# Intramolecular and Environmental Contributions to Electrode Half-Reaction Entropies of M(tacn)$_2$$^{3+/2+}$ (M = Fe, Co, Ni, Ru; tacn = 1,4,7-Triazacyclononane) Redox Couples

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Electrode half-reaction entropies, $\Delta S°_{rc}$, are measured as a function of solvent and electrolyte type and concentration for four M(tacn)$_2$$^{3+/2+}$ (M = Fe, Ni, Co, Ru; tacn = 1,4,7-triazacyclononane) redox couples that experience different amounts of structural change in conjunction with electron transfer. Metal dependent values of $\Delta S°_{rc}$ are observed for these couples and are shown to arise primarily from vibrational and electronic contributions to intramolecular entropy. Vibrational terms become important when frequencies are small and change significantly with a change in oxidation state, as occurs when an increase in number of antibonding electrons weakens metal−ligand bonds upon reduction. Entropy measurements are referenced to the Ru$^{3+/2+}$ couple, which is characterized by small inner-shell reorganization. Experimentally, mean values of $\Delta(\Delta S°_{rc})_{M-Ru}$ = 27 (7), 30 (6), and 69 (14) J mol$^{-1}$ K$^{-1}$ obtained from data in seven solvents are observed for M = Fe, Ni, and Co, respectively. The computed sums of vibrational (obtained using octahedral stretching frequencies of M(NH$_3$)$_6$$^{3+/2+}$ complexes) and electronic entropy differences equal 4, 31, and 69 J mol$^{-1}$ K$^{-1}$ for the same three metals relative to Ru. The unexpectedly large value of $\Delta(\Delta S°_{rc})_{Fe-Ru}$ is the result of a spin-state equilibrium in solution. Temperature-dependent magnetic susceptibility measurements yield $\Delta H°$ = 23.8 (1.0) kJ mol$^{-1}$, $\Delta S°$ = 68.2 (2.8) J mol$^{-1}$ K$^{-1}$, and $K_{SE}$ = 0.25 (298 K) for conversion of low- to high-spin Fe(tacn)$_2$$^{2+}$ in D$_2$O. Observation of uniform values of $\Delta(\Delta S°_{rc})_{M-Ru}$ for each couple in seven solvents indicates that, if inner- and outer-shell reorganizations are coupled during electron transfer, this fact is not reflected in the solvent dependence of $\Delta S°_{rc}$. Ion-pair formation occurs between oxidized complexes and electrolyte anions. Negative and positive contributions to $\Delta S°_{rc}$ result as ion-paired M(tacn)$_2$$^{3+}$: X$^-$ is reduced to dissociated M(tacn)$_2$$^{2+}$ in H$_2$O when X$^-$ = Cl$^-$ and ClO$_4$$^-$, respectively.

## Introduction

Electrode half-reaction entropies ($\Delta S°_{rc} = S°_{red} - S°_{ox}$)[1] are of interest to inorganic chemists and electrochemists because they provide insight to the structural reorganizations of reactants and their environment that accompany electron transfer. Entropic factors also play a role in valence tautomeric equilibria of Co−semiquinone complexes,[2] photoinduced electron transfer reactions,[3] and spin-state transitions.[4] Extensive data have been collected for transition metal redox couples,[1,5−10] from which it is apparent that the Born dielectric continuum model (eq 1)

$$(\Delta S°_{rc})_{Born} = (-Ne^2/8\pi\epsilon_o\epsilon_s)(\partial\epsilon_s/\partial T)(z^2_{ox} - z^2_{red})/r \quad (1)$$

does not accurately predict $\Delta S°_{rc}$. Understanding to date is best summarized by the work of Hupp and Weaver,[5e] who concluded that for cationic, non-aquo couples $\Delta S°_{rc}$ can be represented by a linear combination of terms, one proportional to the electrostatic factor $(z^2_{ox} - z^2_{red})/r$ in eq 1 and another to the acceptor number (AN)[11] of the solvent. Other properties, such as ligand composition and electronic structure of the metal ion, also may contribute to $\Delta S°_{rc}$.

Our interest in the subject arises from electrode kinetic studies[12] of M(tacn)$_2$$^{3+/2+}$ couples (M = Fe, Co, Ni, Ru; tacn = 1,4,7-triazacyclononane; eq 2)

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$$M(tacn)_2^{3+} + e^- \rightleftharpoons M(tacn)_2^{2+} \qquad (2)$$

which exhibit metal-dependent electrochemical rate constants ($k_{s,h}$) and entropies ($\Delta S^\ddagger$) and enthalpies ($\Delta H^\ddagger$) of activation that correlate with the extent of redox-induced M−N bond lengthening. This result is understandable in the context of Marcus theory.[13] However, the members of reaction 2 also exhibit metal-dependent values of $\Delta S^\circ_{rc}$ that correlate with $k_{s,h}$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ and magnitudes of $\Delta S^\circ_{rc}$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ that appear unusually large for M = Fe and Co given the extent of structural change in these cases. One explanation of such findings is that heretofore unrecognized inner-shell reorganizations accompany electron transfer for these species. Another is that inner- and outer-shell reorganizations become coupled when electron transfer causes large structural change, a possibility enhanced by the capacity for hydrogen-bond donation from tacn ligands to solvent.[14,15a] The potential role of solute−solvent interactions of this type in electron-transfer activation has been considered by several investigators.[15] To address the question of inner- versus outer-shell contributions to $\Delta S^\circ_{rc}$ and to better understand the molecular basis for correlation between $\Delta S^\circ_{rc}$ and electrochemical activation parameters, we have determined the electrode half-reaction entropies of M(tacn)$_2$$^{3+/2+}$ couples in nine solvents. We also found $\Delta S^\circ_{rc}$ for aqueous Ni(tacn)$_2$$^{3+/2+}$ to be sensitive to the identity and concentration of supporting electrolyte anion and investigated the influence of these variables on $\Delta S^\circ_{rc}$ for this couple.

