Anomalous Temperature Dependence of Isotropic Nuclear Magnetic Resonance Shifts of Paramagnetic Complexes. Nonzero Intercepts

W. D. Perry and Russell S. Drago*

Contribution from the William A. Noyes Laboratory,
University of Illinois, Urbana, Illinois 61801. *Received July 8, 1970*

Abstract: The significance of nonzero intercepts in the temperature dependence of isotropic shifts for paramagnetic complexes has been investigated. A number of systems have been designed in an attempt to elucidate some of the causes for nonzero intercepts. Ion pairing interactions, hydrogen bonding interactions, and temperature dependent chemical equilibria are established as principal causes in the systems investigated. The effect of nonzero intercepts on the coupling constants calculated from such systems by various procedures is critically examined.

In this laboratory,[1-4] we have been interested in the investigation of the nmr contact and pseudocontact shifts of paramagnetic transition metal complexes. In the course of these studies, we have found that the temperature dependence of the isotropic shift of a wide variety of complexes does not have the temperature dependence predicted by the equations for the contact and pseudocontact shifts.

The observed, isotropic shift, $\Delta\nu_{\mathrm{iso}}$, is the sum of contact and pseudocontact contributions. The contact shift is given by the Bloembergen equation[5] where

$$\frac{\Delta\nu_{\mathrm{p}}}{\nu_0} = \frac{-A_i g_{\mathrm{av}}{}^2\beta_{\mathrm{e}}{}^2 S(S+1)}{g_{\mathrm{N}}\beta_{\mathrm{N}}3kT} \tag{1}$$

ν_0 is the probe frequency, A_i is the nuclear spin–electron spin coupling constant (in gauss), g_{av} the average g value of the electron, β_{e} the Bohr magneton, g_{N} the nuclear g value, β_{N} the nuclear magneton, S is the total electron spin of the system, k the Boltzmann constant, and T is the absolute temperature in °K. The pseudocontact shift is given in general form for axial symmetry by the equation[6]

$$\left(\frac{\Delta\nu_{\mathrm{p}}}{\nu_0}\right)_i = \frac{\beta_{\mathrm{e}}{}^2 S(S+1)}{45kT}F(g)\frac{(3\cos^2 X_i - 1)}{R_i{}^3} \tag{2}$$

Here, $F(g)$ is a function of the principal components of the g tensor,[1] X_i is the angle between the principal axis of the molecule and a vector from the metal to the ith nucleus, and R_i is the length of this vector.

Assumptions made in the derivation of eq 1 and 2 greatly restrict their use on inorganic complexes. It was assumed that there was only one thermally populated energy level in the absence of a magnetic field; that there was no zero-field splitting; and that spin–orbit effects produced no more than first-order effects in the magnetic moment.

As can be seen from the above equations, the isotropic shift should have a linear $1/T$ dependence with a zero intercept

$$\Delta\nu_{\mathrm{iso}} = K\frac{1}{T} \tag{3}$$

where K is a constant for a particular complex which includes the quantity of interest in these experiments, A_i. The existence of a nonzero intercept raises questions as to the significance of the value calculated for A_i in these systems. Since the purpose of many nmr studies on paramagnetic systems is to obtain A_i and interpret this quantity (*i.e.*, infer delocalization mechanisms), the full implications of a nonzero intercept must be established.

We have examined a large number of systems and find that "nonzero" intercepts for $\Delta\nu_{\mathrm{iso}}$ *vs.* $1/T$ plots are very common. This type of behavior has been reported several times in the literature.[7-10] However, little effort has been made in the literature to discuss this phenomenon.

Reuben and Fiat[10] proposed that the nonzero intercepts arose from an exponential dependence of the pseudocontact shift on temperature which arises when the tumbling motion of the complex is not characterized by a correlation time τ such that $1/\tau \gg \hbar^{-1}\cdot(|\beta|H_0|g_\parallel - g_\perp|)$. This explanation, though possibly pertinent to the systems discussed by these authors, should not be valid for the reported systems of octahedral Ni(II) and tetrahedral Co(II) since in these cases $(g_\parallel - g_\perp)$ is small. Kurland and McGarvey[11] discussed the relationship of nonzero intercepts and non-Curie law behavior for systems in which zero-field splitting can occur.

