

Vibrational and Electronic Contributions to Entropy Changes for Oxidation–Reduction Reactions of Metal Complexes

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Entropies for several gas-phase ML_4 and ML_6 neutral and ionic transition-metal complexes are estimated from structural and spectroscopic data. It is demonstrated that vibrational entropies provide a substantial portion (up to 42% in the cases analyzed here) of the total entropy for such complexes as a result of low-frequency skeletal modes. The contributions of vibrational and electronic entropy changes to reaction entropies for a number of related redox couples are also estimated.

Introduction

Considerable attention has been focused on the relationship between the rate of electron-transfer processes between transition-metal compounds in solution and the enthalpic and entropic contributions to the overall driving force of the reaction.¹ This paper concentrates on the entropic aspects of this issue and, in particular, on the contributions of vibrational entropy and electronic entropy to the overall entropy changes that occur in metal complex oxidation–reduction couples and their redox reactions. We have previously² referred to these contributions as *intramolecular* to distinguish them from that portion of entropy that can be related to solvation of the complexes.³ Alternatively, the term *inner-sphere entropy* can be used to separate intramolecular entropies from the contributions of solvation (or outer-sphere entropy). Indeed, the intramolecular contributions are those to be expected in gas-phase experiments⁴ where the solvent is absent.

When a nonisothermal electrochemical cell is used to determine the temperature dependence of an electrode potential, a value for the *reaction entropy*, ΔS_{rc}° , can be obtained. Reaction entropies have been determined for a number of coordination complexes,⁵ organometallics,^{5b,6} and metalloproteins.⁷ The technique eval-

uates the difference between the absolute ionic entropies (ΔS_{rc}°) of the reduced and oxidized halves of the couple (eq 1). The

$$\Delta S_{rc}^\circ = \bar{S}_{red}^\circ - \bar{S}_{ox}^\circ \quad (1)$$

values of ΔS_{rc}° obtained by this method are consistent with the ion convention⁸ for dealing with entropies of electron attachment to gas-phase molecules or ions^{4,9} since the thermochemistry of the electron is ignored.

Theoretical interpretations of reaction entropies have generally centered on the role of solvation, and a Born model based on the dielectric continuum model has been reasonably successful in predicting the overall trends in reaction entropies.^{5c-e,10} Thus, for example, small ammine complex couples ($[M(NH_3)_6]^{3+/2+}$) have large, positive ΔS_{rc}° values in aqueous solution relative to those of larger tris chelate complexes such as $[M(bipy)_3]^{3+/2+}$ (bpy = bipyridine). Some variations from the Born model can be rationalized on the basis of specific solvent–solute interactions or dielectric saturation.¹¹ However, in some cases the ΔS_{rc}° values cannot be interpreted without considering intramolecular contributions. We have previously estimated² vibrational entropy in ruthenium and cobalt hexammine complexes and found that the experimental difference in the ΔS_{rc}° values for the two metals can likely be attributed substantially to larger changes in skeletal vibrational frequencies for the Co(III/II) couple. In addition, electronic entropies were evaluated but were not as large as the vibrational component of the entropies.²

Calculation of vibrational entropy (S_{vib}°) has been applied to a diversity of inorganic compounds. For example, the entropies of solid metal compounds such as metal carbides, nitrides, and

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alloys have been evaluated.¹² In addition, S_{vib}° has been evaluated for defects in solids,¹³ solid solutions,¹⁴ phase transitions,¹⁵ conformations of DNA,¹⁶ and metal complex spin equilibria.¹⁷ Vibrational entropies of discrete metal complexes, however, have not been widely evaluated.¹⁸ In metal complexes, ML_n vibrational degrees of freedom can contribute substantially to the total third law entropy as a result of the low-frequency skeletal modes.³ In the present paper, we estimate the vibrational entropies of a number of common metal complexes and derive the estimated contribution of $\Delta S_{\text{vib}}^{\circ}$ to $\Delta S_{\text{rc}}^{\circ}$ values for related redox couples.