## Experimental Section

**Materials.** The complexes [Fe(tacn)$_2$]Br$_3$·5H$_2$O,[16] [Co(tacn)$_2$]-Br$_3$·H$_2$O,[17] [Ni(tacn)$_2$]Cl$_2$·4H$_2$O,[18] and [Ru(tacn)$_2$]I$_2$·H$_2$O[19] were prepared according to literature procedures, characterized by electronic absorption spectroscopy and converted to the corresponding perchlorate salts by addition of concentrated NaClO$_4$ solutions.

**Caution.** *Although we have experienced no difficulty with these compounds, perchlorate salts of transition metal complexes are potentially explosive and should be handled in small quantities with due caution.*

[Fe(tacn)$_2$]Br$_2$·3H$_2$O was prepared as described in ref 16. The following solvents were obtained commercially in the highest purity available and used as received: acetone, acetonitrile, dimethyl formamide, dimethyl sulfoxide, and propylene carbonate (Burdick and Jackson); deuterium oxide (99.9 at. %) and *N*-methylformamide (Aldrich); formamide (Acros Organics). Aqueous solutions were prepared with Milli-Q deionized water. Lithium perchlorate (Aldrich) and sodium chloride (Mallinckrodt) were obtained commercially.

**Methods.** Formal potentials ($E^{\circ\prime}$) were measured as the average of anodic and cathodic peak potentials by cyclic voltammetry. Voltammograms were recorded for solutions containing 0.5−1 mM reactant at sweep rates of 0.1−0.5 V s$^{-1}$ using a Bioanalytical Systems 100A potentiostat. Chemically

reversible behavior was observed in all cases except for Ni(tacn)$_2$$^{3+/2+}$ and Ru(tacn)$_2$$^{3+/2+}$ in formamide and *N*-methylformamide. The Ni(tacn)$_2$$^{3+/2+}$ and Ru(tacn)$_2$$^{3+/2+}$ couples were examined as oxidations at Pt and Pt or glassy carbon electrodes; the Fe(tacn)$_2$$^{3+/2+}$ and Co(tacn)$_2$$^{3+/2+}$ couples as reductions at Pt and Au or amalgamated Au electrodes. Measurements were conducted in a three-electrode non-isothermal cell[1] with the working and reference compartments independently thermostated by circulating water baths. The reference electrode was a Ag/AgCl (3.0 M KCl) half-cell (Bioanalytical Systems) immersed directly in the reference compartment, which contained the same solvent and supporting electrolyte as the working compartment.

The solution magnetic susceptibility of [Fe(tacn)$_2$]Br$_2$ was determined as a function of temperature in D$_2$O by the $^1$H NMR method of Evans.[20] Measurements were made with a Varian Gemini 2000 spectrometer operating at 200 MHz and employed acetone as internal reference. Mass susceptibility, $\chi_g$, was calculated from

$$\chi_g = -3\Delta f/4\pi fm + \chi_o[1 + (d_o - d_s)/m] \qquad (3)$$

where $\Delta f$ is the frequency shift in Hz of the reference compound, $f$ is the fixed probe frequency of the spectrometer, $\chi_o$ is the mass susceptibility (in cm$^3$ g$^{-1}$) of the solvent, $m$ is the mass (in g) of the complex in 1 cm$^3$ of solution, and $d_o$ and $d_s$ are the densities of the solvent and solution, respectively. Equation 3 is used when frequency shifts are measured with spectrometers having magnetic fields parallel to the sample tube axis.[21] The density difference, $d_o - d_s$, was approximated as that between pure water and an aqueous ferric chloride solution of identical concentration (20 mg/mL).[22] The molar susceptibility, determined as $\chi_m = \chi_g/MW$, was corrected for the diamagnetic contributions of the tacn ligands and Fe(II) core electrons using Pascal's constants[23] to obtain the corrected molar susceptibility, $\chi_m'$.

## Results and Discussion

**Effect of Electrolyte Type and Concentration.** Ion-pairing is anticipated between positively charged reactants and the anion of the supporting electrolyte.[24] Earlier, we found that fluoride ion forms 1:1 ion-pairs with M(tacn)$_2$$^{3+}$ complexes and that the magnitude of the formation constant ($K_{IP} = 5 \pm 1$ M$^{-1}$) is independent of M.[12a] Because of this independence, the Ni(tacn)$_2$$^{3+/2+}$ couple was selected to evaluate the influence of electrolyte type and concentration on half-reaction entropies.

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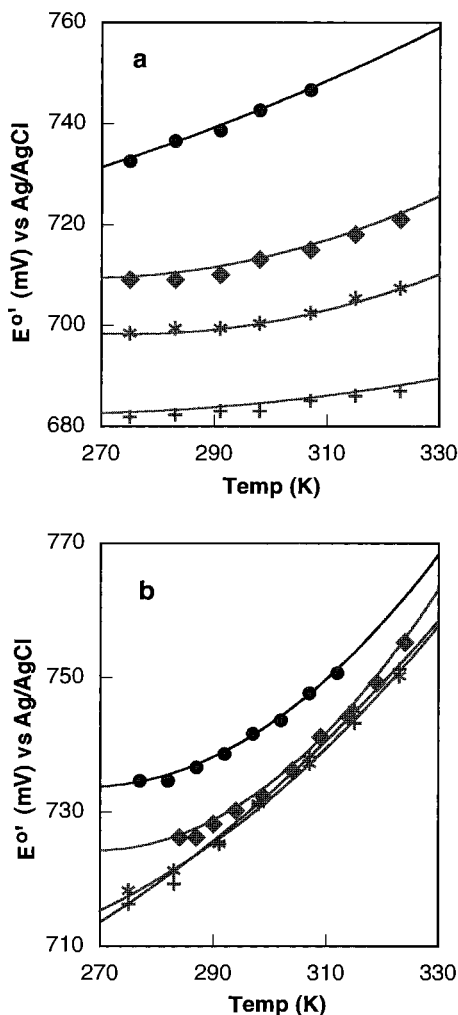
**Figure 1.** Plots of $E^{\circ\prime}$ versus $T$ for Ni(tacn)$_2^{3+/2+}$ in H$_2$O containing (a) NaCl, (b) LiClO$_4$. Electrolyte concentration (M): 0.1 ($\bullet$), 0.75 ($\blacklozenge$), 1.5 (*), 3.0 (+).
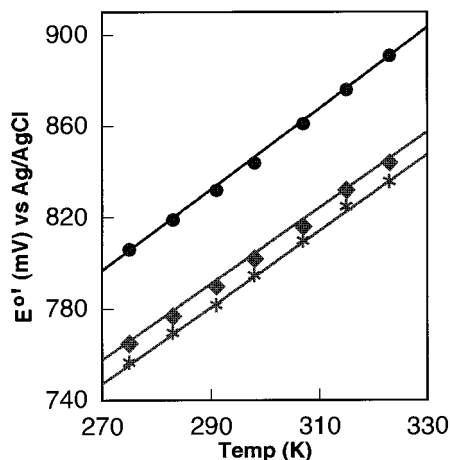