Other factors are reported here which very frequently are part of the cause of a nonzero intercept. Under-

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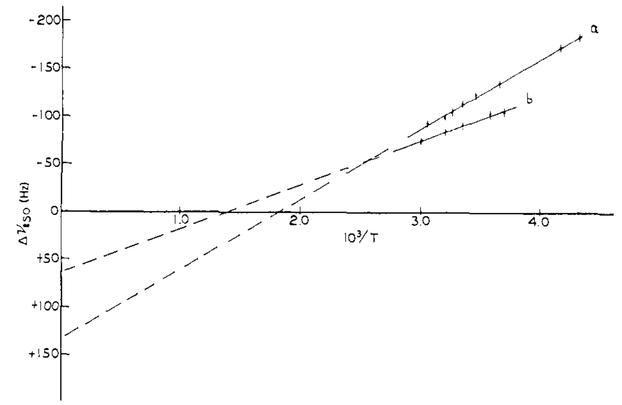

Figure 1. Temperature dependence of isotropic shift for $Co(HMPA)_2Cl_2$: (a) $[Co(HMPA)_2Cl_2]$ = 0.0946 *M*, in $CHCl_3$; (b) $[Co(HMPA)_2Cl_2]$ = 0.0980 *M*, in nitrobenzene.

standing of the causes suggests ways of minimizing the problems and indicates the magnitude of the errors introduced in calculated coupling constants when nonzero intercepts are obtained.

Experimental Section

Apparatus. (a) Nmr Spectra. The nmr spectra were obtained on a Jeolco C-60H spectrometer. All spectra were measured relative to TMS as an internal standard. The temperature was controlled by a Jeolco JES-VT-3 temperature controller to ±0.5° and was measured to ±2° using YSI Model 42SL and 42SC telethermometers. Slopes and intercepts of all plots were determined by a least-squares analysis of the data.

(b) Visible and Near-Infrared Spectra. All near-infrared and visible spectra were determined using a Cary recording spectrophotometer, Model 14RI.

Preparation of Compounds. All compounds measured in this paper were prepared as previously described in the literature or else as described. For each compound, the appropriate reference is given. *Anal.* Calcd for $Co(HMPA)_2X_2$:[12] C, 29.52; H, 7.46; N, 17.22. Found: C, 29.42; H, 7.64; N, 16.95. *Anal.* Calcd for $Co(HMPA)_2Br_2$: C, 24.97; H, 6.30; N, 14.56. Found: C, 25.10; H, 6.50; N, 14.59. *Anal.* Calcd for $Co(pyridine)_2Cl_2$:[13] Co, 20.45; Cl, 24.64. Found: Co, 20.54; Cl, 25.04. *Anal.* Calcd for $Ni(bipyridyl)_3(PF_6)_2$: Ni, 7.18; C, 44.05; H, 2.94. Found: Ni, 7.11; C, 44.00; H, 2.95.

2,2′-Bipyridyl (2 g, 0.0128 mol) and 1 g (0.0042 mol) of $NiCl_2 \cdot 6H_2O$ were added to 50 ml of H_2O and warmed until all solid had dissolved. Benzene was used to extract any excess bipyridyl. HPF_6 (65%) was then slowly added and a pink precipitate formed immediately. The product was filtered, washed with cold water, then with ethanol and ether, and dried over P_2O_5 under vacuum. *Anal.* Calcd for $[Co(CH_3CN)_6](BF_4)_2$:[14] Co, 12.30; C, 30.09; H, 3.76. Found: Co, 12.42; C, 29.37; H, 3.76. *Anal.* Calcd for [Ni(4 methylpyridine *N*-oxide)$_6$]$(ClO_4)_2$:[15] C, 47.40; H, 4.61; N, 9.21. Found: C, 47.29; H, 4.60; N, 9.15. *Anal.* Calcd for $[Co(CH_3CN)_6](ClO_4)_2$:[16] Co, 11.69; C, 28.57; H, 3.57. Found: Co, 11.99; C, 28.35; H, 3.55. *Anal.* Calcd for $[Co(CH_3OH)_6](ClO_4)_2$:[17] Co, 13.09; C, 16.00; H, 5.38. Found: Co, 12.98; C, 15.91; H, 5.22.

Results

In all cases, the experimental shifts were studied over as wide a temperature range as possible. In most systems, the nature of the complex restricted the choice of solvent, the concentrations used, and the temperature range studied. Table I lists the important data for the compounds that will be discussed in this paper.

In Figure 1, we have a plot of $\Delta\nu_{obsd}$ *vs.* $10^3/T$ for $Co(HMPA)_2Cl_2$ in a hydrogen bonding, $CHCl_3$, and a nonhydrogen bonding, nitrobenzene, solvent. The primary coordination sphere of the cobalt in solution was shown to be identical in the two solvents by comparison of the electronic spectra, Table II.

Discussion

In Table I, we have listed a wide range of complexes where the isotropic shifts have been studied as a function of temperature. Most of these data were collected in this laboratory. No attempt is made to discuss each individual complex for which a nonzero intercept is observed. Rather, we shall use a few representative examples in the following discussion to demonstrate the various factors that can give rise to this behavior. The ideas presented here can be easily extended to most of the other complexes found in Table I.