Electronic entropy changes ($\Delta S_{\text{elec}}^{\circ}$) that accompany oxidation-reduction reactions of transition-metal complexes can be significant since substantial changes in multiplicity and orbital degeneracy can be encountered. For example, complexes that go from low spin to high spin when reduced (e.g., $\text{Co}^{\text{III/II}}L_6$) might be expected to have rather large $\Delta S_{\text{elec}}^{\circ}$ terms. In a review¹⁸ on calculation of entropies for inorganic molecules, electronic entropies were treated in an approximate manner (using only the electron spin multiplicity). Given the potential importance of these quantities, S_{elec}° values have been estimated here using a more accurate approach that uses the electronic states that result when spin-orbit coupling is considered.

A second article¹⁹ will consider the contributions of vibrational and electronic entropies to the thermodynamics of ligand substitution reactions at metal centers.

Vibrational and Electronic Contributions to Total Entropies for Metal Complexes

To illustrate the relative importance of vibrational and electronic entropies in the thermodynamics of metal complexes, we have estimated the gas-phase entropies of several complexes via the expression of eq 2, which indicates the additional

$$S_{\text{total}}^{\circ} = S_{\text{trans}}^{\circ} + S_{\text{rot}}^{\circ} + S_{\text{vib}}^{\circ} + S_{\text{int rot}}^{\circ} + S_{\text{elec}}^{\circ} \quad (2)$$

contributions of external rotations, internal rotations, and translation to the total entropy. The equations used to calculate these entropies are derived from statistical mechanics.²⁰ In some cases, certain of the $3N - 6$ vibrational modes are better described as hindered internal rotations, and the necessary calculations have been compiled in tables by Pitzer and Gwinn.²¹ The results of

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Table I. Estimated Gas-Phase Entropies (cal deg⁻¹ mol⁻¹) for Transition-Metal Complexes

complex	S_{vib}° ^a	S_{rot}°	$S_{\text{int rot}}^{\circ}$	S_{trans}°	S_{elec}°	S_{total}°
Cp_2Fe^b	14.9	24.3	5.2	41.6	0	86.0
$\text{Cp}_2\text{Fe}^+{}^b$	17.2	24.4	5.2	41.6	1.7	90.1
RuO_4	6.86	21.0 ^c		41.2	0	69.1
WCl_6	30.0	24.9 ^d		43.8	0	98.7
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	24.1 ^e	25.2 ^f	20.4 ^f	41.8	1.4	112.9
$[\text{Fe}(\text{CN})_6]^{4-}$	49.4 ^g	24.8 ^h		41.9	0	116.1

^a Vibrational frequencies from ref 27 unless otherwise noted. ^b Details of data used are given in ref 4d. Value for S_{total}° (Cp_2Fe) was misstated in ref 4d. ^c Using R-O bond distance of 1.705 Å.³⁰ Symmetry number $\sigma = 12$. ^d Using W-Cl bond distance of 2.26 Å (Ketelaar, J.; Van Oosterhooft, G. *Rec. Trav. Chim. Pays-Bas* **1943**, *62*, 197). $\sigma = 24$. ^e See ref 2 for details of vibrational data. ^f Using M-N distance of 2.104 Å (Stynes, H. C.; Ibers, J. *Inorg. Chem.* **1971**, *10*, 2304). The geometry assumed is D_{3h} and therefore $\sigma = 6$ for the external rotations. Each NH_3 is assumed to be freely rotating on the ML_3 frame and $\sigma_{\text{int}} = 3$. See ref 20a,d for discussion of proper treatment of internal rotations. ^g Vibrational data from ref 31. ^h Using M-C distance of 1.90 Å and C-N distance of 1.138 Å.³¹ $\sigma = 24$.