**Figure 2.** Plots of $E^{\circ\prime}$ versus T for Ni(tacn)$_2^{3+/2+}$ in DMF containing LiClO$_4$. Electrolyte concentration (M): 0.1 ($\bullet$), 0.75 ($\blacklozenge$), 1.5 (*).

Figures 1a and 1b show plots of formal potential versus temperature for Ni(tacn)$_2^{3+/2+}$ in aqueous solutions containing 0.1–3.0 M NaCl and LiClO$_4$, respectively. The corresponding experimental data are collected in Tables S1 and S2 of the Supporting Information. Similar behavior is observed in D$_2$O. Figure 2 shows plots of $E^{\circ\prime}$ versus T for Ni(tacn)$_2^{3+/2+}$ in DMF containing 0.1–1.5 M LiClO$_4$. A negative shift of $E^{\circ\prime}$ with increasing supporting electrolyte concentration is observed in
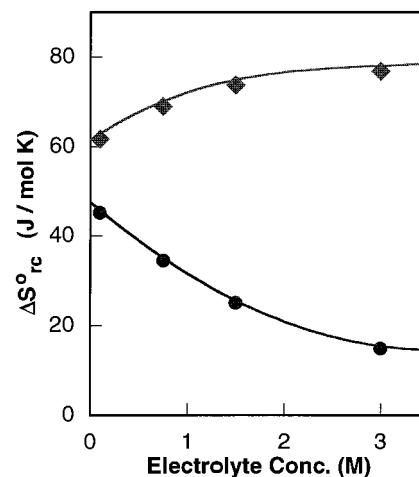


**Figure 3.** Plot of $\Delta S^{\circ}_{rc}$ determined over the interval 290–320 K for Ni(tacn)$_2^{3+/2+}$ as a function of electrolyte concentration in H$_2$O. NaCl ($\bullet$), LiClO$_4$ ($\blacklozenge$).

all cases. This finding is consistent with more extensive ion-pair formation between the oxidized rather than reduced form of the complex and the electrolyte anion. However, there are two unusual aspects to the aqueous solution results: (i) plots of $E^{\circ\prime}$ versus $T$ exhibit noticeable curvature and (ii) comparison of gradients from regions where $E^{\circ\prime}$–$T$ response is approximately linear suggests that $\Delta S^{\circ}_{rc}$ is dependent on electrolyte type and concentration. Because departure from linear $E^{\circ\prime}$–$T$ behavior is more severe at lower temperature, we determined $\Delta S^{\circ}_{rc}$ in H$_2$O over an interval of 290–320 K and plotted results as a function of [X$^-$] (Figure 3). This graph shows that $\Delta S^{\circ}_{rc}$ decreases with increasing NaCl concentration but increases with increasing LiClO$_4$ concentration.

To interpret these findings we begin with the assumption that only reaction 4

$$\text{M(tacn)}_2^{3+} + \text{X}^- \rightleftharpoons \text{M(tacn)}_2^{3+}:\text{X}^- \qquad K_{IP} \qquad (4)$$
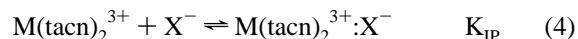
contributes to the shift of $E^{\circ\prime}$ with electrolyte concentration in aqueous solution.[24] The ion-pair formation constant, $K_{IP}$, is evaluated from the expression

$$\exp[(f(E^{\circ\prime}_{3+/2+} - E^{\circ\prime})] = 1 + K_{IP}[\text{X}^-] \qquad (5)$$

where $E^{\circ\prime}_{3+/2+}$ is the potential of reaction 2 in the absence of ion-pairing, $E^{\circ\prime}$ is the observed value, and $f = F/RT$. In H$_2$O at 298 K, $K_{IP} = 3.9 \pm 0.6$ M$^{-1}$ in NaCl and $0.5 \pm 0.1$ M$^{-1}$ in LiClO$_4$. Thus, reduction of M(tacn)$_2^{3+}$ proceeds from a distribution of free and ion-paired M(III) forms to non-ion-paired M(II). The observed half-reaction entropy is

$$\Delta S^{\circ}_{rc} = (\Delta S^{\circ}_{rc})^{\circ} - f_{IP}(\Delta S^{\circ}_{IP}) \qquad (6)$$

where $(\Delta S^{\circ}_{rc})^{\circ}$ is $\Delta S^{\circ}_{rc}$ in the absence of ion-pairing, $f_{IP} = K_{IP}$[X$^-$]/(1 + $K_{IP}$[X$^-$]), and $\Delta S^{\circ}_{IP} = S^{\circ}_{M3+:X} - S^{\circ}_{M3+} - S^{\circ}_{X-}$ is the entropy of ion-pair formation; S$^{\circ}_{M3+:X}$, S$^{\circ}_{M3+}$ and S$^{\circ}_{X-}$ are the entropies of the ion-paired, trivalent, and anionic species, respectively, in reaction 4.

