Table II. Selected NMR Parameters for Triorganotin Compounds

compd[a]	$^{2}J(^{1}H-^{119}Sn)$, Hz	$^{1}J(^{13}C-^{119}Sn)$, Hz	$\delta(^{119}Sn)$, ppm
Me_3SnCl	58.5	379	165.7
$[tmpH_2][Me_3SnCl_2]$	60.0	400	120[c] 56.5[d]
$[Et_4N][Me_3SnCl_2]$	70.5[b]		−53[e]
$[Bu_4N][Me_3SnCl_2]$	70.8	522	−22.13

[a] $CDCl_3$ solution, 33.3 mol %, 303 K, unless otherwise noted. [b] Holmes, R. R.; et al. *J. Organomet. Chem.* **1980**, *197*, 181. [c] CH_2Cl_2 solution, 0.2 M, 303 K. [d] CH_2Cl_2 solution, 0.2 M, 225 K. [e] Reference 18a.

nonequivalence of the Sn–Cl bond contacts exhibited by the tin anion of the cationic Mo(IV) complex cannot be interpreted, since only two structural parameters were communicated.[15] The self-association observed for Me_3SnCl in the solid state is apparently disrupted on melting, as demonstrated from reduced IR and Raman ν(Sn–Cl) stretching frequencies.[16] The essentially linear Cl–Sn–Cl bond angle and dissimilar Sn–Cl bond interactions of **1**, then, would appear to reflect the influence of hydrogen bonding in the solid state for this complex. In the solid state, it seems reasonable to conclude that the protons of the tetramethylpiperidinium cation are involved in strong, hydrogen-bonding interactions with an axial chlorine of the tin anion and would be responsible for weakening the Sn–Cl(2) bonding interaction. Comparison of the structural distortions of the C–Sn–C and C–Sn–Cl bond angles of **1** with the complexes in Table I, as well, further reflects distortions from the idealized TBP geometry for the anion.

The solution-state ^{1}H, $^{13}C\{^{1}H\}$, and $^{119}Sn\{^{1}H\}$ NMR spectra of **1**, along with data for related complexes, were measured, and selected data are summarized in Table II. The important information lies in the magnitudes of the $^{1}J(^{13}C-^{119}Sn)$, $^{2}J(^{1}H-^{119}Sn)$, and $\delta(^{119}Sn)$. Since both the one-bond and the two-bond coupling constants are related via the Fermi contact term to the s electron density in the bond, their magnitudes have been used to infer valence electron distribution in tin–carbon bonds.[17] The self-association observed for Me_3SnCl in the solid state is apparently disrupted on dissolution, as demonstrated from comparisons of the magnitude of the one- and two-bond coupling constants in solution-state[18] and solid-state NMR studies.[19] The magnitude of both the one- and two-bond coupling in **1** (60.0 and 400 Hz, respectively) as compared to the Et_4N and n-Bu_4N derivatives of $[Me_3SnCl_2]^-$ appear to reflect the influence of hydrogen-bonding effects in solution. The interaction could be interpreted in terms of a redistribution of s electron density in the Sn–C bond, with a concomitant increase in the p character in the Sn–Cl bond in accordance with Bent's principle.[20] Comparison of the $\delta(^{119}Sn)$ values for **1** with those of the same tin anion of the tetraalkylammonium derivatives appears to reflect the influence of hydrogen-bonding effects as well. A marked downfield shift for **1** compared to the other pentacoordinated tin anions is observed. This decrease in the shielding of the tin nucleus could be interpreted as a reduction of the Sn(5d)–Cl(3p) orbital overlap. Moreover, the tin chemical shifts for **1** are strongly temperature dependent. At the low-temperature limit, the structure of the tin anion could be described as distorted halfway between idealized four- and five-coordinate geometries.

