermore, in dinuclear complexes, even differences in the ligand charge around the second metal center have insignificant effects on electrostrictive interaction with the solvent. Reduction of the Fe center in the systems $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu\text{-NC})\text{Fe}^{\text{III}}(\text{CN})_5]$ and $[(\text{edta})\text{Ru}^{\text{III}}(\mu\text{-NC})\text{Fe}^{\text{III}}(\text{CN})_5]^{4-}$ is virtually unaffected (-21.8 ± 1.8 cm^3 mol^{-1} and -21.7 ± 2.8 cm^3 mol^{-1}, respectively) when the Ru center is changed from formally cationic (3+) to anionic (1–).

Introduction

Solvent reorganization and electrostriction play an important role in the rate and activation parameters for inorganic reactions in general and electron transfer processes in particular, where solvation effects contribute significantly toward the activation barrier of the process. The mechanistic elucidation of chemical reactions in solution has over the past two decades benefited significantly from activation volume measurements and the construction of reaction volume profiles.[1] The interpretation of such profiles can be complicated by changes in electrostriction that result from charge neutralization or charge creation as part of the overall chemical process. In those cases, solvent electrostriction can overwhelm intrinsic volume contributions resulting from changes in bond lengths and angles. A striking example is the *dissociation* of water into H^+ and OH^- ions, which is accompanied by a volume *decrease* of ca. 22 cm^3 mol^{-1} due to the drastic increase in electrostriction around the ions that are produced.[2]

In some cases, solvational effects and the accompanying volume changes are well understood. For instance, Kitamura et al.[3] measured the reaction volumes for the neutralization of a series of differently charged octahedral aqua and ammine complexes. They found a good correlation between the reaction volume and the difference in the sum of the square of the charges on the reactant and product species. Tregloan and co-workers[4] studied the reduction of differently charged Fe(III) complexes for which it was known that there are effectively no intrinsic volume changes involved, i.e., the observed reaction volumes can be ascribed to changes in electrostriction only. Again they found a very good correlation of the reaction volume with the difference of the square

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of the charges on the oxidized and reduced forms of the complexes. For other redox systems,[5] this correlation could then be used to separate intrinsic volume, ΔV_{intr}, and solvational or electrostrictive volume, ΔV_{electr}, contributions to the overall reduction volume change, $\Delta V_{\text{complex}}$.

An important and unanswered question is the extent to which charge effects operate locally at a specific site or permeate into the extended coordination sphere and the bulk solvent. Furthermore, the introduction of charged reaction partners can cause either local or extended charge neutralization or concentration, which in turn will control the resulting electrostriction of the surrounding solvent molecules. For instance, intermolecular and intramolecular electron transfer reactions on ruthenated cytochrome *c* are accompanied by volume changes that can be accounted for almost entirely by changes in electrostriction on the ruthenium complex itself.[6]

Swaddle and Tregloan have suggested that electrostrictive effects, though they are the major component in the overall reaction volume in some cases, may be quite local in their influence.[7] In this work, we have set out to explore that idea explicitly. We have focused here on the analysis of electrostriction in water caused by the electrochemical reduction of mononuclear and bridged ruthenium complexes, in which differently charged complexes were introduced as bridging partners. The complexes selected include $[\mathrm{Ru^{III}(edta)(H_2O)}]^-$, $[\mathrm{(edta)Ru^{III}(\mu\text{-}NC)Fe^{II}(CN)_5}]^{5-}$, and $[\mathrm{(NH_3)_5Ru^{III}(\mu\text{-}NC)Fe^{II}(CN)_5}]^-$. In the Ru−edta complexes, edta is pentadentate with a pendant carboxylate arm. Solid-state structures have been reported for the chloro-substituted $\mathrm{NH_4[Ru(edta\text{-}H)Cl]\cdot 2H_2O}$[8] and for the aqua−propylenediaminetetraacetate $\mathrm{[Ru(pdta\text{-}H)\text{-}H_2O]\cdot H_2O}$.[9] On the basis of UV−vis spectral data, potentiometric studies of titratable protons, kinetic measurements of the substitution of the aqua ligand, and, at higher pH, substitution of the hydroxo ligand by a range of entering groups, the pendant nature of the edta carboxylate is maintained in solution to quite high pH.[10,11] When we carry out high-pressure electrochemistry at different pH values, the $\mathrm{Ru(edta\text{-}H)(H_2O)}$ complex provides a useful system to test the effects of ionization in the region adjacent to the redox center. In this work we have also extended this idea to some bridged Ru/Fe dinuclear complexes, where the two redox centers, in close physical proximity, can separately undergo reversible electrochemical change. In this case, the objective is also to probe the effects of electronic communication via the bridging ligand on the effective charge of the redox active metal center. The surprising result is that electrostriction is indeed controlled by highly localized charges and is not affected significantly by the charge on the bridging complex partner. This finding is of general importance for the interpretation of rate and activation parameters for the elucidation of inorganic reaction mechanisms.