$(\Delta S^{\circ}_{rc})^{\circ}$ and $\Delta S^{\circ}_{IP}$ can be evaluated from plots of $\Delta S^{\circ}_{rc}$ versus $f_{IP}$ (eq 6). From the data in Figure 3, $(\Delta S^{\circ}_{rc})^{\circ} = 59 \pm 5$ and $\Delta S^{\circ}_{IP} = 41 \pm 7$ J mol$^{-1}$ K$^{-1}$ in NaCl and $(\Delta S^{\circ}_{rc})^{\circ} = 62 \pm 2$ and $\Delta S^{\circ}_{IP} = -28 \pm 5$ J mol$^{-1}$ K$^{-1}$ in LiClO$_4$. An alternate method of data analysis[25] yields $(\Delta S^{\circ}_{rc})^{\circ} = 61 \pm 20$ and $\Delta S^{\circ}_{IP} = 33 \pm 3$ J mol$^{-1}$ K$^{-1}$ in NaCl and $(\Delta S^{\circ}_{rc})^{\circ} = 69 \pm 16$ and $\Delta S^{\circ}_{IP} = -25 \pm 4$ J mol$^{-1}$ K$^{-1}$ in LiClO$_4$. Agreement between

**Table 1.** Electrode Half-Reaction Entropies of M(tacn)$_2^{3+/2+}$ Redox Couples (J mol$^{-1}$K$^{-1}$)[a] and Solvent Parameters

| | Ru | Fe | | Ni | | Co | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta S°_{rc}$ | $\Delta S°_{rc}$ | $\Delta(\Delta S°_{rc})_{M-Ru}$ | $\Delta S°_{rc}$ | $\Delta(\Delta S°_{rc})_{M-Ru}$ | $\Delta S°_{rc}$ | $\Delta(\Delta S°_{rc})_{M-Ru}$ | $(\Delta S°_{rc})_{Born}$[b] | DN[c] | AN[c] | $-a$[d] |
| water | 36(2) | 58(4) | 22 | 63(5) | 27 | 95(2) | 59 | 47 | 18 | 55 | 0 |
| deuterium oxide | 25(7) | 41(3) | 16 | 56(6) | 31 | 84(2) | 59 | | | | −1 |
| formamide | | 106(10) | | | | 140(3) | | 47 | | 40 | 1.5 |
| *N*-methylformamide | | 130(4) | | | | 176(2) | | 39 | | 31 | 5 |
| dimethylformamide | 129(3) | 163(3) | 34 | 149(3) | 20 | 185(3) | 56 | 107 | 27 | 16 | 16 |
| dimethyl sulfoxide | 110(4) | 138(4) | 28 | 142(3) | 32 | 190(3) | 80 | 39 | 30 | 19 | 10 |
| propylene carbonate | 133(2) | 163(5) | 30 | 170(5) | 37 | 196(5) | 63 | 44 | 15 | 18 | 9 |
| acetonitrile | 117(4) | 152(2) | 35 | 155(4) | 38 | 188(10) | 71 | 92 | 14 | 19 | 18 |
| acetone | 130(3) | 157(3) | 27 | 156(6) | 26 | 224(8) | 94 | 184 | 17 | 12.5 | 28 |
| mean | | | 27(7) | | 30(6) | | 69(14) | | | | |

[a] Evaluated over the temperature interval 290−320 K in 0.1 M LiClO$_4$. [b] Calculated from eq 1 using data from Chapter 6 of ref 26. [c] Solvent donor and acceptor numbers from ref 11. [d] Solvent ordering parameter from ref 29.

values of $(\Delta S°_{rc})°$ obtained in two electrolytes and by two methods of data analysis lends confidence to the results. However, the quantitative significance of the values reported should be viewed with caution, because variations in liquid-junction potential and the ionic strength dependences of $K_{IP}$ and $E°'$ have been neglected.

The foregoing results provide a basis for understanding the effects of ion-pairing on electrode half-reaction entropies. Equation 6 predicts that $\Delta S°_{rc}$ will be influenced by the concentration of electrolyte, the magnitude of $K_{IP}$ and the sign and magnitude of $\Delta S°_{IP}$. Aqueous conductivity studies of Co-(III) hexaamine salts[24f,g] show that $\Delta S°_{IP}$ for formation of 1:1 ion pairs correlates with $-\Delta S°_{hyd}$, where $\Delta S°_{hyd}$ is the entropy of hydration of the anion. The $\Delta S°_{hyd}$ of Cl$^-$ is ca. 30 J mol$^{-1}$ K$^{-1}$ more negative than that of ClO$_4^-$,[26] reflecting the greater solvent structure-breaking tendency of the latter ion. Observation of negative and positive contributions to $\Delta S°_{rc}$ as ion-paired M(tacn)$_2^{3+}$:X$^-$ is reduced to dissociated M(tacn)$_2^{2+}$ in the presence of chloride and perchlorate, respectively, is consistent with the relative $\Delta S°_{hyd}$ values of these ions. We believe that similar terms, arising from entropic properties of ions bound or released in the course of electron transfer, account for many of the observations of electrolyte effects on electrode half-reaction entropies.[7,8a,10c]

Plots of $E°'$ versus $T$ exhibit nonlinearity under some conditions, most noticeably in H$_2$O and D$_2$O (Figure 1). Such behavior has not been widely reported in literature. We speculate that it is a consequence of the change in ion-pair stoichiometry that accompanies electron transfer and temperature-dependent properties of liquid H$_2$O and D$_2$O.[27] Yokoyama et al. have shown from aqueous conductivity studies of Co(III) hexaamine salts[24f,g] that $K_{IP}$ and its component thermodynamic quantities ($\Delta H°_{IP}$ and $\Delta S°_{IP}$) exhibit significant temperature dependences.