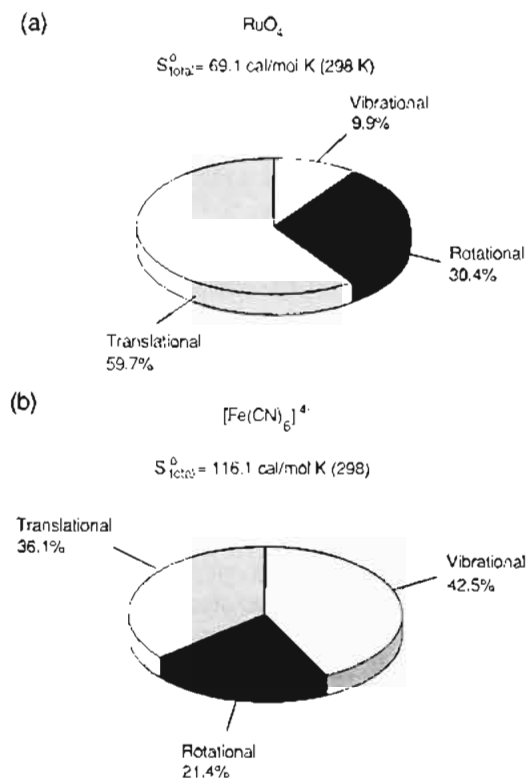


Figure 1. Graphical representations of the contributions of S_{trans}° , S_{vib}° , and S_{rot}° to S_{total}° for (a) RuO_4 and (b) $[\text{Fe}(\text{CN})_6]^{4-}$.

the calculations are given in Table I and are shown schematically for some examples in Figure 1.

The abundance of low-frequency skeletal modes in metal complexes (15 in ML_6) leads to a surprisingly significant part of the S_{total}° deriving from S_{vib}° (~15–45% for the examples in Table I). Because of the increasing entropy for a mode as the frequency gets lower (eq 3), complexes with lower skeletal force

$$S_{\text{vib}}^{\circ} = [1.987uc^{-u}/(1 - e^{-u}) - 4.576 \log(1 - e^{-u})] \text{ cal deg}^{-1} \text{ mol}^{-1} \quad (3)$$

$$u = (1.4388/T)\omega \quad (\omega \text{ in cm}^{-1})$$

constants and higher mass ligands will tend to have a higher portion of the total entropy arising from S_{vib}° . Correction for

Table II. Data for Estimation of S_{total}° for Ferrocyanide

Vibrational Entropy						
mode	vib no.	degeneracy	ω (cm ⁻¹)	ν (298 K)	S/R	S_{vib} (cal deg ⁻¹ mol ⁻¹)
ML ₆	2	1	385	1.86	0.51	1.02
	4	2	409	1.97	0.47	1.86
	7	3	586	2.83	0.24	1.42
	9	3	83	0.401	1.92	11.45
	11	3	105	0.507	1.69	10.08
M-C-N	13	3	61	0.294	2.23	13.27
	5	3	354	1.71	0.58	3.46
	8	3	415	2.00	0.46	2.73
	10	3	506	2.44	0.32	1.93
C≡N	12	3	474	2.29	0.37	2.18
	1	1	2090	10.1	0.0005	0.001
	3	2	2055	9.92	0.0005	0.002
	6	3	2044	9.86	0.0006	0.003
$S_{\text{vib}}(\text{tot.})$						49.39

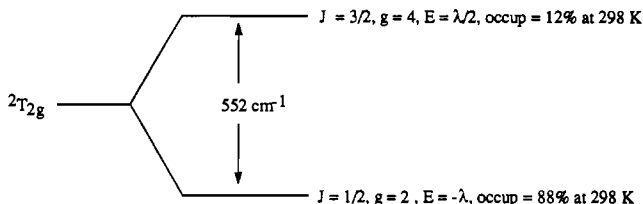
Rotational Energy

$$I_x = I_y = I_z = 4(12.0 \text{ u})(1.90 \text{ \AA})^2 + 4(14.0 \text{ u})(3.038 \text{ \AA})^2 = 690 \text{ u \AA}^2 = 1.15 \times 10^{-37} \text{ g cm}^2; S_{\text{rot}} = 24.76 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

Translational Entropy

$$\text{mass of } [^{56}\text{Fe}(^{12}\text{C}^{14}\text{N})_6]^{4-} = 211.93 \text{ u}; S_{\text{trans}} = 41.95 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

Table III. Details of Electronic Entropy Calculation for Ferricyanide Ion^a

$d^5 \text{ } ^2T_{2g} \zeta(\text{Fe}^{3+}, g) = 460 \text{ cm}^{-1} = -\lambda_0 \lambda[\text{Fe}(\text{CN})_6]^{3-} = 0.80\lambda_0$

$q_{\text{elec}} = 2 + 4(\exp[-(1.439)(552)/298]) = 2.28$
$S = R \ln(q_{\text{elec}}) + E_{\text{therm}} = 1.64 + 0.65 = 2.29 \text{ cal deg}^{-1} \text{ mol}^{-1}$

