$b = 12.75 \pm 0.03$, $c = 24.25 \pm 0.11$ Å, $\beta = 115.20 \pm 0.20°$. The *hl l* level Weissenberg photographs taken of both compounds, each mounted along the *b* crystallographic axis, were virtually indistinguishable in terms of reflection positions and intensities. Thus, the remarkable structure found for $Co_3(DEPAM)_6$ occurs also for $Ni_3(DEPAM)_6$. The latter appears to be somewhat more stable relative to monomers. Although a solution of $Ni_3(DEPAM)_6$ in *m*-xylene, which is green at 25°, turns straw-colored and then light brown at temperatures from 100 to 150°, the spectrum at 80° did not differ significantly from that at room temperature. The observed color changes were reversible.

Correspondence

Evaluation of Dipolar Nuclear Magnetic Resonance Shifts

Sir:

The magnetic resonances of nuclei in paramagnetic complexes often show large isotropic shifts from their diamagnetic positions.[1] These shifts are of two types: contact shifts resulting from the presence of unpaired electron spin density at the resonating nucleus and dipolar shifts caused by a dipolar interaction between the electronic magnetic moment and the nuclear spin which does not vanish in magnetically anisotropic systems. It is the purpose of this article to clarify one method of separating observed isotropic shifts $\Delta\nu^{\mathrm{iso}}$ into dipolar $\Delta\nu^{\mathrm{dip}}$ and contact $\Delta\nu^{\mathrm{con}}$ contributions, and to discuss its application to a system wherein it had been reported to fail.[2] The direct evaluation of dipolar shifts from single-crystal magnetic anisotropy data will also be discussed and applied to the case at hand.

It is possible to separate dipolar and contact contributions to observed isotropic shifts if it can be established, for two series of complexes differing only in central metal ion, that the modes of spin delocalization are identical and that one member is magnetically isotropic (*i.e.*, exhibits no dipolar shifts). This procedure, which will be referred to here as the ratio method, has been applied with apparent success by the present author and his coworkers[3-6] on several occasions and by others[7] to parallel series of magnetically isotropic[8] six-coordinate nickel(II) and magnetically anisotropic[8] cobalt(II) complexes, although the underlying assumptions and limitations of the method were perhaps not properly enunciated at the time. The basic assumption of the method is the following: if the unpaired spin is delocalized in a particular ligand molecular orbital, then it will be distributed according to the MO coefficients of the orbital involved. Only a small change in ligand electronic structure is to be expected when the metal is changed. Cobalt and nickel differ by a single nuclear charge and single extranuclear electron. The quantity of unpaired spin delocalized in a particular MO may be different for cobalt and nickel, say, but the pattern of distribution should be the same. In other words the *ratios* of *contact* shifts for systems differing only in the metal should be identical. This may be expressed quantitatively by eq 1,

$$\frac{\Delta\nu_{\mathrm{Co}}^{\mathrm{con}}(i)}{\Delta\nu_{\mathrm{Co}}^{\mathrm{con}}(j)} = \frac{\Delta\nu_{\mathrm{Ni}}^{\mathrm{con}}(i)}{\Delta\nu_{\mathrm{Ni}}^{\mathrm{con}}(j)} = \frac{\Delta\nu_{\mathrm{Co}}^{\mathrm{iso}}(i) - \Delta\nu_{\mathrm{Co}}^{\mathrm{dip}}(i)}{\Delta\nu_{\mathrm{Co}}^{\mathrm{iso}}(j) - \Delta\nu_{\mathrm{Co}}^{\mathrm{dip}}(j)} \qquad (1)$$

where *i* and *j* refer to the *i*th and *j*th sets of equivalent ligand nuclei. Since dipolar shifts are absent for octahedral nickel(II), $\Delta\nu_{\mathrm{Ni}}^{\mathrm{con}}(i) = \Delta\nu_{\mathrm{Ni}}^{\mathrm{iso}}(i)$. For the axially symmetric systems of interest here the dipolar shift of the *i*th proton resonance is given by eq 2,[9-11]