Experimental Section

Chemicals. $\mathrm{[Ru(NH_3)_5Cl]Cl_2}$, obtained from Aldrich, and $\mathrm{K_4[Fe(CN)_6]\cdot 3H_2O}$, from Merck, were used as purchased. $\mathrm{K[Ru(edta\text{-}H)Cl]\cdot 2H_2O}$ was prepared according to published procedures.[12] All other chemicals used were of AR grade. Distilled Millipore water was used in all experiments. Experimental solutions were around 1 mM in the complex of interest and prepared at an ionic strength of 0.1 M using $\mathrm{KNO_3}$ or $\mathrm{NaNO_3}$ as supporting electrolyte. Solutions of the dinuclear complexes were prepared in situ by dissolving a measured amount of the ruthenium salt, $\mathrm{[Ru(NH_3)_5Cl]Cl_2}$ or $\mathrm{K[Ru(edta\text{-}H)Cl]\cdot 2H_2O}$, in a marginal excess of ferrocyanide solution in 0.1 M $\mathrm{KNO_3}$; the labile chloride ligand was rapidly displaced to produce the bridged blue/green dinuclear complex. Solution pH was controlled using nitric acid, acetate buffer, or CHES buffer (2-cyclohexylaminoethane sulfonic acid; Sigma Aldrich) as indicated in the text. Since pressure may have some effect on the pK_a of buffer components, CHES was chosen because of its particularly low value of ΔV for deprotonation.[2] Taking into account the pK_a's of the complexes presented in reactions 1−3 below, pH conditions were selected where the complexes would be exclusively in the fully protonated, singly deprotonated, or doubly deprotonated form.

Electrochemical Measurements. Measurements were carried out using an EG&G Princeton Applied Research 263 System and the data collected via 270/250 Research Electrochemistry Software 4.00. For electrochemical measurements at elevated pressure, a homemade, high-pressure cell similar to that described in the literature[4,7,13] and thermostated to ±0.1 °C was employed. Prior to use, the 1 mm diameter platinum wire working and auxiliary electrodes were polished with an aqueous suspension of 3 μm followed by 1 μm alumina (Alfa) on a polishing cloth. The wire was then rinsed with distilled water, cleaned in 5 M aqueous $\mathrm{HNO_3}$, rinsed with distilled water, and dried with a tissue. The reference electrode consisted of an Ag wire in 0.01 M $\mathrm{AgNO_3}$/0.1 M $\mathrm{KNO_3}$ solution. Cyclicvoltammograms (CV) were scanned beginning at the upper potential limit, and the second cyclic scan was saved for measurement. Formal reduction potentials for the couple of interest were obtained from the conventional current−potential CV curves using the graphics and analysis program "Igor Pro" (Wavemetrics Inc, Lake Oswego, OR). Initially, in simple quasi-reversible cases, quadratic curve fits around the immediate region of the oxidative or reductive wave peaks were used to calculate the potentials at the current peak and these values then averaged to determine the formal reduction potential. In all the work reported here, in a numerical analogue of our use of differential pulse voltammetry to measure the pressure dependence of reduction potentials,[6] we used Igor to derive a derivative function of the forward and reverse sweeps of the conventional CV curve. These data were then combined into a single $\mathrm{d}i/\mathrm{d}V$ ($=\mathrm{d}i/\mathrm{d}V_{\text{reducing scan}} - \mathrm{d}i/\mathrm{d}V_{\text{oxidizing scan}}$) data set to identify the reduction potential peak position (an example of data processed in this way is shown later in Figure 5). In

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simulations[16] of ideal reversible CV behavior, the maxima (or minima) in the derivative function, corresponding to the inflection points in the reducing or oxidizing CV curve, coincided to within 1 mV. In our experiments on the pressure dependence of ferro-/ferricyanide reduction, these two peaks were within 1 or 2 mV. The pressure dependent plots using data from this technique were more precise than those for the same runs where formal potential had been determined from the original CV current peak positions. This approach was used for all the systems reported in this study and proved particularly powerful in mixed solutions where more than one process was being observed in a single CV experiment (the data shown later in Figures 4−6 are examples of this).

As recommended to ensure reliable data,[7] all pressure runs were carried out in an ascending/descending pressure cycle. For $Fe(CN)_6^{4-/3-}$ present as an internal reference in a mixed solution (Figure 6) using this approach and analysis, the value of $\Delta V_{cell} = -42.2 \pm 0.7$ cm^3 mol^{-1} was in excellent agreement with -42.8 ± 0.6 cm^3 mol^{-1} at $I = 0.1$ M reported previously.[4] Independent runs for $Fe(CN)_6^{4-/3-}$ in this work gave $\Delta V_{cell} = -43.2 \pm 0.9$ cm^3 mol^{-1}.

Nitrogen was bubbled through the solution for several minutes to ensure that oxygen had been purged from the system before sealing the electrochemical cell and mounting it in the high-pressure bomb. This was especially important in experiments on the Ru−edta system at high pH; any oxygen contamination was evident from the highly colored Ru−dioxygen complexes which form over time,[14] and occasional runs indicating oxygen interference over the several hours of a high-pressure experiment were rejected.