To interpret the observed deviations in the temperature dependence of the isotropic shift, at least three possible sources should be considered: first, an extrapolation error in the graph; second, a temperature dependent chemical change taking place in solution; and third, eq 2 and 3 describing the contact and pseudocontact shifts are not valid for the systems being studied because of magnetic complications, *e.g.*, non-Curie behavior.

Extrapolation Error. The intercepts in each case require a very large extrapolation and were determined by a least-squares treatment of the nmr data. A close look at Figure 1 shows that one is unable to force a zero intercept on these systems by proposing reasonable errors in the data.[18] Thus, Table I contains several well-documented cases where the "nonzero" intercepts cannot be attributed to extrapolation error. Some of the values in Table I are only approximate since it was necessary to obtain data points from a graph in a journal.

Non-Curie Behavior. Our primary concern will be with the contributions of magnetic effects to the measured hyperfine coupling constants in systems where the pseudocontact contribution is small. Systems which lead to this situation have been previously described in the literature.[19] Recent progress[11] in factoring out the pseudocontact contribution is encouraging and our conclusions relating to the Fermi contact part of the isotropic shift will be applicable to these systems when the factoring problems are solved and the needed experiments carried out.

The Curie law contact shift equation (1) can be expressed in terms of the susceptibility

$$\frac{\Delta\nu_c}{\nu_0} = -\frac{A_i}{Ng_N\beta_N}\chi_M \qquad (4)$$

where A_i is in units of gauss. Substitution of the Curie law equation for χ_m gives eq 1. It is well known that a good many complexes do not obey the Curie

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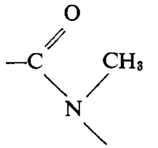
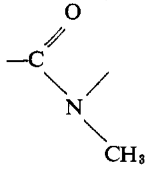
Table I

Complex	Solvent	Proton	Intercept, Hz	$\Delta\nu_{iso}$ (Hz) at 26°	Ref
$Co(HMPA)_2Cl_2$[a]	$CHCl_3$	CH_3	+131	−113	This work
	Nitrobenzene	CH_3	+62	−92	This work
$Co(HMPA)_2Br_2$[a]	$CHCl_3$	CH_3	+115	−157	This work
$Co(HMPA)_2(SCN)_2$[a]	$CHCl_3$	CH_3	+88	−193	*h*
$[Co(HMPA)_4](ClO_4)_2$[a]	Nitrobenzene	CH_3	0	−175	*i*
Co(α-picoline)$_2$Cl$_2$	Acetone and α-picoline	CH_3	+1425	−820	*j*
$Co(pyridine)_2Cl_2$	$CHCl_3$	*m*-H	0	−212	This work
$[Ni(bipy)_3](PF_6)_2$[b]	CH_3CN	4,4′	0	−430	
		5,5′	0	−228	This work
	Propylene carbonate	4,4′	0	−430	
		5,5′	0	−228	
$[Ni(DADPH_2)_2](ClO_4)_2$[c]	Acetone	CH_3	−488	+725	
		m-H	+533	−3800	*k*
		p-H	+202	−720	
$[Ni((CH_3)_2SO)_6](ClO_4)_2$	Dimethyl sulfoxide	CH_3	0		*l*
$[Ni(CH_3OH)_6](ClO_4)_2$	CH_3OH	CH_3	∼+700	∼−2850	*m*
$[Ni(DMF)_6](ClO_4)_2$[d]	DMF	–C(=O)H	−700	+3400	*n*
$Ni(C_5H_4CH_3)_2$	Toluene	CH_3	0	−11,700	*o*
		Ring H	0	+15,000	
[Ni(*p*-$CH_3C_5H_4NO)_6](ClO_4)_2$	CH_3NO_2	*p*-CH_3	+300	−1029	This work
		m-H	+57	−490	
$[Co((CH_3)_2SO)_6](ClO_4)_2$	Dimethyl sulfoxide	CH_3	0		
$[Co(CH_3CN)_6](ClO_4)_2$	CH_3CN	CH_3	∼−788	+350	This work
$[Co(CH_3CN)_6](BF_4)_2$	CH_3CN	CH_3	∼−750	+325	This work
$[Co(CH_3OH)_6](ClO_4)_2$	CH_3OH	CH_3	−600	−3800	This work
		OH	+1500	−5750	
$[Co(H_2O)_6](ClO_4)_2$	H_2O	O—H	−400	−7100	*p*
$[Co(DMF)_6](ClO_4)_2$	DMF	–C(=O)H	∼−700	+4100	*n*
			+30	+296	
			+10	+455	
$Fe(bipy)_3(PF_6)_3$[b]	D_2SO_4	5,5′	0	475	
		4,4′	0	430	*q*
		3,3′	0	+100	
$Fe(PDC)_3$[e]	$CHCl_3$	α-CH_2	∼+900	−4850	*r*
$V(C_6H_5CH_3)_2^+$	Toluene	Ring H	−1458	−16,740	
		CH_3			
V(mesitylene)$_2^+$	Mesitylene	Ring H	−2051	−16,410	
		CH_3	−318	−3860	*s*
$V(C_6H_6)_2^+$	Benzene	Ring H	−10,867	−13,990	
$Co(HMBZ)_2(PF_6)$[f]	CD_2Cl_2	CH_3	+337	−3695	
$Fe(HMBZ)_2(PF_6)$[f]	CD_2Cl_2	CH_3	+24	−255	