$$\frac{\Delta\nu_{(i)}^{\mathrm{dip}}}{\nu} = -DG(\chi,r)_i \qquad (2)$$

where ν is the spectrometer frequency and *D* is a function of temperature and the magnetic properties of the complex[12] (*vide infra*). The geometric factor $G(\chi,r)_i$ is given by eq 3.[9] Here r_i is a vector from the cobalt atom to the *i*th nucleus and χ_i is the angle made by this vector with the symmetry axis. The average is taken over nuclear motions which are rapid on the nmr time scale. Dipolar shifts in a given complex may thus be expressed in terms of the shift for a particular nucleus and ratios of geometric factors. Let X_0 be the dipolar shift for the standard nucleus (0); then the dipolar shifts for all the other nuclei are given by

$$G(\chi,r)_i = \left\langle \frac{3\cos^2\chi_i - 1}{r_i^3} \right\rangle_{\mathrm{av}} \qquad (3)$$

$$\Delta\nu_{\mathrm{Co}}^{\mathrm{dip}}(i) = R(i)X_0 \qquad (4)$$

where

$$R(i) = \frac{G(\chi,r)_i}{G(\chi,r)_0} \qquad (5)$$

is the ratio of the *i*th geometric factor to that of the standard.

Equation 1 becomes

$$\frac{\Delta\nu_{\mathrm{Ni}}^{\mathrm{iso}}(i)}{\Delta\nu_{\mathrm{Ni}}^{\mathrm{iso}}(0)} = \frac{\Delta\nu_{\mathrm{Co}}^{\mathrm{iso}} - R(i)X_0}{\Delta\nu_{\mathrm{Co}}^{\mathrm{iso}}(0) - X_0} \qquad (6)$$

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(1) For a review see D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

(2) M. L. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 2196 (1968).

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(10) J. P. Jesson, *ibid.*, **47**, 579 (1967).

(11) J. P. Jesson, *ibid.*, **47**, 582 (1967).

(12) *D* of eq 2 corresponds to the *D* of ref 11 divided by ν.

TABLE I

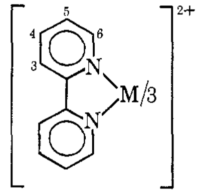
ISOTROPIC SHIFTS[a] AND RATIOS FOR $M(bipy)_3^{2+}$ COMPLEXES

Position[b]	$R(i)$[c]	$\Delta\nu_{Co}^{iso}$ [d]	$\Delta\nu_{Co}^{dip}$	$\Delta\nu_{Co}^{con}$	$\Delta\nu_{Ni}^{iso}$ [e]	$\Delta\nu_{Co}^{iso}(i)/\Delta\nu_{Co}^{iso}(3)$	$\Delta\nu_{Co}^{con}(i)/\Delta\nu_{Co}^{con}(3)$	$\Delta\nu_{Ni}^{iso}(i)/\Delta\nu_{Ni}^{iso}(3)$
3	1.0000	−74.52	−14.33	−60.18	−52.17	1.000	1.000	1.000
4	0.2218	−6.08	−3.18	−2.57	−6.17	0.082	0.043	0.118
5	−0.4408	−38.55	+6.32	−44.87	−36.67	0.517	0.745	0.703
6	−3.918	−80.92	+56.14	−137.07	−128.90	1.086	2.277	2.471

[a] In ppm from diamagnetic complex or ligand resonances. [b] See structure I. [c] $G(\chi,r)_3 = -7.35 \times 10^{-3}$ Å^{-3}, the geometric factors calculated in this work agree reasonably well (to within 12% in all cases) with those of ref 2 when typographical sign errors in G_5 and G_6 are corrected. [d] Measured in ref 2; temperature unspecified. [e] Measured at 40°.

The isotropic shifts are all observable; the $R(i)$'s may be calculated from the geometric factors. X_0 is the single unknown of eq 6. If there are two sets of nuclei with observable isotropic shifts, eq 6 can be solved and the dipolar shifts evaluated. In general there will be $n - 1$ independent equations where n is the number of observed isotropic shifts. Confidence in the validity of this type of analysis comes if the $n - 1$ equations yield identical or nearly identical values of X_0. Only if three or more resonances are observed is such a check possible.