The discussed results imply that reaction 1 represents actually an equilibrium situation which is shifted to the side of $[tmpH_2][Me_3SnCl_2]$ at high concentration or low temperature. Experimental proof comes from further ^{119}Sn NMR studies of this compound in solution. In the concentration range 0.03–1.20 M, $\delta(^{119}Sn)$ changes from 170 to 59.7 ppm, the former value corresponding to a highly diluted solution of Me_3SnCl.[18a] Increased shielding indicates formation of the $[Me_3SnCl_2]^-$ anion, but only time-averaged signals are observed at 303 K. The signal at $\delta(^{119}Sn) = 120$ ppm for a 0.2 M solution of **1** at 273 K is shifted to $\delta = 56.6$ ppm at 225 K. This result also indicates that Cl^- exchange is rapid on the NMR time scale even at low temperature. In a related study, the same result is obtained from CH_2Cl_2 solutions containing equivalent amounts of Me_3SnCl and pyridinium chloride, with $\delta(^{119}Sn)$ changing from 160 to 25.8 ppm for solutions ranging in concentration from 0.02 to 2.2 M. In none of these cases was the ^{119}Sn NMR signal for $[Me_3SnCl_2]^-$ observed, which is extrapolated from the concentration dependence of a CH_2Cl_2 solution of $[Bu_4N][Me_3SnCl_2]$ ($\delta(^{119}Sn) = -17.3$ ppm, $c = 0.06$ M; $\delta(^{119}Sn) = -50.9$ ppm, $c = 1.5$ M) to be −58 ppm. The increase in shielding with increasing coordination number is a well-known phenomenon in tin chemistry. However, the observed importance of hydrogen bonding on the stability of higher coordination tin complexes is, to our knowledge, a new feature, in the present case the competition of a Lewis acid and a protic acid for chloride as a base. It is conceivable that such an interaction will play an important role in the bioinorganic chemistry of organotin compounds.[21] A full study of the influence of cation–anion interactions on the pentacoordinated state of triorganotin anions is forthcoming.

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Supplementary Material Available: Details of crystallographic data collection (Table S1), atomic coordinates (Table S2), full bond parameters (Table S3), and anisotropic and isotropic thermal parameters (Tables S4 and S5) (3 pages); observed and calculated structure factors (Table S6) (10 pages). Ordering information is given on any current masthead page.

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Intramolecular Entropy Changes for Transition-Metal Complex Redox Couples: Hexaammineruthenium(III/II) and -cobalt(III/II) Couples

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The entropy change associated with an electron-transfer reaction is equivalent to the difference in the reaction entropies ($\Delta S_{rc}°$) for the two redox couples involved. A reaction entropy value can be derived from the temperature dependence of the electrode potential for a redox couple, and values of $\Delta S_{rc}°$ for a number of transition-metal complex couples have been reported.[1-5]

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Table I. Assignments of Vibrational Frequencies (cm^{-1}) in Hexaamminemetal Complexes[a]

	skeletal M–N vib						ammonia rocking vib[e]			
	ν_1 A_{1g}	ν_2 E_g	ν_3 T_{1u}	ν_4 T_{1u}	ν_5 T_{2g}	ν_6 T_{2u}	T_{1g}	T_{1u}	T_{2g}	T_{2u}
$Ru(NH_3)_6^{3+}$	500	475	463	273	248	175[b]	788	788	788	788
$Ru(NH_3)_6^{2+}$	450	430	409	245[c]	245[c]	170[b]	763	763	763	763
$Co(NH_3)_6^{3+}$	494	442	475	331	322	228[b]	831	831	830	831
$Co(NH_3)_6^{2+}$	357	255	325	192	187[d]	132[b]	654	654	654	654

[a] Data for chloride salts. Except where noted, the frequencies are from the compilations in ref 9. Some frequencies given are averages of observed multiplets. [b] Value for ν_6 obtained from $\nu_6 = 2^{-1/2}\nu_5$. This approximation ignores the contributions of interaction constants to ν_5 and ν_6.[8] [c] T_{1u} bending mode frequency determined in this work. The frequency of the T_{2g} Raman-active mode has not been determined, so the T_{1u} value is used. [d] Value obtained from approximate parallel relationship between variations in frequencies for Co^{3+} and Co^{2+} complexes. [e] T_{1g} and T_{2u} rocking vibrations are infrared and Raman inactive, and the T_{2g} value may be unavailable. Frequencies given are assumed to be the same as for the T_{1u} mode.

