frequency of 409 cm^{-1} for $[Ru(NH_3)_6]$ Cl_2 is a very rational compromise between the two extremes which have been considered plausible for this vibration. Some precedent for this range of frequencies for ruthenium(II) ammines exists in the reported Ru–NH$_3$ stretching modes assigned from ~390 to 450 cm^{-1} for a series of $[Ru(NH_3)_5(N_2)]^{2+}$ salts.[14]

The factors which determine the intensity of the T_{1u} metal–ligand vibration in the infrared spectrum are not well understood. The controversy which persisted for years regarding assignment of the T_{1u} stretching vibration in $[Co(NH_3)_6]Cl_3$ was a direct result of the low intensity exhibited by this symmetry allowed T_{1u} vibrational mode. Shimanouchi and Nakagawa[15] have suggested a correlation between the ionicity of the M–N bond and the intensity of the infrared T_{1u} absorption which seems applicable in the case of the two hexaamminecobalt complexes. The Co(II)–N bond is more ionic than the Co(III)–N bond, and a lower frequency, more intense T_{1u} mode is observed for hexaamminecobalt(II) than for $[Co(NH_3)_6]^{3+}$. However, this intensity pattern is reversed for hexaammineruthenium complexes where the $[Ru(NH_3)_6]^{3+}$ T_{1u} vibration is sufficiently intense to be observed at 463 cm^{-1} in routine spectra while the $[Ru(NH_3)_6]^{2+}$ Ru–N stretching mode is extremely weak and therefore difficult to locate. It may be that a more valid correlation between infrared intensity and metal properties lies in the electronic structure since both of the hexaammines with very weak M–N infrared absorptions are low-spin d^6 metal ions. It should be noted, however, that Griffith's vibrational study of the low-spin d^6 $[M(NH_3)_6]^{3+}$ (M = Rh, Ir) ions does not indicate an anomalously low intensity for ν_3 (T_{1u}) in these complexes.[12]

The original goal of comparing Ru(II)–N force constants for the octahedral pyridine and ammine complexes of ruthenium(II) is now accessible. Utilizing the rigid-ligand MX_6 model leads to eq 2.[3] Insertion of 326 cm^{-1} for $\tilde{\nu}_3$(py) and

$$\frac{(f_d - \delta)_{py}}{(f_d - \delta)_{NH_3}} = \left[\frac{m_{py}(m_{Ru} + 2m_{NH_3})}{m_{NH_3}(m_{Ru} + 2m_{py})}\right]\frac{[\tilde{\nu}_3(py)]^2}{[\tilde{\nu}_3(NH_3)]^2} \quad (2)$$

409 cm^{-1} for $\tilde{\nu}_3(NH_3)$ as measured for $[Ru(NH_3)_6]Cl_2$ leads to a ratio of 1.54 for the force constants characterizing pyridine and ammonia bound to ruthenium(II). As discussed previously, the interaction force constant for trans M–X bonds, δ, is expected to be small compared to the bond-stretching force constants, f_d.[3] To the extent that the δ term is not negligible it would only serve to reinforce the conclusion that the ruthenium–pyridine bond has a substantially larger force constant than the ammine analogue since coupling in the ammine complex is through σ-only bonds and is likely to be small.[12]

Identification of the T_{1u} (Ru–N) stretching frequency in $[Ru(NH_3)_6]Cl_2$ allows one to calculate a ratio of Ru(III)/Ru(II) force constants on the basis of the square of the observed frequencies since the mass factors are identical and thus cancel. A ratio of $f_3(Ru(III)–N)/f_2(Ru(II)–N) = (463\ cm^{-1}/409\ cm^{-1})^2 = 1.28$ results for the $Ru(NH_3)_6{}^{3+/2+}$ complexes.