Results and Discussion

Ru(III)−edta System. When K[Ru(edta-H)Cl] is dissolved in aqueous solution, it rapidly aquates to form the corresponding aqua complex.[10,11] The electrochemistry of the aqua−ruthenium(III)−edta system has been reported previously.[14] The pK_a's of reactions 1−3 are given below.[14] These complexes provide a tunable environment to test the effects of local charge on electrostrictive volume change.

$$\mathrm{Ru(edta\text{-}H)(H_2O)} \rightleftharpoons \mathrm{Ru(edta)(H_2O)^-} + \mathrm{H^+} \quad \mathrm{p}K_a = 2.4 \quad (1)$$

$$\mathrm{Ru(edta)(H_2O)^-} \rightleftharpoons \mathrm{Ru(edta)(OH)^{2-}} + \mathrm{H^+} \quad \mathrm{p}K_a = 7.6 \quad (2)$$

$$\mathrm{Ru(edta)(OH)^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Ru(edta)(OH)_2^{3-}} + \mathrm{H^+} \quad \mathrm{p}K_a = 11.0 \quad (3)$$

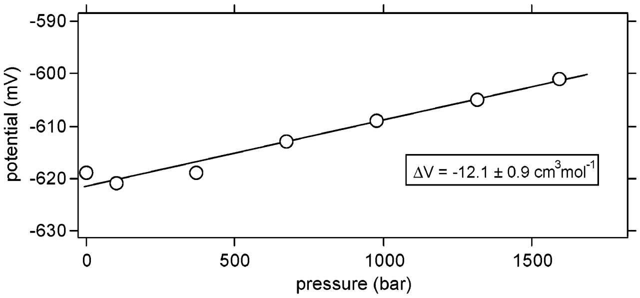

Figure 1. Dependence of formal reduction potential on pressure for 0.011 M $[Ru(edta)(H_2O)]^-$ in 0.1 M KNO_3 (pH 4 acetate buffer; Pt working electrode; Ag/0.01 M $AgNO_3$ in 0.1 M KNO_3 reference electrode; potential data from fitted cyclic differential CV peaks).

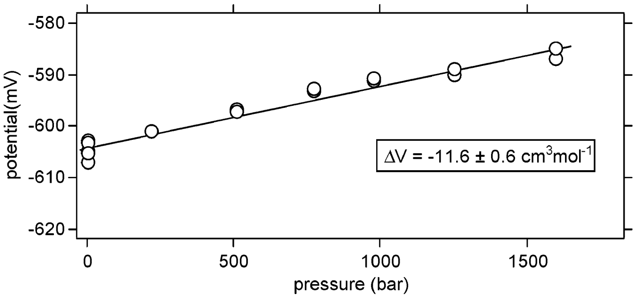

Figure 2. Dependence of formal reduction potential on pressure for 0.0090 M $[Ru(edta\text{-}H)(H_2O)]$ in 0.1M KNO_3 (pH 1.3 using HNO_3; Pt working electrode; Ag/0.01 M $AgNO_3$ in 0.1 M KNO_3 reference electrode; potential data from fitted cyclic differential CV peaks).

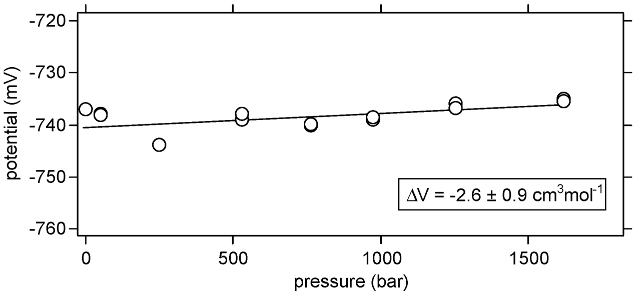

Figure 3. Dependence of formal reduction potential on pressure for 0.008 M $[Ru(edta)OH]^{2-}$ in 0.1 M KNO_3 (pH 9.6 CHES buffer; sample prepared under N_2; Pt working electrode; Ag/0.01 M $AgNO_3$ in 0.1 M KNO_3; formal potential data from fitted cyclic differential CV peaks).

Plots of the pressure dependence of the redox potentials for the Ru(edta)−aqua complex system at pH 4.0, 1.3, and 9.6 are given in Figures 1−3; the slope of each plot is $-nF\Delta V_{cell}$.[7] Table 1 lists the experimental cell reaction volumes and derived data for the $[(edta\text{-}H)Ru(H_2O)]^{0/-}$, $[(edta)Ru(H_2O)]^{-/2-}$, and $[(edta)Ru(OH)]^{2-/3-}$ systems. The cell reaction volumes have then been corrected for the contribution of the reference electrode half cell, −13 cm^3 mol^{-1} at this ionic strength,[4] to obtain the volume change due to the reduction of the metal complex, $\Delta V_{complex}$. The data in Table 1 do not simply reflect the formal electrostrictive volume change since $\Delta V_{complex}$ for the $[(edta\text{-}H)Ru(H_2O)]^{0/-}$ and $[(edta)Ru(H_2O)]^{-/2-}$ systems are practically identical. For the reduction of metal complexes at this ionic strength, we have shown[4,5,7] that electrostrictive volume change is described well by $4.3\Delta(z^2)$, where $\Delta(z^2)$ = (charge of the oxidized form of the complex)^2 − (charge of the reduced form of the complex)^2. We propose that the most reasonable interpretation of these data is that the complexes are best modeled as $HO_2C-[lig-Ru^{III/II}-OH_2]^{0/1-}$ and $^-O_2C-[lig-Ru^{III/II}-OH_2]^{0/-}$, respectively, and that the ionized carboxylate at pH 4, although only a few Å away, has no influence at all on the electrostrictive change around the redox site. If $4.3\Delta(z^2)$, where $\Delta(z^2)$ is now the change in square of "local" charge, is used to estimate ΔV_{electr}, then this indicates intrinsic volume changes of +5.7 and +5.2 cm^3 mol^{-1} for these complexes, respectively (Table 1).