[a] HMPA, hexamethylphosphoramide. [b] Bipy, α,α′-bipyridine. [c] DADPH$_2$, 2,6-diacetylpyridine dioxime. [d] DMF, dimethylformamide. [e] PDC, pyrrolidyl dithiocarbamate. [f] HMBZ, hexamethylbenzene. [g] All shifts are reported relative to free ligand or whenever possible to the diamagnetic analog. [h] M. Rosenthal, Ph.D. Thesis, University of Illinois, 1965. [i] B. B. Wayland, Ph.D. Thesis, University of Illinois, 1964. [j] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 4319 (1967). [k] E. Baucom and R. S. Drago, to be published. [l] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 2579 (1969). [m] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058 (1964). [n] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966). [o] M. Rettig, Ph.D. Thesis, University of Illinois, 1967. [p] N. A. Matwiyoff, *J. Phys. Chem.*, **72**, 2659 (1968). [q] R. E. DeSimone, private communication. [r] R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, **45**, 2688 (1966). R. M. Golding, "Applied Wave Mechanics," Van Nostrand, Princeton, N. J., 1969, p 372. [s] S. Anderson and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 4244 (1970).

Table II. Electronic Spectra of $Co(HMPA)_2Cl_2$

Solvent	Concn, *M*	λ_{max}, mμ[a]				
$C_6H_5NO_2$	0.0133	660 (533)	640 (465)	610 (331)	590 (308)	580 sh
$CHCl_3$	0.0197	664 (487)	640 (411)	610 (299)	596 (284)	580 sh
CH_2Cl_2	0.0201	665 (537)	640 (453)	610 (323)	597 (318)	580 sh

[a] Numbers in parentheses represent molar extinction coefficients at band maxima.

law, $\chi_m = c/T$, but follow an empirical Curie–Weiss law, $\chi_m = c/(T + \Theta)$, where Θ is the Weiss constant in °K. Since the contact shift is derived for simple Curie law behavior, it seemed possible that, for systems which obey the Curie–Weiss law, one may not observe a zero intercept. The Weiss constant can be incorporated by substituting it into eq 4

$$\frac{\Delta\nu_c}{\nu_0} = -\frac{A_i}{Ng_N\beta_N}\frac{c}{(T + \Theta)} \qquad (5)$$

For this case, we would expect $\Delta\nu_c \propto [1/(T + \Theta)]$ and $\Delta\nu_c \propto \chi_m$. Thus, a plot of $\Delta\nu$ *vs.* $1/T$ would give rise to an intercept because of a displaced temperature axis. If Θ is a contributing factor to the temperature dependence of the contact shift, then the effect can be empirically accounted for by plotting $\Delta\nu_c$ *vs.* χ_m, where χ_m and $\Delta\nu_c$ were determined for the same solutions at the same temperatures. This plot in effect cancels out any Θ contribution to the intercept and comparison of the intercepts in the $\Delta\nu$ *vs.* χ_m and $\Delta\nu$ *vs.* $1/T$ plots would reveal the magnitude of complications from this effect. This procedure was carried out for the complexes $[Co(HMPA)_2Cl_2]$, $[Co(CH_3CN)_6](ClO_4)_2$, and $[Ni(bipy)_3](PF_6)_2$. In all cases, the intercepts were essentially the same as reported in Table I.

For systems in which there are appreciable pseudocontact contributions, one has at least two components to the susceptibility, $\chi_\parallel$ and $\chi_\perp$. If it can be shown experimentally that the total susceptibility, χ_m, follows a Curie–Weiss law, then it may be reasonable that each individual component, $\chi_\parallel$ and $\chi_\perp$, will also follow a similar relationship. However, it is possible that the Weiss constants, in the parallel and perpendicular directions, would not be the same and could give rise to nonideal behavior of the pseudocontact portion of the isotropic shift potentially leading to a nonzero intercept. For reasons previously stated, the problem of the pseudocontact shift contribution to the intercept will not be considered further.

From the above arguments, it can be concluded that the Weiss constant is not important in the temperature dependence of the contact shifts for $Co(HMPA)_2Cl_2$, $Co(CH_3CN)_6(ClO_4)_2$, and $Ni(bipy)_3(PF_6)_2$, but no general conclusions can be drawn regarding other systems. For complexes clearly different than those studied here, χ_m should be determined as a function of temperature.