Calculation of the inner-sphere rearrangement energy for the rate of electron transfer in the $Ru(NH_3)_6{}^{3+/2+}$ exchange reaction can be accomplished in terms of eq 3[2] where the force

$$\Delta G_{in}* = 6f_2f_3(\Delta a)^2/2(f_2 + f_3) \quad (3)$$

constants, f_i, refer to the Ru–N bonds for the divalent and trivalent metal centers and Δa is the 0.04-Å difference between the equilibrium Ru–N bond distances.[9] Brown and Sutin calculated $\Delta G_{in}*$ to be 0.9 kcal mol^{-1} on the basis of the assumption that $f_3 = f_2 = 2.5$ mdyn/Å. Employing the f_3/f_2 ratio of 1.28 reported here and retaining the f_3 value of 2.5 mdyn/Å imply that f_2 is approximately 2.0 mdyn/Å and $\Delta G_{in}*$ for $Ru(NH_3)_6{}^{3+/2+}$ is then 0.8 kcal mol^{-1}. It is clear that the inner-sphere reorganizational energy is indeed very small for the hexaammineruthenium redox couple regardless, but the quantitative basis provided by the $Ru(NH_3)_6{}^{2+}$ infrared data reported here supplies the final piece of experimental information required to eliminate discrepancies in the input for such calculations.[2,9]

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Registry No. $[Ru(NH_3)_6](BF_4)_2$, 16446-60-9; $[Ru(NH_3)_6](PF_6)_2$, 72496-76-5; $[Ru(NH_3)_6]Cl_2$, 15305-72-3; $[Ru(NH_3)_6]I_2$, 16446-59-6; $[Ru(NH_3)_6]Br_2$, 16446-58-5; $[Ru(ND_3)_6]Br_2$, 72496-75-4.

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Functional Dependence upon Ligand Composition of the Reaction Entropies for Some Transition-Metal Redox Couples Containing Mixed Ligands

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Although a knowledge of the entropies and enthalpies of reaction $\Delta S°$ and $\Delta H°$ is important for unraveling the factors influencing the kinetics of electron-transfer processes,[1] such information has been surprisingly scarce for transition-metal redox couples. We have recently pointed out that measurements of the temperature dependence of formal potentials using a nonisothermal cell arrangement provide a simple method of evaluating the difference $\Delta S°_{rc}$ ($=\bar{S}°_{red} - \bar{S}°_{ox}$) between the absolute ionic entropies $\bar{S}°$ of the reduced and oxidized halves of the redox couple.[2] Besides furnishing a direct route to the determination of $\Delta S°$ and $\Delta H°$ for appropriate pairs of redox couples, these "reaction entropies" $\Delta S°_{rc}$ are of particular interest since they provide a sensitive monitor of the changes in solvent polarization that are necessary in order for electron transfer to occur.[2,3] An approximately linear correlation has also been found between $\Delta S°_{rc}$ and the activation free energies of corresponding outer-sphere self-exchange processes.[3] The experimental values of $\Delta S°_{rc}$ for simple octahedral M(III/II) couples in aqueous media have been found to be dependent upon the nature of the ligands to a much greater extent than predicted by the dielectric-continuum Born model.[2] These latter results suggest that specific interactions between individual ligands and surrounding water molecules play an important role by influencing the extent of overall solvent polarization induced by changes in the metal oxidation state.[2]

Of interest in this connection is the effect of stepwise alterations in the ratio of the number of the ligands L′ and L″ upon $\Delta S°_{rc}$ for redox couples such as $M^{III}L'_mL''_n + e^- \rightleftarrows M^{II}L'_mL''_n$. Fundamental studies of electron-transfer kinetics typically employ such "mixed-ligand" complexes. It is therefore desirable to understand the functional dependences of $\Delta S°_{rc}$ upon m and n both to yield further insight into the various ligand influences upon the solvent polarization and to