^a See ref 24 for details of the electronic states of d^5 complexes.

vibrational anharmonicity is not included in eq 3, but its effect on S_{vib}° is small.^{18,22}

Ferrocyanide ion has the highest estimated gas-phase entropy among the complexes in Table I, and a detailed entropic analysis is given in Table II to illustrate the procedures used. The large total entropy is primarily due to the contribution of S_{vib}° (49.4 cal deg⁻¹ mol⁻¹). Of the 12 normal modes in this ion, 3-fold degenerate bending modes (nos. 9, 11, 13) contribute 71% of the total vibrational entropy (Table II)! It is clear that analyses of vibrational entropies for metal complexes must be based on accurate assignments and experimental frequencies for such low-frequency modes (<400 cm⁻¹). Unfortunately, these modes are generally the least well characterized experimentally.

At the other extreme, relatively small S_{vib}° contributions are found for metal-oxide complexes such as RuO_4 , which has formal $\text{Ru}=\text{O}$ bonds and generally higher frequency skeletal modes (for RuO_4 , the stretching modes are at 885 and 921 cm⁻¹, and the bending modes are at 319 and 336 cm⁻¹; compare to ferrocyanide, Table II).

With respect to electronic entropies, it should be noted that the electronic partition function, q_{elec} , and S_{elec}° (eq 4) are not always evaluated accurately from the molecular term symbol for the ground electronic state. Thus, the total electron spin and orbital

$$S_{\text{elec}}^{\circ} = R \ln(q_{\text{elec}}) + E_{\text{therm}} \quad (4)$$

degeneracies expressed in the term symbol cannot always be used in eq 4 since spin-orbit coupling and lowered symmetry can lead to splitting of the ground-state term. The necessary information on the ground-state electron quantum levels can often be deduced from fits of theory to magnetic susceptibility and electron paramagnetic resonance spectra.²³ For our purposes, any low-symmetry components are ignored and only spin-orbit coupling is considered. Species with A or E terms are assumed to have quenched orbital angular momentum,^{23,24} and the multiplicity and orbital degeneracies are used to obtain the electronic partition function q_{elec} in eq 4 (e.g., for FeCl_4^- , which has a 6A ground state, $q_{\text{elec}} = 6 \times 1 = 6$, and for MnO_4^{2-} , which is 2E , $q_{\text{elec}} = 2 \times 2 = 4$).

In the case of T terms, we use the J levels that result from spin-orbit coupling and take thermal occupancy of the higher lying states (E_{therm}) into account. As an example, a $^4T_{2g}$ state in O_h high-spin Co^{II}L_6 has a degeneracy of $4 \times 3 = 12$ in the absence of LS coupling, but the actual S_{elec}° is much lower than $R \ln(12)$ since the coupling lifts the degeneracy of the ground state.² The fit of theory to experiment does not always give unique parameters, so only estimates of energy levels can be made for most compounds. In the cases of $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, we assume that the value of the one electron spin-orbit coupling constant λ is $0.8\lambda_0$ (λ_0 is the free ion value). In terms of ligand field theory, this factor of 0.8 approximately accounts for electron delocalization of electron density onto the ligands and is in the range usually estimated for those two complexes.^{23c} Table III shows an example of the resulting states for ferrocyanide along with thermal occupancies at 298 K.

For the cases of $d^5 \text{ IrCl}_6^{2-}$ and $d^1 \text{ WCl}_6^-$, both with $^2T_{2g}$ ground states, the spin-orbit coupling constants are so large that only the lowest states are significantly occupied at room temperature ($J = 1/2$ and $J = 3/2$, respectively).²³ Therefore, q_{elec} values are readily estimated by the state degeneracies (2 and 4, respectively) and $S_{\text{elec}}^{\circ} = R \ln(q_{\text{elec}})$.