Another possible magnetic contribution is from temperature independent paramagnetism, TIP, which is a second-order Zeeman effect. This contribution to the susceptibility can be estimated from electronic spectral data. The susceptibility is given by

$$\chi_m = \frac{c}{T} + N\alpha \qquad (6)$$

where $N\alpha$ is the TIP contribution to the susceptibility. Substituting this expression into eq 4 yields

$$\frac{\Delta\nu_c}{\nu_0} = \frac{-A_i}{Ng_N\beta_N}\frac{c}{T}\frac{-A_i}{Ng_N\beta_N}(N\alpha) \qquad (7)$$

If TIP is a contributing factor to the observed temperature dependence, its effect would be to change the intercept but *not* the slope of a $\Delta\nu_c$ *vs.* $1/T$ plot.

The TIP, as expressed in eq 4, may be a contributing factor in some cases to the nonzero intercepts. However, this contribution only predicts an intercept with the same sign as the observed shift and therefore cannot account for the large majority of the available data since it is quite common for the intercept to have a sign opposite to that of the observed shift and often to have a different sign for different protons in the same complex. Again, it should be emphasized that these arguments hold only for systems in which the pseudocontact shift is negligible.

Equations 1 and 2 were derived for free-radical systems and Curie law behavior. Thus, it should not be completely unexpected if these equations break down when used on paramagnetic complexes. It is important to note that there are many cases where these equations do seem to be completely valid; see Table I. If the equations are valid for a particular complex, then it does not seem unreasonable to expect them to hold for complexes whose magnetic behavior is very similar. For example, it is seen from the data in Table I that $Ni(bipy)_3(PF_6)_2$ is a well-behaved complex. However, the complex with the tridentate ligand $DAPDH_2$, $[Ni(DAPDH_2)_2](ClO_4)_2$, is not well behaved with respect to its temperature dependence of the isotropic shift. If eq 1 and 2 are valid for the $[Ni(bipy)_3](PF_6)_2$ complex with regard to the magnetic behavior of the system, then it seems reasonable to expect it to be valid for the magnetic behavior of the $[Ni(DAPDH_2)_2(ClO_4)_2$ complex. The deviation of the temperature dependence in the latter complex is due mainly to the hydrogen-bonding interactions (*vide infra*) known to occur with this compound.

Equations 1 and 2 are undoubtedly invalid for many inorganic complexes and what is really needed is a complete theoretical investigation leading to appropriate equations for all inorganic coordination compounds. The general expression for the proton contact shift is

$$\Delta H = \frac{A_i\langle S_z\rangle}{g_N\beta_N}$$

where $\langle S_z\rangle$ is the average value of the electron spin in the z direction. The difficulty arises in the evaluation of $\langle S_z\rangle$. This evaluation is simple and straightforward under conditions of Curie law behavior and eq 1 results (after substitution of $\Delta\nu/\nu_0$ for $\Delta H/H_0$). In systems which exhibit spin–orbit coupling of ground to nearby excited states and/or zero field splitting, $\langle S_z\rangle$ must be evaluated including these effects. When the spin–orbit levels are greatly separated ($\gg kt$) g_{av} is constant and takes orbital angular momentum into account, but when the levels are closely spaced, g_{av} may change and non-Curie behavior can be expected even in an isotropic system. The effects of zero-field splitting are comparable. Preliminary work[11,20] has shown that the resulting expressions for this type of system do not have a simple inverse temperature dependence as do eq 1 and 2. Additional complications can be encountered when the delocalization pattern from the populated excited level is different from that of the ground level. Although this magnetic phenomena is a very likely reason for the observation of nonzero intercepts, in some cases, the existence of other nonmagnetic effects will be conclusively shown

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[20] R. M. Golding, *Mol. Phys.*, **8**, 561 (1964).

to cause significant nonzero intercepts in the following sections.

Chemical Change. There are two general types of chemical change that accompany dissolution of a solute: one that is temperature independent and one that is temperature dependent. If a temperature independent change took place upon dissolution of a substance (*i.e.*, the equilibrium constant is so large that there is no significant change in the concentration of species present over the temperature range studied), the isotropic nmr shift would be due to the same compound at each temperature. Even though we may not know the exact nature of the compound in solution, we would expect a temperature dependence as predicted by eq 1 and 2 (assuming a magnetically nonideal substance was not produced). One of the important conditions for the use of the equations for contact and pseudocontact shifts is that one is looking at the same species at each temperature. If a temperature dependent chemical change took place, the position of the equilibrium or the nature of the species in solution would be altered at each temperature. If the species were interconverted by a process which is fast on the nmr time scale, the observed nmr shift at each temperature would be due to an average system which differs from that at any other temperature. Under these conditions, a straight line may or may not result, depending upon the magnitude of the change over the temperature region studied and the differences in the isotropic shifts of the compounds involved. A nonzero intercept will inevitably result if the isotropic shifts differ.