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Table I. Reaction Entropies ΔS°_{rc} for Various Redox Couples of the Type $ML'_mL''_n$III/II

redox couple[a]	E°,[b] mV vs. SCE at 25 °C	ΔS°_{rc},[c] eu	$(\Delta S^\circ_{rc})^{estd}$,[d] eu	$(\Delta S^\circ_{rc})^{Born}$,[e] eu
$Ru(bpy)_3{}^{3+/2+}$	1048 (0.1),[f] 1100[g]	1,[f,i,k] 0[g,j]		7.0
cis-$Ru(NH_3)_2(bpy)_2{}^{3+/2+}$	642 (0.1)[f]	6.5[f,i,k]	7	8.6
$Ru(NH_3)_4bpy^{3+/2+}$	284 (0.1)[f]	12.5[f,i,k]	12.5	10.9
$Ru(NH_3)_4phen^{3+/2+}$	289 (0.1)[f]	14.5[f,i,k]		10.5
$Ru(NH_3)_5py^{3+/2+}$	73 (0.1)[f]	17[f,i,k]	15.5	12.6
$Ru(NH_3)_6{}^{3+/2+}$	−175 (0.1)[f]	18.5[f,i,k]		14.6
$Ru(NH_3)_5OH_2{}^{3+/2+}$	−162 (0.2)[h]	25[h,i]	21.5	14.5
cis-$Ru(NH_3)_4(OH_2)_2{}^{3+/2+}$	−135 (0.1)[h]	26[h,i]	24.5	14.5
$Ru(OH_2)_6{}^{3+/2+}$	−16 (0.3)[h]	36[h,i]		14.5
cis-$Ru(OH_2)_2(bpy)_2{}^{3+/2+}$	640 (1.0)[f]	6[f,i,l]	12.5	8.5
trans-$Ru(OH_2)_2(bpy)_2{}^{3+/2+}$	457 (1.0)[f]	6[f,i,l]	12.5	8.5
$Fe(bpy)_3{}^{3+/2+}$	845 (0.05),[h] 875 (0)[g]	2,[d,h] −1.5[e,g]		7
$Fe(CN)_4bpy^{-/2-}$	298 (0)[g]	−29[e,g]	−28	−5.5
$Fe(CN)_6{}^{3-/4-}$	110(0)[g]	−41.5[e,g]		−15
ferricinium/ferrocene	127 (0.1)[f]	−5[f,i,k]		2.5

[a] bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, py = pyridine. [b] Standard (or formal) electrode potential for redox couple vs. saturated calomel electrode in isothermal cell at 25 °C, determined at ionic strength indicated in parentheses. From reference sources indicated. [c] Experimental reaction entropy of redox couple.[6] Determined at or extrapolated to ionic strength $\mu = 0.1$ M. From reference sources indicated. [d] Reaction entropy for mixed-ligand couples, estimated from the experimental values for the corresponding two pure ligand couples by linear interpolation (see text). [e] Reaction entropy calculated from the Born model.[11] [f] This work. [g] References 7, 9, 10. [h] Reference 2. [i] ΔS°_{rc} determined from cyclic voltammetry by using nonisothermal cell arrangement as described in ref 2. Precision of quoted values ±1 eu. [j] Recalculated from isothermal cell data.[6] [k] Obtained from cyclic voltammetry by using platinum and glassy carbon indicator electrodes. Supporting electrolyte was 0.1 M CF_3COONa/CF_3COOH (results were pH independent). Sources of redox couples: ferrocinium picrate; $Ru(bpy)_3\cdot Cl_2\cdot 6H_2O$; $Ru(NH_3)_2(bpy)_2\cdot(ClO_4)_2$; $Ru(NH_3)_4phen\cdot(CF_3SO_3)_2\cdot 3H_2O$. Solutions of $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_4bpy^{2+}$ were prepared by cathodically electrolyzing solutions of $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_4Cl_2{}^{+}$ and by adding a slight stoichiometric excess of pyridine and bipyridine, respectively. [l] Values at $\mu = 0.1$ unobtainable due to hydrolysis.[16] (The value given in ref 2 that was obtained in 0.1 M acid is unreliable for this reason.) Quoted values estimated at $\mu = 0.1$ from experimental values of ΔS°_{rc} obtained in 1 M *p*-toluenesulfonic acid (8.5 eu for both cis and trans isomers) by using values obtained for corresponding conditions for *cis*-$Ru(NH_3)_2(bpy)_2{}^{3+/2+}$ [9 eu ($\mu = 1$), 6.5 eu ($\mu = 0.1$)]. *cis*-$Ru(OH_2)_2(bpy)_2{}^{2+}$ obtained by dissolving $Ru(bpy)_2CO_3\cdot 2H_2O$ in 1 M acid and *trans*-$Ru(OH_2)_2(bpy)_2{}^{2+}$ by exposing solutions of the cis isomer to daylight.[15]