The entry given for $S_{\text{int rot}}^{\circ}$ in Table I for $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is based on the assumption of unhindered rotation of the ammonias in the complex.²¹ If the ammonias were to have large barriers to internal rotation, a total of six torsion vibrational modes would be present and would contribute to S_{vib}° .²⁵ However, the assumption of unhindered rotation seems reasonable in view of results for $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ hexaammines (as the iodide salts), which have rotational barriers in the range of $\sim 200 \pm 50 \text{ cm}^{-1}$.²⁵ Such low barriers will have only a small effect on the estimated $S_{\text{int rot}}^{\circ}$ at 298 K (on the order of 1–2 cal deg⁻¹ mol⁻¹ for the molecule). Furthermore, the barriers determined for salts depend on the counterion²⁶ and therefore have questionable validity for the complex ions in solution. In our previous publication on metal hexaammines,² the entropic contributions of these internal NH_3 rotations were assumed to cancel out for the 2+ and 3+ complexes and thus do not contribute to $\Delta S_{\text{rc}}^{\circ}$.

Note that estimates based on eq 2 for gas-phase ions in Table I will be poorer than those for neutrals since structural and spectroscopic data are for condensed-phase forms (i.e., salts or

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Table IV. Estimated Contributions of Vibrational and Electronic Entropy Changes to Reaction Entropies for Transition-Metal Redox Couples^a

complex	S_{vib}°	S_{elec}°	$\Delta S_{\text{vib,elec}}^{\circ}$	$\Delta S_{\text{rc}}^{\circ}$
Cp_2Fe^+	17.2	1.7		
Cp_2Fe	14.9	0	-4.0	-5 to +14 ^b
$[\text{Fe}(\text{CN})_6]^{3-}$	51.1	2.3		
$[\text{Fe}(\text{CN})_6]^{4-}$	49.4	0	-4.0	-41.5 ^c
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	24.1	1.4		
$[\text{Ru}(\text{NH}_3)_6]^{2+}$	26.1	0	0.6	18.5 ^d
$[\text{Co}(\text{NH}_3)_6]^{3+}$	20.0	0		
$[\text{Co}(\text{NH}_3)_6]^{2+}$	34.9	2.5	17.4	~45 ^e
IrCl_6^{2-}	30.5	1.4		
IrCl_6^{3-}	30.5	0	-1.4	
WCl_6	30.0	0		
WCl_6^-	31.5	2.8	4.3	
RuO_4	6.86	0		
RuO_4^-	7.19	2.8	3.1	
RuO_4^{2-}	6.99	2.2	-0.8	
MnO_4^-	6.01	0		
MnO_4^{2-}	7.09	2.8	3.9	
MnO_4^{3-}	7.39	2.2	-0.3	
FeCl_4^-	19.4	3.6		
FeCl_4^{2-}	23.1	4.6	4.7	

^a All entropy values have units of $\text{cal deg}^{-1} \text{mol}^{-1}$. ^b Taken from ref 6. $\Delta S_{\text{rc}}^{\circ}$ values were solvent dependent, ranging from -5 to 14 $\text{cal deg}^{-1} \text{mol}^{-1}$ in nine different solvents. ^c Taken from ref 5b. Values obtained in water. ^d Taken from ref 5a. Values obtained in water. ^e Estimated. Values of $\Delta S_{\text{rc}}^{\circ}$ for $[\text{M}(\text{bpy})_3]^{3+/2+}$, $[\text{M}(\text{en})_3]^{3+/2+}$, $[\text{M}(\text{NH}_3)_6]^{3+/2+}$, and $[\text{M}(\text{H}_2\text{O})_6]^{3+/2+}$ couples are typically determined or estimated to be $22 \pm 4 \text{ cal deg}^{-1} \text{mol}^{-1}$ higher for $\text{M} = \text{Co}$ than for $\text{M} = \text{Ru}$.³³

solution). However, it is clear for both neutrals and ions that the contributions of S_{vib}° are relatively much larger than normally encountered for small organic and nonmetal inorganic molecules.

Vibrational and Electronic Contributions to Reaction Entropies of Redox Couples

In order to calculate $\Delta S_{\text{vib}}^{\circ}$ and $\Delta S_{\text{elec}}^{\circ}$ contributions to $\Delta S_{\text{rc}}^{\circ}$ values, spectroscopic data for both members of the redox couple are required. Again, vibrational data are usually taken from studies of solids or salts²⁷ and must be considered approximations of the frequencies in solution where the electrode potentials are determined. However, this approximation is probably not severe.²⁸

Calculations for a variety of metal complexes are summarized in Table IV. Where possible, experimentally determined values of $\Delta S_{\text{rc}}^{\circ}$ have also been included. The estimates in Table IV show that $\Delta S_{\text{vib}}^{\circ}$ is expected to be a small contributor to $\Delta S_{\text{rc}}^{\circ}$ in cases where the occupancy of strongly antibonding or bonding molecular orbitals does not change ($\Delta S_{\text{vib}} < 2 \text{ cal deg}^{-1} \text{mol}^{-1}$,

(27) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986.