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Table 1. High-Pressure Electrochemistry of the edta)−$Ru^{III/II}$−H_2O System

pH	complex III/II	$E°$ [a] (mV)	ΔV_{cell} ($cm^3\ mol^{-1}$)	$\Delta V_{complex}$ [b] ($cm^3\ mol^{-1}$)	$\Delta(z^2)$	ΔV_{electr} [c] ($cm^3\ mol^{-1}$)	ΔV_{intr} [d] ($cm^3\ mol^{-1}$)
1.1	$[(edta\text{-}H)Ru(H_2O)]^{0/-}$	−603	−11.6 ± 0.6	1.4 ± 1.6	−1	−4.3	+5.7
4.0	$^{-}[(edta)Ru(H_2O)]^{0/-}$	−621	−12.1 ± 0.6	0.9 ± 1.6	−1[e]	−4.3	+5.2
9.6	$^{-}[(edta)Ru(OH)]^{-/2-}$	−740	−2.6 ± 0.9	10.4 ± 1.9	−3[e]	−12.9	see text

[a] E vs Ag/0.01 M Ag^+ in 0.1 M KNO_3, extrapolated to 1 bar. [b] Calculated from ΔV_{cell} using $\Delta V_{ref} = -13 \pm 1$ $cm^3\ mol^{-1}$ for Ag/Ag^+ at $I = 0.1$ M.[4] [c] ΔV_{electr} is calculated on the basis of $4.3\Delta(z^2)$,[4] and $\Delta(z^2)$ refers to the "local" change in charge as described in the text. [d] $\Delta V_{intr} = \Delta V_{complex} - \Delta V_{electr}$. [e] $\Delta(z^2)$ is the change in charge within the immediate first coordination sphere of the redox metal center; evidence is that the pendant carboxylate does not contribute to this local charge.

At pH 9.6 the redox reactant is $[(edta)Ru^{III}(OH)]^{2-}$, and if the local electrostrictive charge is taken as being defined by the metal ion and ligands coordinated into the first coordination sphere, the local charge change is better represented as $^{-}[(edta)Ru^{III/II}(OH)]^{-/2-}$, where the charge at the left-hand side of the formula represents the pendant charge, remote from the metal redox site. Using the arguments outlined above, the local electrostrictive change is therefore estimated to be $4.3(-3) = -12.9$ $cm^3\ mol^{-1}$, which would imply an intrinsic change of $(10.4 + 12.9) = 23.3$ $cm^3\ mol^{-1}$, clearly out of line with expectations from other Ru(III/II) systems[5,7] and the data for this system at lower pH in Table 1. However, the pK_a of $[(edta)Ru^{II}OH_2)]^{3-}$ has been reported as 10.6,[10,15] so that, at pH 9.6, the $[(edta)Ru^{II}(OH)]^{3-}$ redox product would rapidly protonate at the hydroxo ligand. Reaction volume data are available for the protonation of complexes such as $Co(CN)_5(OH)^{3-}$ (+19.7 $cm^3\ mol^{-1}$) and $Co(nta)(OH)_2^{2-}$ (+13.1 $cm^3\ mol^{-1}$).[3] Assuming ΔV for the protonation of the Ru(II) product to be approximately the average of these (+16 $cm^3\ mol^{-1}$), ΔV_{electr} for the redox step to be determined by the local charge change, and ΔV_{intr} for the redox step to be similar to the values proposed at lower pH (Table 1), the volume changes for reduction of $[(edta)Ru^{III}(OH)]^{2-}$ at pH 9.6 are summarized in the scheme (4)−(6) below, with a net predicted change of $(-12.9 + 5.5 + 16) = +8.6$ $cm^3\ mol^{-1}$, in sensible agreement with the observed $\Delta V_{complex}$ of +10.4 $cm^3\ mol^{-1}$. If the protonation reaction volume is also seen as simply electrostrictive and so determined by $4.3((-2)^2 + (+1)^2 - (-1)^2)$ to be 17.2 $cm^3\ mol^{-1}$, the predicted $\Delta V_{complex}$ at pH 9.6 is $(-12.9 + 5.5 + 17.2) = +9.8$ $cm^3\ mol^{-1}$, i.e., again in good agreement with the observed value.

$$^{-}(edta)Ru^{III}(OH)^{-} \rightarrow {}^{-}(edta)Ru^{II}(OH)^{2-} \quad \Delta V_{electr} = -12.9 \tag{4}$$

$$^{-}(edta)Ru^{III}(OH)^{-} \rightarrow {}^{-}(edta)Ru^{II}(OH)^{2-} \quad \Delta V_{intr} = +5.5 \tag{5}$$

$$^{-}(edta)Ru^{II}(OH)^{2-} + H^{+} \rightarrow {}^{-}(edta)Ru^{II}(OH_2)^{-} \quad \Delta V_{prot} = +16 \text{ or } +17.2 \text{ (see text)} \tag{6}$$

Binuclear Ru(III)−Fe(II) Complexes. The binuclear Ru(III)−Fe(II) complexes, $[(NH_3)_5Ru(\mu\text{-}NC)Fe(CN)_5]^-$ and $[(edta)Ru(\mu\text{-}NC)Fe(CN)_5]^{2-}$, extended this study to situations where two redox centers are held in close proximity via a bridging ligand to create an extreme test of the effects of the local and overall charge environment. The edta ligand is again pentadentate with, at pH 5−6, a pendant carboxylate. In these complexes, the Ru or Fe centers may undergo independent electrochemical redox, and our hypothesis is that the "local" charge environment is determined by the metal and its immediate coordination sphere. However, in these examples the chemical environment is complicated further by (a) the close proximity of the redox center to the partner metal center and its ligand set, (b) the bridging ligand being shared between the metal centers, and (c) the possibility of redistribution of charge via the bridging ligand.