Wicholas and Drago[2] set out to prove that the spin-delocalization mechanisms in tris(bipyridyl)cobalt(II) and -nickel(II) complexes, I, are different by demonstrating the failure of the ratio method when applied to this system. It is one purpose of this note to examine the basic assumptions of the ratio method and the reasons for its reported failure[2] and to demonstrate that a reasonable estimate of the dipolar shifts in this system can be obtained by its judicious application. The ratio method will fail unless its basic assumptions are met. The spin must be delocalized in an identical MO or through an identical exchange polarization mechanism in the two complexes. If more than one orbital is involved or more than one mode of delocalization is present, then failure is to be expected. For instance, if two different π MO's are involved (with different delocalization patterns), or a σ and a π MO, then the relative contribution of each would be expected to vary, perhaps drastically, as the metal is changed. Eaton[13] has discussed at length the change in mode of spin delocalization to be expected for tris-acetylacetonate complexes as the central metal is varied. Success may be expected if a single ligand orbital is involved in both the cobalt and nickel cases. This is a likely situation for π spin delocalization in coordinated phosphines,[3] isocyanides,[3] and amine N-oxides[4,5] to which the method has been applied with apparent success. Convincing evidence has been presented that spin is delocalized in the highest filled π MO of coordinated quinoline N-oxide and isoquinoline N-oxide.[5] For pyridine-type ligands there is evidence that while σ spin delocalization is dominant,[14] some π-type delocalization is present which becomes particularly apparent at the γ position.[15] In such ligands, if two sorts of orbital are involved, there is no reason to expect the π/σ ratio to be invariant to a change in metal. Wicholas and Drago[2] demonstrated the variable π contribution at the 4-position proton by noting the discrepancy in the two independent ratios based on this resonance. It should be noted, however, that the geometric factor for the 4 position is small and quite sensitive to minor changes in geometry (a 5° rotation of the bipyridyl ligands about the three twofold axes of the D_3 complex changes $G(\chi,r)_4$ by 25%). For the present analysis data for the 6-position proton (not reported by Wicholas and Drago) are included and the ratios are based on the 3-position resonance, which is less affected by the variable π contribution and has a larger isotropic shift and a geometric factor quite insensitive to changes in geometry (a 5° rotation causes less than 1% change). Reasonable agreement is obtained for the independent ratios based on the 3-position resonance except at the 4 position, where the variable π contribution and uncertain geometric factors become important. This is shown in Table I.



I, M = Co, Ni

Independent evidence which lends support to the above analysis of dipolar shifts in tris(bipyridyl)cobalt(II) comes from single-crystal magnetic anisotropy data obtained on $Co(bipy)_3Br_2 \cdot 6H_2O$ which contains the complex cation of interest.[16] The principal molecular magnetic susceptibilities extrapolated to 40° are $^M\chi_{\parallel} = 7500 \times 10^{-6}$ and $^M\chi_{\perp} = 12{,}250 \times 10^{-6}$ cgsu/mol.

Some time ago it was pointed out[17] that the dipolar shift equation, originally derived[9] for systems devoid of residual ground-state orbital angular momentum, was not strictly applicable to six-coordinate cobalt(II). The ground state of this ion consists of a manifold of six Kramer's doublets, several of which are thermally populated at room temperature. An equation for dipolar shifts in terms of the susceptibility anisotropy valid for the solid state was proposed.[17] Subsequently, Jesson presented a theoretical study of isotropic nuclear resonance shifts in octahedral cobalt(II) systems[10]

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wherein he took into account the thermal population of several Kramer's doublets. He presented equations in terms of the g values of the various levels for the several averaging conditions which depend on the relative magnitudes of the electronic spin-lattice relaxation time T_{1e}, the correlation time for tumbling in solution τ, and the Zeeman anisotropy energy $|g_\parallel - g_\perp|\beta H\hbar^{-1}$. T_{1e} values for octahedral cobalt(II) complexes are known to be very small and only two of the four possible situations might be expected to obtain in reality. The first, with $(1/\tau) \ll |g_\parallel - g_\perp|\beta H\hbar^{-1}$ and $T_{1e} \ll \tau$, leads to eq 7 (Jesson's case (a))[10] while the

$$\frac{\Delta\nu_{(i)}{}^{\text{dip}}}{\nu} = K'[(g_\parallel + g_\perp)(g_\parallel - g_\perp)/3]G(\chi,r)_i \qquad (7)$$

second with $(1/\tau) \gg |g_\parallel - g_\perp|\beta H\hbar^{-1}$ and $T_{1e} \ll \tau$ results in eq 8 (Jesson's case (c))[10] where $K' = -[\beta^2 S'\cdot$

$$\frac{\Delta\nu_{(i)}{}^{\text{dip}}}{\nu} = K'[(3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)/15]G(\chi,r)_i \qquad (8)$$