(28) Comparison of cases in ref 27 indicates shifts are generally <10%.

$T\Delta S_{\text{vib}}^{\circ} < 0.6 \text{ kcal mol}^{-1}$ at 298 K). The case of $\text{Co}(\text{III}/\text{II})$, which involves a spin change, illustrates an upper limit ($\sim 15 \text{ cal deg}^{-1} \text{mol}^{-1}$ for the hexaammine couple in Table III) to what might be expected for typical one electron couples of octahedral complexes. Reduction of $\text{Co}(\text{III})$ to $\text{Co}(\text{II})$ leads to an additional two electrons in the antibonding e_g^* level causing a significant decrease in skeletal frequencies. In addition, the $\text{FeCl}_4^{-/2-}$ couple has an estimated $\Delta S_{\text{vib}}^{\circ}$ of $\sim 4 \text{ cal deg}^{-1} \text{mol}^{-1}$. Here, the symmetrical stretching mode goes from 330 to 266 cm^{-1} . It is interesting to note that reduction can lead to a negative value for $\Delta S_{\text{vib}}^{\circ}$. For the couples $\text{Cp}_2\text{Fe}^{+/0}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$ (Table IV), reduction causes a stiffening of the M-L skeletal modes resulting in a loss of entropy.

In comparison of the relative magnitudes of $\Delta S_{\text{vib,elec}}^{\circ}$ and $\Delta S_{\text{rc}}^{\circ}$ in Table IV, and other values,⁵ for highly charged ions of small radii a large $\Delta S_{\text{solv}}^{\circ}$ accompanying the change in charge renders the contribution of $\Delta S_{\text{vib,elec}}^{\circ}$ to $\Delta S_{\text{rc}}^{\circ}$ small for the majority of cases. For 0/- and +/0 couples, or for ions of large radii such as $[\text{M}(\text{bipy})_3]^{3+}$, $\Delta S_{\text{solv}}^{\circ}$ is smaller and so $\Delta S_{\text{vib,elec}}^{\circ}$ can make a relatively larger contribution to $\Delta S_{\text{rc}}^{\circ}$. For example, $\Delta S_{\text{vib,elec}}^{\circ}$ for $\text{Cp}_2\text{Fe}^{+/0}$ is $-4 \text{ cal deg}^{-1} \text{mol}^{-1}$, while $\Delta S_{\text{rc}}^{\circ}$ values ranging from -5 to 14 $\text{cal deg}^{-1} \text{mol}^{-1}$ have been obtained in different solvents⁶ (Table IV). For the redox couple $[(\text{COT})\text{Fe}(\text{CO})_3]^{0/-}$ ($\text{COT} = \text{cyclooctatetraene}$) a value for $\Delta S_{\text{total}}^{\circ}$ in the gas phase has recently been experimentally determined to be 8.7 $\text{cal deg}^{-1} \text{mol}^{-1}$.²⁹ For this couple the Born model predicts a value for $\Delta S_{\text{solv}}^{\circ}$ to be negative by a few $\text{cal deg}^{-1} \text{mol}^{-1}$.

Conclusions

Vibrational degrees of freedom can contribute significantly to absolute entropies of metal complexes and to reaction entropies for redox couples. It appears that it is inadequate to attribute $\Delta S_{\text{rc}}^{\circ}$ entirely to $\Delta S_{\text{solv}}^{\circ}$ when considering entropy changes for redox couples involving complex metal ions. In special cases such as the $\text{Co}(\text{III})/\text{Co}(\text{II})$ couples considered here, intramolecular entropy changes may contribute significantly to $\Delta S_{\text{rc}}^{\circ}$ even for ions of quite small radii. In the case of redox couples involving large ions such as $[\text{Co}(\text{bipy})_3]^{3+/2+}$ differential solvation effects are small and $\Delta S_{\text{rc}}^{\circ}$ can be attributed almost entirely to intramolecular entropy changes.

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