allow interpolation and extrapolation of ΔS°_{rc} values between related redox couples. Aside from the Born model which treats such nonsymmetrical complexes as uniformly charged spheres, the simplest approach is to consider that the observed values of ΔS°_{rc} arise from independent additive contributions from each ligand. This latter model also forms the basis of the empirical entropy correlations of George et al.[4] In this communication, the suitabilities of such simple treatments for predicting reaction entropies for mixed-ligand complexes are scrutinized by using the presently available experimental data, including some new values of ΔS°_{rc} for Ru(III/II) couples containing ammine, aquo, and polypyridine ligands. These ruthenium couples are of particular interest since there are only small and known differences in size between the oxidized and reduced forms.[5]

In Table I are summarized experimental values of ΔS°_{rc} for octahedral redox couples of the type $ML'_mL''_n$ III/II for which values are also available for the corresponding "pure-ligand" couples ML'_x III/II and ML''_y III/II.[6] Listed for each couple is the reaction entropy $(\Delta S^\circ_{rc})^{Born}$ that is calculated by using the Born model.[11] Also given for the mixed-ligand couples are reaction entropies $(\Delta S^\circ_{rc})^{estd}$ that were estimated by linear interpolation from the experimental values of ΔS°_{rc} for the corresponding two pure ligand couples, i.e., by assuming that the two types of ligands provide additive contributions to ΔS°_{rc} that are proportional to the number of each ligand type present in the mixed-ligand couples.

For the Ru(III/II) couples containing ammine and bipyridine ligands, excellent agreement is seen between ΔS°_{rc} and $(\Delta S^\circ_{rc})^{estd}$, whereas the Born model fails to predict the marked decreases in ΔS°_{rc} that are observed as the number of bipyridine groups increases, particularly in going from *cis*-$Ru(NH_3)_2(bpy)_2{}^{3+/2+}$ to $Ru(bpy)_3{}^{3+/2+}$. These results suggest that differences in local solvation of the individual ligands of a type determined by the ligand structure, rather than changes in the average distance of closest approach of the solvent to the metal charge center, are largely responsible for the observed large variations in ΔS°_{rc}. This is perhaps not surprising for complexes containing large ligands such as bipyridine where a number of the solvating water molecules will lie in the vicinity of the aromatic rings away from the metal charge center and the other ligands. The addition of an electron to such Ru(III) complexes to form Ru(II) could well give rise to two competing effects upon the surrounding solvent structure. The water molecules close to the ruthenium center, including those surrounding any ammine ligands, will be less polarized and therefore less "ordered" in the lower oxidation state, giving rise to a positive contribution to ΔS°_{rc}. However, the water molecules adjacent to the bipyridine rings