$E°'$ versus $T$ responses are more linear in nonaqueous solvents (Figure 2). Unfortunately, $(\Delta S°_{rc})°$ cannot be determined under these conditions because ion-pair formation is extensive.[28] For example, a plot of $E°'$ versus log[ClO$_4^-$] taken from data in DMF containing 0.050−0.125 M LiClO$_4$ at 300 K (Table S3, Supporting Information) is linear with a slope of $-0.061 \pm$

0.001 V, indicating that the oxidized form is associated with one more counter ion than the reduced form. However, the fraction of dissociated material is small; thus, the ion-pair stoichiometry and magnitude of $K_{IP}$ cannot be evaluated and the contribution of $\Delta S°_{IP}$ to $\Delta S°_{rc}$ cannot be determined.

**Effects of Solvent and Metal Ion.** Electrode half-reaction entropies of the four M(tacn)$_2^{3+/2+}$ couples in various solvents containing 0.1 M LiClO$_4$ are reported in Table 1. The quantities in parentheses are uncertainties at the 90% confidence limit. Values of $\Delta S°_{rc}$ are determined over the temperature interval 290−320 K and are uncorrected for ion-pair formation. $\Delta S°_{rc}$ could not be established for Ru(tacn)$_2^{3+/2+}$ and Ni(tacn)$_2^{3+/2+}$ in formamide and *N*-methylformamide because of irreversible electrochemical response in these solvents.

The electrode half-reaction entropies in Table 1 exhibit a marked dependence on solvent. The range of values exceeds 100 J mol$^{-1}$ K$^{-1}$ for each redox couple. However, the experimental quantities do not correlate with $(\Delta S°_{rc})_{Born}$ calculated from eq 1. Failure of the Born dielectric continuum model to predict the solvent dependence of $\Delta S°_{rc}$ is well documented.[5,15c] $\Delta S°_{rc}$ also does not correlate with Gutmann's solvent donor number (DN).[11] It has been argued[5e] that the half-reaction entropy is influenced more directly by the extent to which solvent order is created or destroyed by the change in charge of the reactant. Weakly self-interacting solvents characterized by small values of acceptor number[11] or large values of the solvent ordering parameter $(-a)$ of Criss[29] are considered to be more susceptible to this change. The pronounced increases in $\Delta S°_{rc}$ with decreasing solvent acceptor number and with increasing solvent ordering parameter are consistent with this interpretation.

One objective of our work has been to ascertain whether inner- and outer-shell reorganizations become coupled when large changes in reactant structure accompany electron transfer. If this were to occur, an abnormal solvent dependence of $\Delta S°_{rc}$ may be anticipated for couples characterized by large structural change. The structural and compositional homogeneity of the M(tacn)$_2^{3+/2+}$ complexes affords an opportunity to explore this question by considering the differential quantity $\Delta(\Delta S°_{rc})_{M-Ru}$. This term equals the half-reaction entropy of each M(tacn)$_2^{3+/2+}$ couple minus that of Ru. On the basis of the structural data for closely related compounds,[30] Ru(tacn)$_2^{3+/2+}$ is expected to exhibit little inner-shell reorganization as a consequence of

(25) In this procedure $(\Delta S°_{rc})°$ is determined by correcting $E°'$ for the effects of ion-pairing and plotting $E°'_{3+/2+}$ versus $T$. $\Delta S°_{IP}$ is evaluated from the temperature dependence of $K_{IP}$; i.e., $\Delta S°_{IP} = R[\ln K_{IP}^{298} - (1/T) \partial \ln K_{IP}/\partial(1/T)]$. From this analysis, also: $\Delta H°_{IP} = 6.5 \pm 0.2$ kJ mol$^{-1}$ in NaCl and $-5.7 \pm 0.3$ kJ mol$^{-1}$ in LiClO$_4$.

(26) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.

(27) Lang, E. W.; Lüdemann, H.-D. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 315−329.

(28) More extensive ion-pairing in nonaqueous solvents is consistent with a reported value of $K_{IP} = 10^{2.4}$ for Co(en)$_3^{3+}$:ClO$_4^-$ in DMF: Tanaka, N.; Harada, K. *Electrochim. Acta* **1976**, *21*, 615−620.
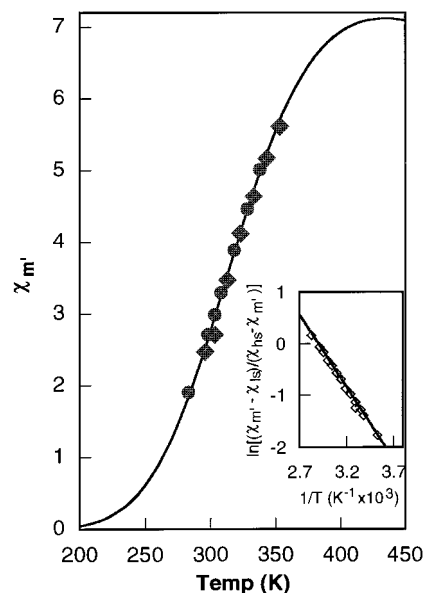
(29) Criss, C. M. *J. Phys. Chem.* **1974**, *78*, 1000−1002.

(30) From structural data for [Ru(sar)](CF$_3$SO$_3$)$_3$ and [Ru(Mesar)](CF$_3$SO$_3$)$_2$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; Mesar = 1-methyl derivative of sar). Bernhard, P.; Bürgi, H.-B.; Raselli, A.; Sargeson, A. M. *Inorg. Chem.* **1989**, *28*, 3234−3239.

electron transfer. Thus, nonspecific solvent contributions and ion-pair effects are cancelled by referencing measurements to this couple.