$(S' + 1)/3kT]$ and the appropriate statistical average is to be taken over the thermally populated levels. Unfortunately, this analysis neglects the second-order Zeeman (SOZ) terms (the summation within the braces of eq 9) in Van Vleck's expression[18] for paramagnetic susceptibility

$$^{\text{M}}\chi_\alpha = \frac{N\beta^2 \sum_i \left\{\dfrac{\langle i|L_\alpha + 2S_\alpha|i\rangle^2}{kT} - 2\sum_{j\neq i}\dfrac{\langle i|L_\alpha + 2S_\alpha|j\rangle^2}{E_i - E_j}\right\} \times \exp(-E_i^0/kT)}{\sum_i \exp(-E_i^0/kT)} \qquad (9)$$

where for the axially symmetric case $\alpha = \parallel$ or $\perp$, N is Avogadro's number, β is the Bohr magneton, $L_\alpha + 2S_\alpha$ is the magnetic dipole operator, and the first sum is over the i electronic states whose energies in the absence of an applied magnetic field are E_i^0. Application of the theory of Abragam and Pryce[19] to a magnetic susceptibility calculation, using the parameters necessary to describe the epr results[20] on the lowest Kramer's doublet of bis(tris(pyrazoyl)borate)cobalt(II) complexes to which Jesson applied his analysis,[11] shows that the SOZ terms contribute about 45% of the bulk magnetic susceptibility at room temperature. Furthermore the SOZ terms contribute more heavily to $\chi_\perp$ than to $\chi_\parallel$ indicating that g tensor and susceptibility anisotropy are not strictly proportional. Evaluation of μ_{eff} from eq 8 neglecting SOZ terms and employing the standard relationship $\mu_{\text{eff}} = 2.828(^{\text{M}}\chi T)^{1/2}$ results in less than spin-only values for μ_{eff}. These findings suggest that neglect of SOZ terms in the evaluation of the electronic–nuclear dipolar interaction is invalid.

Since the SOZ contribution is contained in the measured principal susceptibility values, it is reasonable that a valid determination of the factor D in the dipolar shift expression (eq 2) may be made from these quantities. Furthermore it is easily shown[17,21] that for eq 7 one has

$$D = \frac{1}{3N}[^{\text{M}}\chi_\parallel - {}^{\text{M}}\chi_\perp] \qquad (10)$$

while eq 8 corresponds to

$$D = \frac{1}{N}\left[\frac{\chi_\parallel}{5} + \frac{(\chi_\parallel\chi_\perp)^{1/2}}{15} - \frac{4\chi_\perp}{15}\right] \qquad (11)$$

Dipolar shifts for the 3-position proton resonance of I (M = Co) are calculated to be −19.3 and −13.8 ppm from eq 10 and 11, respectively. These calculated shifts bracket the value (—14.3 ppm) determined independently by application of the ratio method to the pmr data (Table I). The particularly good agreement with the results of eq 11 suggests that the averaging conditions applicable to eq 8 may be operative in the present case.

Although subject to numerous sources of error and various degrees of approximation, the satisfactory agreement between the independent ratio and magnetic anisotropy methods of estimating dipolar shifts in the present case lends support to the validity of applying the ratio method to the tris(bipyridyl)cobalt(II) system. The basic assumptions and approximations of the ratio method (*vide supra*) must nevertheless be kept firmly in mind when it is applied.

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[18] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," The Clarendon Press, Oxford, 1932.

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[21] This follows directly from the simple expression for the suceptibility of a ground-state manifold well separated from all excited levels (SOZ contributions are then negligible): $^{\text{M}}\chi_\alpha = Ng_\alpha{}^2\beta^2S(S + 1)/3kT$.