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(6) It should be noted that the values of ΔS°_{rc} quoted here are the quantities measured by using (or recalculated for) nonisothermal electrochemical cell measurements with the reference electrode held at a fixed temperature.[2] Since in all probability the thermal junction potentials can be arranged to be very small,[2] such quantities are essentially equal to $(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})$. Such "absolute" values of ΔS°_{rc} should be carefully distinguished from other commonly quoted "reaction entropies" such as those referring to the overall cell reaction ox + $^1/_2H_2 \rightleftarrows$ red + H^+ (ΔS°_H) or those obtained by arbitrarily setting the ionic entropy of the aqueous proton, $\bar{S}^\circ_{H^+}$, equal to zero.[2,7] Since $\bar{S}^\circ_{H_2} = 31.2$ eu and from nonisothermal cell measurements and other considerations[8] $\bar{S}^\circ_{H^+} \simeq -5$ eu, then $\Delta S^\circ_{rc} \simeq \Delta S^\circ_H + 20.5$ eu.

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(11) Determined by using the relation[12] $(\Delta S^\circ_{rc})^{Born} = 9.65(Z_{ox}^2/\bar{a}_{ox} - Z_{red}^2/\bar{a}_{red})$, where Z_{ox} and Z_{red} are the net charges and $\bar{a}_{ox}$ and $\bar{a}_{red}$ are the equivalent radii[5] (in Å) of the oxidized and reduced species, respectively. Values of $\bar{a}$ either taken from ref 5 or estimated from ionic radii.

(12) For example, see R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

could well experience an increase in polarization in going to the Ru(II) state since the added t_{2g} electron will be significantly delocalized around the aromatic rings, acting to increase their net charge density. This latter effect would yield a negative contribution to $\Delta S^\circ_{\rm rc}$ which will be roughly proportional to the number of pyridine rings. Therefore the stepwise replacement of ammine by bipyridine or pyridine ligands would result in an approximately linear decrease in $\Delta S^\circ_{\rm rc}$, as observed. For $Ru(bpy)_3^{3+/2+}$, these two effects presumably cancel, yielding $\Delta S^\circ_{\rm rc} \approx 0$. The small (or slightly negative) values of $\Delta S^\circ_{\rm rc}$ observed for Ru(III/II), Fe(III/II), and Os(III/II) polypyridine couples have been previously ascribed to the efficient shielding of the metal center from the solvent by these ligands.[10] This latter explanation seems less reasonable since the polypyridine ligands will allow some solvent molecules to approach close to the metal center along the open channels formed by the planar aromatic rings. Also, the markedly larger values of $\Delta S^\circ_{\rm rc}$ (22 eu) observed for both $Co(bpy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ [2] can be more easily understood on the basis of the present model. These Co(III) → Co(II) reactions involve the electronic conversion $t_{2g}^6 \rightarrow t_{2g}^5e_g^2$ which should minimize the extent of electron delocalization in the reduced state and therefore discourage any increase in solvent polarization in the vicinity of the pyridine rings. This change in electronic configuration will also yield a marked expansion of the cobalt center[13] and hence an especially large decrease in the polarization of nearby water molecules.[3]

We have obtained further evidence that favors the present interpretation from the observation that the ferrocinium/ferrocene couple has a distinctly *negative* value of $\Delta S^\circ_{\rm rc}$ in aqeous media (−5 eu, Table I). Since this couple is of the charge type +1/0, the simple dielectric polarization model predicts a small positive value of $\Delta S^\circ_{\rm rc}$. Although the added electron will be substantially delocalized around the cyclopentadienyl rings in a manner similar to the polypyridine couples, the "sandwich" structure of the ferrocinium/ferrocene couple should largely prevent the close approach of solvent molecules to the metal center. Consequently in this case the predominant contribution to $\Delta S^\circ_{\rm rc}$ is anticipated to be the increased polarization of water molecules adjacent to the aromatic rings in the lower oxidation state, in accordance with the observed negative value of $\Delta S^\circ_{\rm rc}$. Negative values of $\Delta S^\circ_{\rm rc}$ have also been observed for some blue copper protein couples having the charge type +1/0 and have been interpreted in terms of hydrophobic effects in the vicinity of the copper redox center.[14]