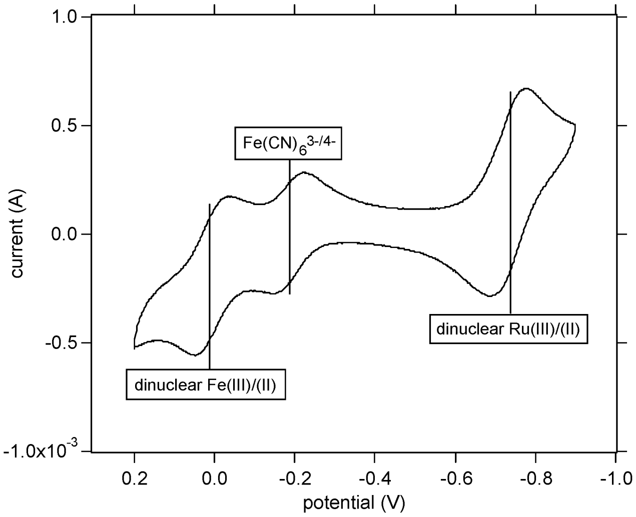

Figure 4. Cyclic voltammetric scan at 985 bar of 0.005 M $Na[(NH_3)_5Ru(\mu\text{-}NC)Fe(CN)_5]$ in 0.1 M $NaNO_3$ (pH 5−6 adjusted with nitric acid; sample prepared under N_2; Pt working electrode; Ag/0.01 M $AgNO_3$ in 0.1 M KNO_3 reference electrode; scan rate 100 mV/s).

Figure 4 shows a typical high-pressure voltammogram, in this case of $[(NH_3)_5Ru(\mu\text{-}NC)Fe(CN)_5]^-$ in a solution containing a small excess of ferrocyanide, which acts as an independent internal reference; all potentials were measured with respect to a Ag/Ag^+(0.01 M) reference electrode. Figure 5 shows the computed current/potential derivative data from which the reduction potentials were determined. Figure 6 presents a plot of the three reduction potentials from this experiment as a function of pressure. Tables 2 and 3 present our results for a range of mononuclear and dinuclear Fe and Ru complexes. High-pressure voltammograms of a partially hydrolyzed solution of $Ru(NH_3)_5Cl^{2+}$ were resolved to obtain reduction potentials and reduction volumes for both $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_5(H_2O)^{3+}$; the experiments at the higher scan rate of 2500 mV/s achieved better resolution of the component peaks, but the cell reaction volumes for each process ($[Ru(NH_3)_5Cl]^{2+/+}$, +8.7 ± 0.8 $cm^3\ mol^{-1}$ (100 mV/s), +7.0 ± 0.8 $cm^3\ mol^{-1}$ (2500 mV/s); $[Ru(NH_3)_5(H_2O)]^{3+/2+}$,

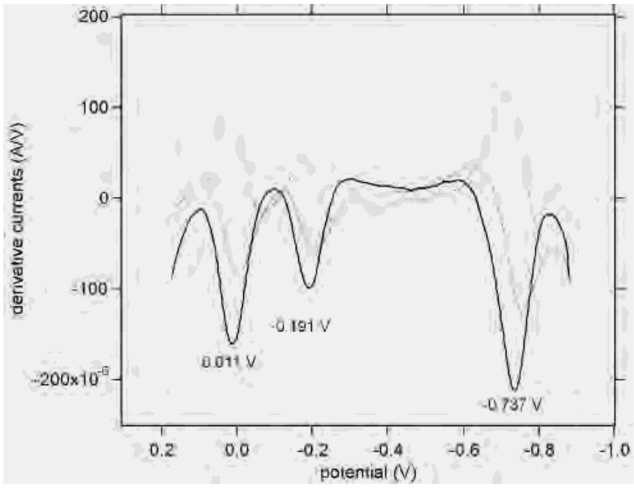

Figure 5. Derivatives of CV data at 985 bar of 0.005 M Na[$(NH_3)_5$Ru-(μ-NC)Fe$(CN)_5$] in 0.1 M $NaNO_3$ in Figure 4. Light lines are the derivatives of the forward and reverse sweeps; the black line represents the scaled mean derivative data.

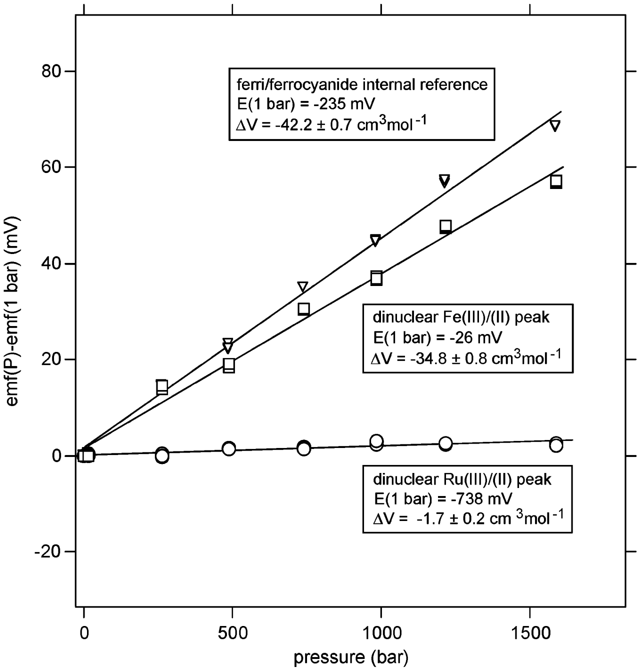

Figure 6. Dependence of formal reduction potentials on pressure for 0.005 M Na[$(NH_3)_5$Ru(μ-NC)Fe$(CN)_5$] with $Fe(CN)_6^{3-/4-}$ internal reference in 0.1 M $NaNO_3$ (pH 5−6 adjusted with nitric acid; sample prepared under N_2; Pt working electrode; Ag/0.01 M $AgNO_3$ in 0.1 M KNO_3 reference electrode; data equals difference in formal potential at pressure *P* and 1 bar; potential data from fitted cyclic differential CV peaks).