Values of $\Delta(\Delta S°_{rc})_{M-Ru}$ in seven solvents containing 0.1 M LiClO$_4$ are included in Table 1. Mean values of $\Delta(\Delta S°_{rc})_{M-Ru}$ = 27 ± 7, 30 ± 6, and 69 ± 14 J mol$^{-1}$ K$^{-1}$ are observed for M = Fe, Ni, and Co, respectively. Although the values of $\Delta(\Delta S°_{rc})_{M-Ru}$ are relatively uniform for each redox couple, some deviations exist. Specifically, results of $\Delta(\Delta S°_{rc})_{Fe-Ru}$ = 22 J mol$^{-1}$ K$^{-1}$ in H$_2$O, $\Delta(\Delta S°_{rc})_{Fe-Ru}$ = 16 J mol$^{-1}$ K$^{-1}$ in D$_2$O and $(\Delta S°_{rc})_{Ni-Ru}$ = 20 J mol$^{-1}$ K$^{-1}$ in DMF appear to be unusually small, and results of $(\Delta S°_{rc})_{Co-Ru}$ = 80 J mol$^{-1}$ K$^{-1}$ in DMSO and 94 J mol$^{-1}$ K$^{-1}$ in acetone appear to be unusually large. An explanation of the small values for $\Delta(\Delta S°_{rc})_{Fe-Ru}$ in H$_2$O and D$_2$O is provided in the following section; however, there is no apparent rationalization of the $\Delta(\Delta S°_{rc})_{Ni-Ru}$ result in DMF. It is tempting to speculate that the large values of $\Delta(\Delta S°_{rc})_{Co-Ru}$ in DMSO and acetone arise from interactions between amine hydrogens on the tacn ligands and lone-pair electrons on the O atoms of the solvent. This finding would be in accord with the large donor number of DMSO and its demonstrated ability to selectively solvate amine hydrogen bearing reactants.[31] However, the DN of acetone is smaller than DMF and scarcely larger than several other solvents in Table 1 which do not exhibit unusual values of $\Delta(\Delta S°_{rc})_{Co-Ru}$. Moreover, anomalous behavior is not observed for the other redox couples. Thus, we conclude there is no systematic pattern to the observed deviations in $\Delta(\Delta S°_{rc})_{M-Ru}$ and that, if inner- and outer-shell reorganizations are coupled during M(tacn)$_2^{3+/2+}$ electron transfer, the fact is not reflected in the solvent dependence of their half-reaction entropies.

**Metal Dependence of $\Delta S°_{rc}$ and Its Origins.** The results in Table 1 demonstrate that the entropy of reaction 2 exhibits a significant dependence on the identity of the metal ion. The difference in $\Delta S°_{rc}$ between Co$^{3+/2+}$ and Ru$^{3+/2+}$ is particularly large. This fact has been noted previously.[5,32] Generally, it is considered that $\Delta S°_{rc}$ for Co$^{3+/2+}$ exceeds that for Ru$^{3+/2+}$ by 90 J mol$^{-1}$ K$^{-1}$ or more. However, comparative values of $\Delta(\Delta S°_{rc})_{Co-Ru}$ = 63 to 100 J mol$^{-1}$ K$^{-1}$ are found in the literature, if conditions of identical ligand, solvent and electrolyte counter ion and concentration are adhered to.[33] This range compares favorably with that found in Table 1. It appears that a typical value of $\Delta(\Delta S°_{rc})_{Co-Ru}$ is ca. 70 J mol$^{-1}$ K$^{-1}$, although we are unable to account for observations that significantly exceed this figure. There are insufficient data to make similar comparisons with M = Fe and Ni. However, large values of $\Delta(\Delta S°_{rc})_{Ni-Ru}$ in addition to $\Delta(\Delta S°_{rc})_{Co-Ru}$ are not surprising given that Ni(tacn)$_2^{3+/2+}$ and Co(tacn)$_2^{3+/2+}$ experience significant inner-shell reorganizations as a consequence of a change in number of antibonding electrons with electron transfer. The difference in M−N bond lengths is 0.09 Å in the case of Ni[34]

(31) (a) Ennix, K. S.; McMahon, P. T.; de la Rosa, R.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660−2666. (b) Curtis, J. C.; Blackbourn, R. L.; Ennix, K. S.; Hu, S.; Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1989**, *28*, 3791−3795.

(32) (a) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1991**, *30*, 1412−1414. (b) Richardson, D. E.; Sharpe, P. *Inorg. Chem.* **1993**, *32*, 1809−1812.

(33) Data meeting these criteria with resultant $\Delta(\Delta S°_{rc})_{Co-Ru}$ values (J mol$^{-1}$ K$^{-1}$) in parentheses are as follows: M(en)$_3^{3+/2+}$, 0.1 M LiClO$_4$ or Et$_4$NClO$_4$, DMF (63)[5c]; M(bpy)$_3^{3+/2+}$, 0.1 M LiClO$_4$ or 0.1 M KPF$_6$, CH$_3$CN (65);[5b,d] M(en)$_3^{3+/2+}$, 0.1 M LiClO$_4$, DMSO (80);[5c] M(tacn)$_2^{3+/2+}$, 0.75 M NaF, H$_2$O (89);[12a] M(en)$_3^{3+/2+}$, 0.1 M LiClO$_4$, H$_2$O (100).[5b]

(34) From structural data for (a) [Ni(tacn)$_2$]$_2$(S$_2$O$_6$)$_3$·7H$_2$O: Wieghardt, K.; Walz, W.; Nuber, B.; Weiss, J.; Ozarowski, A.; Stratemeier, H.; Reinen, D. *Inorg. Chem.* **1986**, *25*, 1650−1654. (b) [Ni(tacn)$_2$](NO$_3$)-(Cl)·H$_2$O: Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157-L159.

**Figure 4.** Plot of corrected molar susceptibility of Fe(tacn)$_2^{2+}$ in D$_2$O as a function temperature. Measurements were initiated at room temperature and cycled through an interval of 280−350 K. Points obtained on heating and cooling are represented by (♦) and (•), respectively. Inset: Evaluation of thermodynamic parameters.

and 0.18 Å in the case of Co.[35] The result $\Delta(\Delta S°_{rc})_{Fe-Ru}$ = 27 J mol$^{-1}$ K$^{-1}$ is surprising because little structural change is anticipated for Fe(tacn)$_2^{3+/2+}$ based on X-ray crystal structures of isolated solids.[36] Both oxidation states are isolated as low-spin complexes and exhibit a difference of only 0.04 Å in Fe−N bond distance. However, the solution structures of Fe(tacn)$_2^{3+/2+}$ have not been characterized, and spin-crossover behavior is prevalent in Fe(II) chemistry.[4]