Theoretical interpretations[1c,d,2b,6] of the experimental values of $\Delta S_{rc}°$ for substitution-inert complexes have centered on the solvation of the species involved, and the approach taken typically has been based on a Born ion solvation model. Although the general trends in the experimental $\Delta S_{rc}°$ values can be explained by this approach, such models have not been completely satisfactory. For example, an explanation for the consistently greater values[1a,c,d] of $\Delta S_{rc}°$ for many Co(III/II) couples compared to isostructural Ru(III/II) couples has not been given. Values of $\Delta S_{rc}°$ for $[M(bpy)_3]^{3+/2+}$, $[M(en)_3]^{3+/2+}$, $[M(NH_3)_6]^{3+/2+}$, and $[M(H_2O)_6]^{3+/2+}$ couples are typically determined or estimated to be 22 ± 4 cal deg^{-1} mol^{-1} higher for M = Co than for M = Ru. Part of this difference can be attributed to electronic entropy changes ($\Delta S_{in}(el)°$), but the remaining difference is not convincingly explained by models that consider solvation entropies (or "outer-sphere" entropies) alone.

We suggest that a substantial portion of the differences in $\Delta S_{rc}°$ values for these isostructural Co and Ru couples can be attributed to *intramolecular* vibrational entropy changes ("inner-sphere" entropy changes) that accompany oxidation state changes. The role of the inner-sphere entropy changes in redox thermochemistry of metal complexes does not appear to have been considered extensively, and discussions in the literature typically ignore such inner-sphere contributions or assume them to be unimportant.[7] However, changes in metal–ligand bonding that result from a change in metal oxidation state can shift the frequencies of metal–ligand skeletal vibrations. Changes in the vibrational partition function value associated with these degrees of freedom will contribute to an intramolecular entropy change (ΔS_{in}) when the oxidation state changes for a particular metal complex. Furthermore, the magnitude of ΔS_{in} depends on the extent to which various molecular properties change and may be thermochemically significant in some cases.

The total change in entropy attributed to the degrees of freedom of a polyatomic molecule can be expressed as the sum of the translational, rotational, vibrational, and electronic entropy contributions (eq 1). The contributions $\Delta S_{in}(vib)°$ etc. can be

$$\Delta S_{in}° = \Delta S_{in}(vib)° + \Delta S_{in}(rot)° + \Delta S_{in}(trans)° + \Delta S_{in}(el)° \tag{1}$$

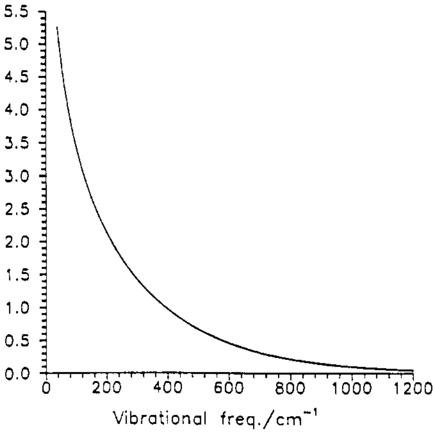

Figure 1. Plot of the entropy contribution of a vibrational mode as a function of the vibrational frequency of the mode (298 K).

evaluated by using the methods of statistical thermodynamics, and values of the molecular entropies for each complex ion can be calculated from the appropriate partition functions q_{vib} etc. We focus here on the $\Delta S_{in}(vib)°$ term, which is given by statistical mechanics by eq 2 (under the harmonic oscillator approximation.)

$$\Delta S_{in}(vib) = R\sum_{i=1}^{n}\left[\left(\frac{x_R}{e^{x_R}-1}\right)-\left(\frac{x_O}{e^{x_O}-1}\right)+\ln\left(\frac{1-e^{-x_O}}{1-e^{-x_R}}\right)\right] \tag{2}$$

In eq 2, the sum is over the n normal modes of the molecules, and x_R and x_O are given by $hc\nu_i/kT$ for the reduced (R) and oxidized (O) forms, respectively, where the ν_i are the vibrational frequencies (in cm^{-1}) of the corresponding normal modes. Equation 2 applies for O/R couples of the type considered here, in which the number of atoms in the complex is the same for O and R (both nonlinear).