$+15.2 \pm 0.8$ cm^3 mol^{-1} (100 mV/s), $+16.5 \pm 1.0$ cm^3 mol^{-1} (2500 mV/s)) agreed to within experimental error.

For the $Fe^{III/II}(CN)_6^{3-/4-}$ system there is no intrinsic volume change on reduction, (ref. 4 and literature cited therein) but for the Ru(III/II) systems, while ΔV_{intr} values are expected to be small compared to for example Co(III/II) systems,[5,7] we propose that they can be estimated for a given system from the difference between the experimental value of $\Delta V_{complex}$ and that predicted by $4.3\Delta(z^2)$. Data for the mononuclear complexes reported in Table 2 are plotted in Figure 7 to illustrate this correlation. The deviation of data points from the $4.3\Delta(z^2)$ line indicates that ΔV_{intr} for Ru−ammine complexes, whether the sixth ligand is ammonia, water, or chloride, has an average value of $+7.8$ cm^3 mol^{-1}, and for Ru−edta complexes, $\Delta V_{intr} \sim +5.5$ cm^3 mol^{-1}.

Data for the dinuclear Ru/Fe complexes, together with reduction potential data for some relevant mononuclear complexes, are presented in Table 3. Clearly, $\Delta V_{complex}$ does not correlate at all with the total charge on the dinuclear complex and a more detailed analysis is necessary. As the next more complex model, we have examined the effect on the reduction potentials and the redox volume changes of sharing the bridging ligand and of the influence of the other metal center. In both the edta and ammine dinuclear systems, effects on the Fe(III/II) center are virtually identical. The reduction potential for Fe(III/II) becomes ~200 mV less negative, i.e., the iron is easier to reduce, suggesting that charge has been removed from the iron−cyano moiety. On the basis of a 3−/4− local charge change, $\Delta V_{electr} = \Delta V_{complex}$ is expected to be -30.1 cm^3 mol^{-1}. However, for a local charge change of 2−/3−, the estimated value of ΔV_{electr} becomes -21.5 cm^3 mol^{-1}, which in conjunction with an expected ΔV_{intr} of zero is in very close agreement with the measured $\Delta V_{complex}$ values of -21.8 and -21.7 cm^3 mol^{-1}. These results suggest that $\Delta V_{complex}$ for the Fe(III/II) center is not affected at all by the overall anionic or cationic nature of the ruthenium bridging partner, viz. $Ru(edta)^-$ or $Ru(NH_3)_5^{3+}$, but rather only by the local charge effects of the Fe(III/II) and its surrounding ligands modified by movement of a charge of 1− away from the Fe center group through the bridging cyanide.

The situation for the Ru redox centers is more complex. In the case of the Ru−ammine center, the reduction potential becomes more negative, i.e., the Ru is more difficult to reduce, consistent with a move of charge onto the metal center. By the modeling for environments of 2+/1+ or +/0, in conjunction with an intrinsic volume change of $+7.8$ cm^3 mol^{-1} at the Ru−ammine center, a local $\Delta(z^2)$ of $+1$, corresponding to a shift in negative charge from the Fe center and associated cyanides to the Ru moiety, fits the experimental data best. Note that the iron center is also reduced at this stage. This indicates that the cationic Ru−ammine complex senses the bridge to the $Fe^{II}(CN)_6^{4-}$ partner as a -2 charge unit, one charge unit presumably coming from the cyanide bridge and a further charge unit derived from the reduced and highly negatively charged $Fe^{II}(CN)_5^{3-}$ unit. In the anionic Ru−edta case the opposite trend is observed. The reduction potential becomes less negative in the dinuclear environment; i.e., there is a loss of charge on the ruthenium center, which is able to distribute charge to the Fe moiety. If one recognizes that the pendant carboxylate is not part of the redox environment at all and with modeling for a −/2− and 0/− Ru(edta)−NC environment, the best fit to the experimental $\Delta V_{complex}$ is obtained for $\Delta(z^2) = -1$. This is in agreement with the fundamental nature of Ru^{III} complexes that behave as weaker Lewis acids than expected for 3+ charged cations. This is supported by the surprising lability of the Ru(edta)−chloro complex[10,11] and the tendency not to coordinate the ring-opened carboxylate ion.