The large values of $\Delta S^\circ_{\rm rc}$ typically observed for aquo couples have been attributed to field-assisted hydrogen bonding between the aquo ligands and surrounding water molecules.[2] As noted previously,[2] substitution of a single aquo ligand into $Ru(NH_3)_6^{3+/2+}$ yields a proportionately larger increase in $\Delta S^\circ_{\rm rc}$ than those which result from subsequent aquo substitutions (Table I). However, there is reasonable agreement between $\Delta S^\circ_{\rm rc}$ and $(\Delta S^\circ_{\rm rc})^{\rm estd}$ for *cis*-$Ru(NH_3)_4(OH_2)_2^{3+/2+}$ (Table I). On the other hand, substitution of one bipyridine in $Ru(bpy)_3^{3+/2+}$ by two aquo ligands in either a cis or trans configuration[15] yields somewhat smaller values of $\Delta S^\circ_{\rm rc}$ compared with $(\Delta S^\circ_{\rm rc})^{\rm estd}$ (Table I). It is possible that the extent of hydrogen bonding involving aquo ligands is very sensitive to the electrostatic and steric environment. It therefore may be generally difficult to predict accurate values of $\Delta S^\circ_{\rm rc}$ for mixed-ligand couples containing aquo ligands.

Since a large number of complexes employed in redox kinetics contain anionic as well as neutral ligands, it is of interest to examine the stepwise changes in $\Delta S^\circ_{\rm rc}$ that occur as anions are substituted into the coordination sphere. Substantial and even qualitative changes in $\Delta S^\circ_{\rm rc}$ are generally expected from the Born model as well as from local solvation effects due to the variations in the overall charges of the complexes. Unfortunately, suitable data are extremely sparse. Table I contains data for three Fe(III/II) couples containing bipyridine and/or cyanide ligands. Again it is seen that the estimated values $(\Delta S^\circ_{\rm rc})^{\rm estd}$ for the mixed-ligand couple $Fe(CN)_4bpy^{-/2-}$ is in reasonable agreement with the experimental value of $\Delta S^\circ_{\rm rc}$, whereas the Born model fails to provide adequate estimates of $\Delta S^\circ_{\rm rc}$ for all three couples.

It therefore appears that the assumption that the reaction entropies for mixed-ligand couples arise from simple linear additive contributions from each ligand can provide a useful, albeit approximate, means of estimating $\Delta S^\circ_{\rm rc}$ under some circumstances. However, often one or both $\Delta S^\circ_{\rm rc}$ values for the corresponding pure ligand couples are unavailable. Inasmuch as the values of $\Delta S^\circ_{\rm rc}$ are often expected to depend chiefly on the ligands and the charge type of the redox couple,[2] the required reaction entropies could be inferred from those for other couples containing the same ligands. George et al.[4] have given empirical parameters for various ligands obtained from ionic entropy data that allow estimates of $\Delta S^\circ_{\rm rc}$ to be obtained for couples containing these ligands. We have pointed out that this approach has limitations since in some cases $\Delta S^\circ_{\rm rc}$ can be significantly dependent on the nature as well as the charges of the central metal ions.[2,3] Nevertheless, the method could be usefully employed, albeit with caution, to estimate the *changes* in $\Delta S^\circ_{\rm rc}$ resulting from minor alterations in ligand composition.

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Registry No. Ru, 7440-18-8; Fe, 7439-89-6; bpy, 366-18-7; phen, 66-71-7; py, 110-86-1.

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Formation of Extrinsic (Pt^{3+}-Doped) Magnus' Green Salt in the Platinum(II)-Catalyzed Substitution Reactions of Platinum(IV) Complexes

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Magnus' green salt (MGS), $Pt(NH_3)_4PtCl_4$, has long been of interest as a quasi-one-dimensional semiconductor.[1,2] This is because the alternate cation and anion stacking in the crystal structure[3] permits strong overlap of the Pt(II) d_{z^2} orbitals and

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