The vibrational properties of metal complexes suggest that values of $\Delta S_{in}(vib)°$ could be significant for certain metal complex redox couples. The potential for an increased importance of vibrational entropy changes for metal redox complexes compared to organic couples arises from the frequency dependence of the vibrational partition function and resulting total vibrational entropies for the reduced and oxidized members of the couples. In Figure 1, vibrational entropy is plotted as a function of vibrational frequency at 298 K. It can be seen that $S_{in}(vib)°$ increases dramatically as the frequency of a vibrational mode decreases. For organometallic and coordination compounds, vibrations associated with metal–ligand skeletal modes are typically in the range 100–700 cm^{-1}.[8] Shifts in these frequencies of the magnitude that often accompany a change in formal oxidation state at the metal center may cause significant changes in entropy per vibrational mode, especially for the low-frequency skeletal modes. For octahedral ML_6 complexes, 15 skeletal vibrations enter into the summation in eq 2. Higher frequency vibrations (generally ligand based) contribute less to total entropies, but for hexaammine

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complexes, shifts in the relatively low frequency NH_3 rocking modes (600–800 cm^{-1}) can be significant to entropy changes in redox couples.

In this note we present the results of calculations based on eqs 1 and 2 for the hexaammine couples of cobalt(III/II) and ruthenium(III/II). These couples were chosen since the vibrational properties of hexaammine complexes have been studied in detail by a number of workers.[9] Table I presents the vibrational frequencies observed or estimated for chloride salts of the complexes of interest. It is assumed that the solid-state frequencies are comparable to the actual frequencies in solution (reported[9] skeletal frequencies from Raman spectra of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]^{3+}(aq)$ differ by ≤ 10 cm^{-1}). The least satisfactory compilation is for $[Ru(NH_3)_6]^{2+}$, for which surprisingly few vibrational data are available.[10] The far-infrared spectrum of $[Ru(NH_3)_6]Cl_2$ was therefore determined in this work to provide a value for the T_{1u} bending vibrations.[11] Details of the estimates used are given in the footnotes of Table I. It is clear that frequency shifts in the cobalt case are significant, with the observed T_{1u} M–N stretching band (ν_3) shifting ~150 cm^{-1}, while, in the ruthenium case, the observed shift is ~50 cm^{-1}. The much reduced M–N force constant for Co^{II} relative to Co^{III} can be attributed to the $(d\pi)^5(d\sigma^*)^2$ to $(d\pi)^6$ change in electronic configuration at the metal center.

From the data in Table I and eq 1, the values of $\Delta S_{in}(vib)°$ at 298 K for the $[Co(NH_3)_6]^{3+/2+}$ and $[Ru(NH_3)_6]^{3+/2+}$ couples are estimated to be 15 ± 2 and 2 ± 2 eu, respectively. The estimated error in these values is based on an assumption that the vibrational frequencies in Table I are within 10 cm^{-1} of the true value in aqueous solution, but larger errors in the assumed vibrational frequencies, especially for the estimated ν_6 T_{1u} mode, could lead to a values of $\Delta S_{in}(vib)°$ outside the ranges given.

Another important contribution to $\Delta\Delta S_{rc}$ for these two couples arises from the $\Delta S_{in}(el)°$ values, which are estimated[12] to be ~2.0–2.5 cal deg^{-1} mol^{-1} for the conversion of low-spin cobalt(III) to high-spin cobalt(II) complexes and −1.4 cal deg^{-1} mol^{-1} for reduction of low-spin ruthenium(III) to low-spin ruthenium(II). The total ΔS_{rc} difference between the two couples due to changes in the vibrational and electronic partition functions is therefore estimated as 16 ± 3 eu, which accounts for much of the estimated[2a] experimental difference of ~27 eu. Unfortunately, the hexaamminecobalt(III/II) couple is not conveniently studied electrochemically, so the actual $\Delta S_{rc}°$ value has not been determined. However, given the consistent differences between $\Delta S_{rc}°$ values for Co(III/II) and Ru(III/II) couples,[1,2] the calculations here suggest that approximately half of the difference in $\Delta S_{rc}°$ values for these complexes is attributable to the inner-sphere vibrational term, with the $\Delta S_{in}(el)°$ term accounting for an additional ~4 eu. The remaining difference may be related primarily to the outer-sphere contributions arising from the large Co–N distance change in the cobalt couple.