To address this question we examined the solution magnetic behavior of Fe(tacn)$_2^{2+}$ using the Evans NMR method. Figure 4 shows a plot of the corrected molar susceptibility, $\chi_{m'}$, of Fe-(tacn)$_2^{2+}$ in D$_2$O as a function of temperature. $\chi_{m'}$ exhibits no hysteresis as temperature is cycled over an interval of 280−350 K. In addition, the ligand proton resonances are paramagnetically broadened and shifted to lower field with increasing temperature. These behaviors are consistent with an equilibrium between low- and high-spin forms of Fe(tacn)$_2^{2+}$ in solution.[37] Thermodynamic parameters are determined from a plot of ln-$[(\chi_{m'} - \chi_{ls})/(\chi_{hs} - \chi_{m'})]$ versus $1/T$ (inset, Figure 4), where $\chi_{ls}$ and $\chi_{hs}$ are the molar susceptibilities of the low- and high-spin forms, respectively. Low- and high-temperature limits cannot be achieved under the experimental conditions; therefore, we assume $\chi_{ls} = 0$ and $\chi_{hs} = 5.4\mu_B$.[38] The quantities obtained are $\Delta H°_{SE}$ = 23.8 ± 1.0 kJ mol$^{-1}$, $\Delta S°_{SE}$ = 68.2 ± 2.8 J mol$^{-1}$ K$^{-1}$, $T_c$ = 349 K, and $K_{SE}$ = 0.25 at 298 K. These results fall within the range of values commonly observed for ls−hs equilibria of Fe(II) complexes with N donor ligands.[4c,39] The

(35) From structural data for (a) [Co(Metacn)$_2$]I$_3$·5H$_2$O (Metacn = (R)-2-methyl-1,4,7-triazacyclononane): Mikami, M.; Kuroda, R.; Konno, M.; Saito, Y. *Acta Crystallogr.* **1977**, *B33*, 1485−1489. (b) [Co(tacn)$_2$]-I$_2$·2H$_2$O: Küppers, J.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400−2408.

(36) From structural data for [Fe(tacn)$_2$]Cl$_3$·5H$_2$O and [Fe(tacn)$_2$]Cl$_2$·4H$_2$O: Boeyens, J. C. A.; Forbes, A. G. S.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 2926−2931.

(37) At the conclusion of this work an unpublished report of the ls−hs conversion of Fe(tacn)$_2^{2+}$ in solution was cited in the following paper: Diebold, A.; Hagen, K. S. *Inorg. Chem.* **1998**, *37*, 215−223.

(38) Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1071−1075.

**Table 2.** Vibrational and Electronic Contributions to Electrode Half-Reaction Entropies (J mol$^{-1}$ K$^{-1}$)

| M | $S^\circ_{vib,3+}$[a] | $S^\circ_{vib,2+}$[a] | $\Delta S^\circ_{vib}$ | $S^\circ_{el,3+}$ | $S^\circ_{el,2+}$ | $\Delta S^\circ_{el}$ | $\Delta S^\circ_{vib+el}$ | $\Delta(\Delta S^\circ_{vib+el})_{M-Ru}$ |
|---|---|---|---|---|---|---|---|---|
| Ru | 90 | 97 | 7 | 6[c] | 0 | −6 | 1 | |
| Fe | 94 | 137 (hs) | 43 (hs) | 10[c] | 20 (hs)[c] | 10 (hs) | 5[d] | 4 |
|  | 94 | 97 (ls)[b] | 3 (ls)[b] | 10[c] | 0 (ls) | −10 (ls) | | |
| Ni | 78 | 113 | 35 | 12 | 9 | −3 | 32 | 31 |
| Co | 75 | 128 | 53 | 0 | 17[c] | 17 | 70 | 69 |

[a] Calculated from eq 7 using the data in Table S4. [b] Value assumed equal to $S^\circ_{vib}$ for Ru(NH$_3$)$_6^{2+}$. [c] Calculated from eq 8 with $q_{el} = \sum g_i e^{-1.439\epsilon_i/T}$, where $g_i$ is the degeneracy and $\epsilon_i$ is the energy (cm$^{-1}$) of state $i$. Degeneracies and energies determined as described in ref 43a using a spin−orbit coupling constant of $\lambda = -0.8\zeta/2S$, where $\zeta$ is the one-electron free ion value (Table A.8, ref 43b) and $S$ is the total spin angular momentum of the complex. [d] Calculated assuming 20% hs−80% ls Fe(II) in solution.

magnitude of $K_{SE}$ is equivalent to the presence of 20% hs-Fe-(tacn)$_2^{2+}$ in solution at 298 K. The value $\Delta(\Delta S^\circ_{rc})_{Fe-Ru} = 16$ J mol$^{-1}$ K$^{-1}$ in D$_2$O is consistent with this distribution assuming that reduction of Fe(tacn)$_2^{3+}$ to low-spin Fe(tacn)$_2^{2+}$ makes a small contribution to the entropy difference. Somewhat larger values of $\Delta(\Delta S^\circ_{rc})_{Fe-Ru}$ are observed in non-aqueous solvents, which may indicate greater fractions of hs-Fe(tacn)$_2^{2+}$ under these conditions.

The entropy of molecular systems can be represented as a sum of translational, rotational, vibrational, and electronic terms. Translational and rotational contributions should be nearly equal for all members of the structurally homologous M(tacn)$_2^{3+/2+}$ couples. Therefore, entropic differences are more likely to arise from differences in vibrational and electronic terms. Richardson and Sharpe[32] noted that vibrational contributions to $\Delta S^\circ_{rc}$ become important when frequencies are small and change significantly with a change in oxidation state. This property should characterize Co$^{3+/2+}$, Ni$^{3+/2+}$, and ls-Fe$^{3+}$/hs-Fe$^{2+}$ couples for which an increase in number of antibonding electrons weakens metal−ligand bonds upon reduction. In addition, there will be a contribution to $\Delta S^\circ_{rc}$ from the change in electronic configuration of each couple. Thus, the principal intramolecular components of $\Delta S^\circ_{rc}$ can be represented as a sum of vibrational ($\Delta S^\circ_{vib}$) and electronic ($\Delta S^\circ_{el}$) terms.