Table 2. High-Pressure Electrochemistry of Mononuclear Ru(III/II) and Fe(III/II) Systems

complex III/II	ref from Figs 7, 8	$\Delta V_{\mathrm{complex}}{}^{b}$ (cm^3 mol^{-1})	$\Delta(z^2)$	$\Delta V_{\mathrm{electr}}{}^{c}$ (cm^3 mol^{-1})	$\Delta V_{\mathrm{intr}}{}^{d}$ (cm^3 mol^{-1})	ref
$Ru(NH_3)_5Cl^{2+/+}$	1	21.7 ± 1.8	3	12.9	8.8	*a*, 100 mV/s
$Ru(NH_3)_5Cl^{2+/+}$	2	20.0 ± 1.8	3	12.9	7.1	*a*, 2500 mV/s
$Ru(NH_3)_5(H_2O)^{3+/2+}$	5	28.2 ± 2.0	5	21.5	6.7	*a*, 100 mV/s
$Ru(NH_3)_5(H_2O)^{3+/2+}$	6	29.5 ± 1.8	5	21.5	8.0	*a*, 2500 mV/s
$Ru(NH_3)_6{}^{3+/2+}$	7	30.3 ± 1.4	5	21.5	8.3	5
$[(edta\text{-}H)Ru(H_2O)]^{0/-}$	10	1.4 ± 1.6	−1	−4.3	5.7	*a*
$^{-}[(edta)Ru(H_2O)]^{0/-}$	11	0.9 ± 1.6	−1	−4.3	5.2	*a*
$Fe(CN)_6{}^{3-/4-}$	3	−29.2 ± 1.7	−7	−30.1	0[g]	*a*, *e*
$Fe(CN)_6{}^{3-/4-}$	4	−29.8 ± 1.6	−7	−30.1	0[g]	5
$Fe(CN)_6{}^{3-/4-}$	9	−30.2 ± 1.9	−7	−30.1	0[g]	*a*
$Fe(CN)_6{}^{3-/4-}$	8	−27.6 ± 1.6	−7	−30.1	0[g]	*a*, *f*

[a] This work. [b] Calculated from ΔV_{cell} using $\Delta V_{\mathrm{ref}} = -13 \pm 1$ cm^3 mol^{-1} for Ag/Ag$^+$ at $I = 0.1$ M.[4] [c] $\Delta V_{\mathrm{electr}}$ is calculated on the basis of $4.3\Delta(z^2)$,[4] and $\Delta(z^2)$ refers to the "local" change in charge as described in the text. [d] $\Delta V_{\mathrm{intr}} = \Delta V_{\mathrm{complex}} - \Delta V_{\mathrm{electr}}$. [e] Internal reference in $[(NH_3)_5Ru(\mu\text{-}NC)Fe(CN)_5]$ experiments. [f] Internal reference in $[(edta)Ru(\mu\text{-}NC)Fe(CN)_5]$ experiments. [g] See ref 4 and references therein.

Table 3. High-Pressure Electrochemistry of Dinuclear $Ru^{III/II}(\mu\text{-}NC)Fe^{III/II}$ Systems

complex III/II	$E°$ [a] (mV)	$\Delta V_{\mathrm{complex}}{}^{b}$ (cm^3 mol^{-1})	local $z_{\mathrm{ox}}/z_{\mathrm{red}}$ → local $\Delta(z^2)$	$\Delta V_{\mathrm{electr}}{}^{c}$ (cm^3 mol^{-1})	$\Delta V_{\mathrm{intr}}{}^{d}$ (cm^3 mol^{-1})	$\Delta V_{\mathrm{complex\ calcd}}$ (cm^3 mol^{-1})
$[Fe(CN)_6]^{3-/4-}$	*−235*					
$[(NH_3)_5Ru^{III}(\mu\text{-}NC)Fe^{III/II}(CN)_5]^{0/-}$	−26	−21.8 ± 1.8	3−/4− → −7	−30.1	0	−30.1
			2−/3− → −5	−21.5	0	−21.5
$[Ru(NH_3)_6]^{3+/2+}$	*−592*[e]					
$[(NH_3)_5Ru^{III/II}(\mu\text{-}NC)Fe^{II}(CN)_5]^{-/2-}$	−738	+11.3 ± 1.2	2+/+ → 3	+12.9	8	+21
			+/0 → 1	+4.3	8	+12.3
$[Fe(CN)_6]^{3-/4-}$	*−242*					
$^{-}[(edta)Ru^{III}(\mu\text{-}NC)Fe^{III/II}(CN)_5]^{3-/4-}$	−45	−21.7 ± 2.8	2−/3− → −5	−21.5	0	−21.5
$^{-}[(edta)Ru(H_2O)]^{0/-}$	*−620*					
$^{-}[(edta)Ru^{III/II}(\mu\text{-}NC)Fe^{II}(CN)_5]^{4-/5-}$	−514	+0.2 ± 2.4	1−/2− → −3	−12.9	5.2	−7.7
			0/− → −1	−4.3	5.2	+0.9

[a] E (mV) vs Ag/0.01 M Ag$^+$ in 0.1 M KNO$_3$, extrapolated to 1 bar. Italicized $E°$ values are for unbridged M(III/II) centers. [b] Using $\Delta V_{\mathrm{ref}} = -13 \pm 1$ cm^3 mol^{-1} for Ag/Ag$^+$ at $I = 0.1$ M;[4] quoted errors are the sum of experimental and reference uncertainties. [c] $\Delta V_{\mathrm{electr}}$ is calculated on the basis of $4.3\Delta(z^2)$,[4] and $\Delta(z^2)$ refers to the "local" change in charge as described in the text. [d] ΔV_{intr} here is the intrinsic volume change for appropriate metal(III/II) centers from Table 2. [e] Reference 5.