The types of temperature dependent changes that are manifested by the systems in Table I are ion pairing, hydrogen bonding, and an equilibrium among chemical species with different primary coordination spheres (*e.g.*, tetrahedral and square planar Ni^{2+}).

It has been shown[21] that hydrogen bonding solvents, such as chloroform, strongly interact with some complexes. As the temperature is varied, the relative amount of hydrogen bonding may change, less hydrogen bonding being expected at higher temperature for an exothermic interaction. For this type system, as the nmr is studied as a function of temperature, one is in effect observing various mixtures of different species whose contact shifts may differ. If the extent of hydrogen bonding changes in a regular fashion, a linear $1/T$ dependence on the shift could result over the region studied, but a "nonzero" intercept would result.

A test for the hypothesis that hydrogen bonding is one cause of the observed "nonzero" intercepts is to study a complex in a hydrogen bonding and a nonhydrogen bonding solvent. A comparison of the magnitude of the intercept for the same complex (one capable of hydrogen bonding) in the two types of solvents would reveal the potential existence and the magnitude of such an effect. It has been shown[22] by an infrared study that $Co(HMPA)_2Cl_2$ and $Co(HMPA)_2Br_2$ complexes are hydrogen bonded to the solvent, $CHCl_3$, presumably *via* the halides. We report here a study of $Co(HMPA)_2Cl_2$ in the hydrogen bonding solvent chloroform and in the nonhydrogen bonding solvent nitrobenzene. Figure 1 demonstrates the solvent dependence of the isotropic shift for this system. As is readily seen from the graph, there is a large difference in the isotropic shift behavior in these two solvents. From Table I, we see that even in nitrobenzene, there still exists a slight "nonzero" intercept outside the 25 Hz expected from extrapolation errors. Clearly, though, the effect of hydrogen bonding is to give rise to a significant nonzero contribution to the intercept and straight line $\Delta\nu$ *vs.* $1/T$ behavior of the isotropic shift. It is to be emphasized that if the hydrogen bonding interaction was so extensive and there was no significant change in the extent of it with temperature, a nonzero intercept could not result from this effect, since the mole fractions of species in solution would not be changing as a function of temperature.

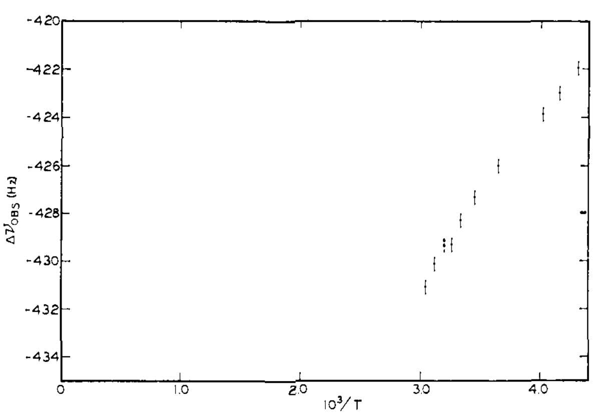

Figure 2. Temperature dependence of chloroform resonance for 0.0946 *M* $Co(HMPA)_2Cl_2$ in $CHCl_3$.

Other evidence for a change in the amount of hydrogen bonding with temperature change is obtained from the temperature dependence of the chloroform resonance for solutions of $Co(HMPA)_2Cl_2$ in chloroform. Figure 2 shows nonlinear behavior of the chloroform resonance as a function of $1/T$. If the amount of hydrogen bonding was constant, then we would expect a linear $1/T$ dependence with an intercept corresponding to the value for the chloroform hydrogen bonded to a diamagnetic analog.

The complex $[Co(HMPA)_4](ClO_4)_2$ is well behaved in nitrobenzene. Since hydrogen bonding occurs at a coordinated halide in $[Co(HMPA)_2X_2]$, there are no sites available for hydrogen bonding in the former complex. Thus, we would predict that the isotropic shift of this complex would not be effected by a hydrogen bonding solvent. This is the behavior reported for this system.[23] Golding[24] investigated the temperature dependence of the magnetic moment and the isotropic shift of tris(pyrrolidyl dithiocarbamato)iron(III). From the magnetic moment measurements, he determined that the complex has a $^6A_1$ ground state. This implies that the Curie law equation for the isotropic shift should be valid for this complex. Using the data presented in his paper, an intercept of +900 Hz is obtained for the α-CH_2 group (see Table I). The isotropic shift measurements were carried out in chloroform. In light of the previous discussion, it seems reasonable that the chloroform could hydrogen bond

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[21] M. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 2966 (1966).

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[23] B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 2372 (1965).

[24] See Table I, footnote *r*.