$\Delta S^\circ_{vib}$ is evaluated as $S^\circ_{vib,2+} - S^\circ_{vib,3+}$. The entropies of the individual oxidation states are calculated from[40]

$$S^\circ_{vib} = R\sum[u/(e^u - 1) - \ln(1 - e^{-u})] \tag{7}$$

where $u = 1.439\omega/T$ and $\omega$ is the vibrational frequency in cm$^{-1}$. Vibrational spectra have not been obtained for the structurally complex M(tacn)$_2^{3+/2+}$ molecules. Therefore, data for M(NH$_3$)$_6^{3+/2+}$ complexes are used.[41] The rationale is that, because low-energy M−N frequencies make the largest contribution to entropy, $\Delta S^\circ_{vib}$ will be similar for the two families of compounds. Richardson and Sharpe[32] adopted this approach in estimating vibrational contributions to $\Delta S^\circ_{rc}$ for Co$^{3+/2+}$ and Ru$^{3+/2+}$. Values of $\Delta S^\circ_{vib}$ calculated from eq 7 are collected in Table 2. In each case, the sum is over the fifteen octahedral modes of the corresponding M(NH$_3$)$_6^{n+}$ complex. The vibrational data are presented in Table S4 of the Supporting Information. In instances where experimental frequencies are unavailable, they are estimated from Badger's rule[42] and characteristic bond distances. Data for Fe(NH$_3$)$_6^{2+}$ correspond to the hs form of

the complex. $S^\circ_{vib}$ for non-existent ls-Fe(NH$_3$)$_6^{2+}$ is assumed to equal that for Ru(NH$_3$)$_6^{2+}$.

$\Delta S^\circ_{el}$ is evaluated as $S^\circ_{el,2+} - S^\circ_{el,3+}$. For species with A or E ground electronic states, it is assumed that $S^\circ_{el} = R \ln q_{el}$ and that the electronic partition function, $q_{el}$, equals the product of the spin multiplicity and orbital degeneracy. Thus, for Ru$^{2+}$-($^1A_{1g}$), ls-Fe$^{2+}$($^1A_{1g}$), Co$^{3+}$($^1A_{1g}$), Ni$^{2+}$($^3A_{1g}$), and Ni$^{3+}$($^2E_g$), $q_{el}$ = 1, 1, 1, 3, and 4, respectively. For other forms the effects of spin−orbit coupling must be considered,[43] and the electronic entropy is determined from[40]

$$S^\circ_{el} = R \ln q_{el} + RT\, \partial(\ln q_{el})/\partial T \tag{8}$$

Values of $S^\circ_{el}$ calculated in this manner for Ru$^{3+}$($^2T_{2g}$), Fe$^{3+}$-($^2T_{2g}$), hs-Fe$^{2+}$($^5T_{2g}$), and Co$^{2+}$($^4T_{1g}$) are entered in Table 2. Details are provided in the footnotes.

Values of $\Delta S^\circ_{vib}$ and $\Delta S^\circ_{el}$ are set out for each redox couple in Table 2. Their sum is expressed as $\Delta S^\circ_{vib+el}$. Separate terms are entered for the high- and low-spin forms of iron(II), and $\Delta S^\circ_{vib+el}$ for this couple is calculated assuming 20% hs−80% ls Fe$^{2+}$ in solution. The calculated quantities can be compared with experimental ones by taking differences with respect to Ru. Values of $\Delta(\Delta S^\circ_{vib+el})_{M-Ru}$ = 4, 31, and 69 J mol$^{-1}$ K$^{-1}$ in Table 2 compare favorably with the mean values of $\Delta(\Delta S^\circ_{rc})_{M-Ru}$ = 27, 30, and 69 J mol$^{-1}$ K$^{-1}$ in Table 1 for M = Fe, Ni, and Co, respectively. Use of vibrational data for Ru-(NH$_3$)$_6^{2+}$ to approximate $S^\circ_{vib}$ for ls-Fe(NH$_3$)$_6^{2+}$ may account for the low result for $\Delta(\Delta S^\circ_{vib+el})_{Fe-Ru}$.

The overall agreement between $\Delta(\Delta S^\circ_{vib+el})_{M-Ru}$ and $\Delta$-($\Delta S^\circ_{rc})_{M-Ru}$ is satisfying given the use of data for NH$_3$ complexes to estimate vibrational contributions for M(tacn)$_2^{3+/2+}$. It is anticipated for tacn complexes that low-frequency modes may differ in energy because of the greater rigidity of the macrocyclic ligand and that the effects of structural differences may be distributed over a large number of modes. The impact of these factors on calculated entropies cannot be assessed until vibrational data for tacn complexes become available. Nevertheless, it is apparent that intramolecular contributions arising from vibrational and electronic sources account in large measure for the metal-dependent differences in $\Delta S^\circ_{rc}$ of M(tacn)$_2^{3+/2+}$ couples.

## Conclusions

Metal-dependent values of $\Delta S^\circ_{rc}$ for M(tacn)$_2^{3+/2+}$ redox couples arise from intramolecular sources. Vibrational terms become important when frequencies are small and change significantly with oxidation state, as occurs when an increase in number of antibonding electrons weakens metal−ligand bonds upon reduction. Electronic terms make a smaller, but significant,

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contribution to $\Delta S^{\circ}_{rc}$. An unexpectedly large value of $\Delta S^{\circ}_{rc}$ for $Fe(tacn)_2^{3+/2+}$ results from a ls−hs equilibrium in the Fe(II) oxidation state, for which $K_{SE} = 0.25$ at 298 K in $D_2O$.

**Supporting Information Available:** Tables S1−S3 (electrochemical data) and Table S4 (vibrational frequencies of $M(NH_3)_6^{3+}$ and $M(NH_3)_6^{2+}$ complexes) (4 pages). Ordering information is given on any current masthead page.