Although complete vibrational assignments are not available for other related complexes with L = en, bpy, and H_2O, the known vibrational frequency shifts for the Co couples are consistent with the same explanation for the observed higher $\Delta S_{rc}°$ values in comparison to those for low-spin/low-spin Ru and Fe couples. For example, $[Fe(bpy)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ couples have $\Delta S_{rc}°$ values of 2 and 22 eu in water, respectively.[1c] The observed M–N stretching frequencies[8] in the Fe complexes are essentially unchanged between the iron(III) and iron(II) complexes, while the same frequencies shift lower by ~130 cm^{-1} in going from cobalt(III) to cobalt(II). Assuming comparable shifts in other bending and stretching modes of the ML_3 unit, much of the 20 eu difference in $\Delta S_{rc}°$ values could be attributable to the vibrational entropy component, as demonstrated here for the hexaammine case.

In general, changes in vibrational frequencies and electronic degeneracies are expected to dominate intramolecular contributions to redox entropy changes (rotational entropy changes are likely small, on the order of 10^{-1} eu, for typical bond length changes). The emergence of gas-phase methods[14] for assessing entropies of electron attachment and ionization of metal complexes could lead to direct comparisons of experimental and calculated intramolecular entropy changes for redox processes. Details of the statistical mechanical evaluation of entropy changes for a variety of transition-metal complex redox couples will be given in a future article.

Finally, it should be noted that any chemical change at a metal center that leads to significant alteration of the skeletal frequencies of the complex can have an appreciable vibrational contribution to the entropy change of the reaction. Spin equilibrium is an excellent example of such a process, and evaluation of the thermochemistry of such processes with respect to intramolecular vibrational entropies has been illuminating but surprisingly limited.[15]

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(11) Far-IR spectra were obtained for $[Ru(NH_3)_6]Cl_2$ in a polyethylene pellet. The complex was produced via zinc reduction of an aqueous solution of $[Ru(NH_3)_6]Cl_3$ under argon followed by precipitation with NH_4Cl. Isotope studies to confirm the band assignments have not been completed. Assignment of the observed band at ~245 cm^{-1} as the T_{1u} mode must be considered tentative.

(12) In the case of octahedral low-spin d^6 ML_6 complexes of Ru^{II} and Co^{III}, the electronic partition function, q_{el}, is equal to 1 for these $^1A_{1g}$ complexes. For Ru^{III} and high-spin Co^{II} the calculation of q_{el} is complicated by the effects of spin–orbit coupling and Jahn–Teller distortion. For O_h Ru^{III}, the ground state including spin–orbit coupling is $J = {}^1/_2$, with the $J = {}^3/_2$ state higher in energy by $3\lambda/2$ (~1800 cm^{-1} higher on the basis of the free ion value of ζ). Since the higher state is not significantly populated at 298 K, $q_{el} \simeq (2(1/2) + 1) = 2$, and $\Delta S_{in}(el)°$ for $Ru^{III/II}$ $\simeq R \ln (1/2)$. For high-spin O_h Co^{II}, the ground state is also a Kramers doublet with $J = {}^1/_2$, but the two higher lying states ($J = {}^3/_2$ and $J = {}^5/_2$) are thermally accessible. The value of q_{el} will therefore be >2, but the necessary parameters are not available to allow an accurate estimate. For a range of λ values of $0.75\lambda_0$–$1.0\lambda_0$ and an A value[13] of 1.5 and with distortions from cubic symmetry ignored, q_{el} is estimated to be ~2.6–3.2.

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X-ray Diffraction Study of Pentacarbonyl(μ-hydrido)(nonacarbonyldimanganese)rhenium, $HMn_2Re(CO)_{14}$

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Among the large number of polynuclear transition-metal complexes containing bridging hydride ligands, those which contain a hydride bridging two *different* metals are rare.[1] Reliable, high-yield methods for the synthesis of such species are still being

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