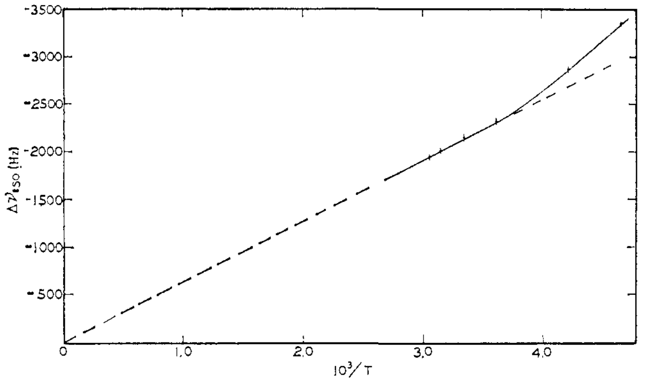

Figure 3. Temperature dependence of isotropic shift of Co(pyridine)$_2$Cl$_2$ in CHCl$_3$.

to the uncoordinated nitrogen atom on the ligand, thus giving rise to the observed nonzero intercept.

From Table I it can be seen that [Ni(CH$_3$OH)$_6$](ClO$_4$)$_2$ and [Ni(DMF)$_6$](ClO$_4$)$_2$ both have rather large nonzero intercepts. The shifts for these two compounds were obtained in the ligand as solvent and thus can easily be explained on the basis of hydrogen bonding of the solvent to the coordinated ligand. The complex [Ni(4-CH$_3$-pyNO)$_6$](ClO$_4$)$_2$ also has a nonzero intercept, as seen from Table I, but we would not predict extensive hydrogen bonding in CH$_3$NO$_2$. Thus, the behavior of this complex cannot be rationalized in this context and will be discussed later.

A great deal of work has been done[25–28] on the nature of ion pairing for charged complexes in solution. The formation of an ion pair could distort a complex and change the isotropic nmr shift by changing the value of the pseudocontact and/or contact shift. Ion pairing in solution is a much more complex problem than that of hydrogen bonding. As pointed out by Fanning and Drago,[25] if the enthalpy of association is negative as expected, then a decrease in association would be expected as the temperature increases. However, as the temperature increases, the dielectric constant of a solvent decreases, and the degree of association would be expected to increase. Both effects give rise to a temperature-dependent change in the species in solution. As previously shown,[26] ion pairing can induce a pseudocontact contribution to the shift giving rise to different isotropic shifts in the ion-paired and dissociated species. We would not expect this effect to be very important in systems that are nearly isotropic, *e.g.*, octahedral Ni(II). Since even D_{4h} Ni(II) complexes do not exhibit pseudocontact shifts, we feel that ion pairing will not be sufficient to produce pseudocontact shifts in six-coordinate Ni(II) *via* distortion. However, in six-coordinate Co(II), where a large pseudocontact contribution to the isotropic shift is possible, ion pairing could have a very significant effect on the temperature dependence of the isotropic shift. We believe this is the cause of a substantial contribution to the nonzero intercept in Co(CH$_3$CN)$_6$(ClO$_4$)$_2$.

An equilibrium among more than one structurally different species in solution would also affect the temperature dependence of the isotropic shift. An example of this effect was found in Co(py)$_2$Cl$_2$. Figure 3 demonstrates the temperature dependence. Although we are not able to identify the species, electronic spectra over the temperature region covered in Figure 3 indicate that there is an equilibrium involving complexes of different coordination number and that the position of equilibrium is changing with temperature. Interconversion between the species is fast on the nmr time scale. Here the interaction is such as to give rise to nonlinearity in the $\Delta\nu$ *vs.* $1/T$ plot. However, it can be seen that if the system were studied over the temperature range −58 to +20°, a straight line with nonzero intercept would be obtained because of an equilibrium possibly involving octahedral (bridging chlorines)–tetrahedral species. Thus equilibria of this sort are a potential cause of nonzero intercepts.

In this case, we were unable to observe any shift in the chloroform resonance as a function of temperature presumably because, in the dilute solutions of complex that had to be used, the chloroform shift would be too small to be observed. The zero intercept for the high-temperature region implies essentially tetrahedral species and such extensive hydrogen bonding to CHCl$_3$ that the solvation number is not changing appreciably over this temperature range.

The complex, [Ni(4-CH$_3$pyNO)$_6$](ClO$_4$)$_2$, previously mentioned, may also fall in this category. The possibility of hydrogen bonding or ion pairing being the cause of the nonzero intercept has already been discounted. The shifts for this system were determined in nitromethane with excess 4-methylpyridine *N*-oxide by use of the mole fraction equation over the temperature range +25 to +85°. It is very possible that at the higher temperatures some 4-methylpyridine *N*-oxide is displaced from the first coordination sphere (by CH$_3$NO$_2$ or anion), producing more than one species in solution. A very small amount of this could account for the observed nonzero intercept in this complex.