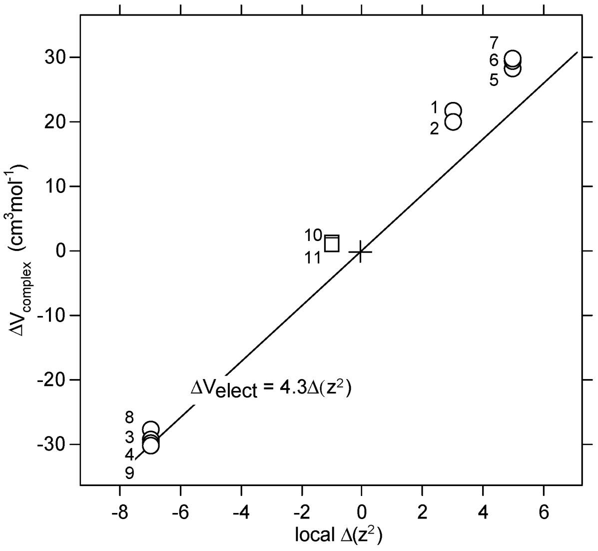

Figure 7. Dependence of ΔV for reduction of metal centers in mononuclear complexes on local $\Delta(z^2)$ in the first coordination sphere of the reduced center. Key to plotted points: 1 = $[(NH_3)_5Ru^{III/II}Cl]^{2+/+}$; 2 = $[(NH_3)_5Ru^{III/II}Cl]^{2+/+}$; 3 = $[(CN)Fe^{III/II}(CN)_5]^{3-/4-}$; 4 = $[(CN)Fe^{III/II}(CN)_5]^{3-/4-}$; 5 = $[(NH_3)_5Ru^{III/II}(H_2O)]^{3+/\ 2+}$; 6 = $[(NH_3)_5Ru^{III/II}(H_2O)]^{3+/2+}$; 7 = $[(NH_3)_5Ru^{III/II}(NH_3)]^{3+/2+}$; 8 = $[(CN)Fe^{III/II}(CN)_5]^{3-/4-}$; 9 = $[(CN)Fe^{III/II}(CN)_5]^{3-/4-}$; 10 = $[(edta\text{-}H)Ru^{III/II}(H_2O)]^{0/-}$; 11 = $^{-}[(edta)Ru^{III/II}(H_2O)]^{0/-}$.

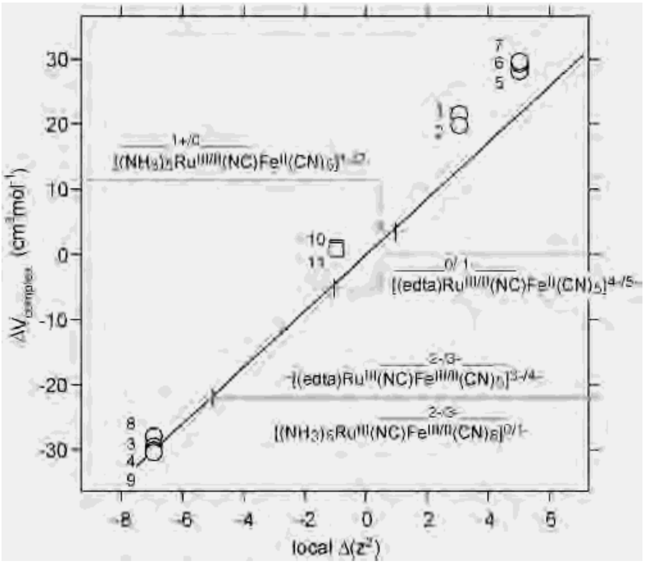

Figure 8. Dependence of ΔV for reduction of metal centers on local Δz^2 in the first coordination sphere of the reduced center. The partitioning of redox volumes for the dinuclear complexes is described in the text. The notation for charge shows any pendant charge at the left, the residual formal charge at the right, and the effective local charge and change at the redox center over the redox center in the formula here. See Figure 7 for the key to the plotted points.

The adjustment of the effective charge on the Fe and Ru redox centers in the bridged complexes studied here, on the basis of the measured values of $\Delta V_{\mathrm{complex}}$ and its correlation with contributions from ΔV_{intr} and $4.3\Delta(z^2)$, is presented schematically in Figure 8 on the basis of the data summarized in Figure 7 and Table 3. The Fe centers behave very similarly in both cases, whereas the Ru centers behave totally differently depending on their anionic or cationic character, i.e., their ability to donate electron density to, or to accept electron density from, the bridging iron–cyano complex, respectively.

Conclusions

The results from this study demonstrate that electrostriction effects caused by the reduction of metal centers in monomeric and bridged complexes have a highly localized character in a polar solvent such as water. A simple model based on the difference in the square of the charges on the oxidized and reduced forms of the complexes can be adopted to separate the intrinsic and electrostrictive volume effects and to analyze the influence of charge distribution in bridged complexes. Furthermore, the reaction volumes for reduction correlate well with the effect of the bridging ligand on the redox potentials of the metal centers involved. The $Fe(CN)_6^{3-/4-}$ component in the bridged complexes responds as if it has lost a single charge via the cyano ligand and apparently does not experience anything from the cationic or anionic nature of the Ru center. The cationic Ru–ammine complex accepts a double negative charge from the iron–cyano center, whereas the anionic Ru–edta center loses electron density and, in terms of volume changes, behaves as if the bridge to the iron–cyano complex has no overall effect. These results will provide a very useful model to assist in the interpretation of solvational changes in electron transfer reactions in monomeric and bridged complexes.

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