Another possible contribution to nonzero intercepts is the temperature dependence of conformational equilibria which could be important in systems such as 4-methylpyridine *N*-oxide and dimethylformamide. The significance of these effects was dramatically indicated in an analysis of the contact shifts of some alkylamine complexes of nickel(II).[29]

Evaluation of A_i for Nonzero Intercept Systems. The problem of a nonzero intercept has profound implications on the meaning of the values calculated for A_i by eq 1. Significantly different results are obtained if A_i is evaluated from the slope of the line or from a single room temperature measurement as shown for some representative systems in Table III. Clearly, nonzero intercepts should be avoided to obtain meaningful coupling constants. The work described in the previous sections suggests ways of doing this by proper selection of conditions, *e.g.*, nonhydrogen bonding, poorly coordinating, and high dielectric constant solvents.

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Table III

Compound		$A_i{}^a$ (single temp, 26°)	$A_i{}^a$ (slope of $1/T$ plot)
$Co(HMPA)_2Cl_2$		$+1.175 \times 10^4$	$+2.526 \times 10^4$
$Ni(DAPDH_2)_2(ClO_4)_2$	p-H	$+1.56 \times 10^5$	$+1.87 \times 10^5$
	m-H	$+8.25 \times 10^5$	$+9.27 \times 10^5$
	CH_3	-1.58×10^5	-2.67×10^5
$[Ni(4\text{-}CH_3pyN{\rightarrow}O)_6](ClO_4)_2$	p-CH_3	$+2.205 \times 10^5$	$+2.861 \times 10^5$
	m-H	$+1.050 \times 10^5$	$+1.179 \times 10^5$

[a] In units of hertz.

If the nonzero intercept arises in the case of nickel(II) complexes because of reaction with the solvent (as proposed for $Ni(ONC_5H_4CH_3)_6{}^{2+}$) and if spectroscopic studies are available to show that the desired species is predominant (95% or better), the most accurate A_i values can be expected from a single measurement at the temperature of the spectroscopic studies. Using typical values for $NiL_6{}^{2+}$, $NiLX^{2+}$, etc., complexes, errors less than 5% in A_i should be expected from a single temperature measurement, whereas 20–30% discrepancies are noted in Table III.

In conclusion, the temperature dependence should be studied in any investigation of isotropic shifts. The potential influence of error from a nonzero intercept on the conclusions being drawn should be investigated in the manner described above. As additional systems are investigated, other factors giving rise to nonzero intercepts will undoubtedly arise.

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Nuclear Magnetic Resonance Studies of Phosphate Esters. I. Conformational Study of Trisneopentyl Phosphate and Tris(β-chloroethyl) Phosphate

A. A. Bothner-By* and W.-P. Trautwein

Contribution from Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received August 20, 1970*

Abstract: The temperature dependences of the $^3J_{POCH}$ of trisneopentyl phosphate and of the $^3J_{POCH}$ and the two $^3J_{HH}$ of tris(β-chloroethyl) phosphate have been measured. In both cases the preferred conformations for rotation about the CO bonds are those with the phosphate and alkyl groups in trans orientations. In the chloroethyl derivative the chlorine and phosphate oxygen are preferentially gauche.

The phosphate ester linkage is a common structural feature of biological molecules, including sugar phosphates, phospholipids, nucleotides, RNA's, and DNA's, etc. A study of the conformation of such molecules, centering on rotational isomerism about the P–O and O–C bonds, may yield information useful in understanding the binding of these substances to enzymes, and the mechanisms of their chemical reactions.

Studies by Sasikekharan and Lakshminarayanan[1] based on X-ray diffraction results and on empirical calculations have established that the groups on the O–C bond tend to occupy staggered positions, as in substituted ethane (Figure 1).

Rotation about the O–C bond may be studied *via* the ^{31}P–H vicinal coupling constant, $^3J_{POCH}$, in suitable systems. Different values of $^3J_{POCH}$ in diverse trialkyl phosphates were observed by Axtmann, Shuler, and Eberly[2] in 1959. That these differences arose from conformational effects was suggested by Dudek.[3] Measurements on rigid compounds of known geometry[4–7] have generally been concordant with the idea that the value of $^3J_{POCH}$ depends on the POCH dihedral angle, and that the form of the dependence is similar to the well-known Karplus[8] curve for $^3J_{HCCH}$.

Tsuboi, *et al.*,[9] observed the $^3J_{POCH}$ values in a series of mono- and dialkyl phosphates in heavy water solution, and have estimated the conformational equilibria from these values, as well as the values $J_t = 28$ and $J_g = 1.5$ Hz derived from the couplings observed in methyl esters and in the rigid compound 1-phenyltrimethylene phosphate. In rigid model compounds, however, J_t has usually been smaller, of the order of 20 Hz.[4,6]

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