J. Am. Chem. Soc. 1987, 109, 2589-2594

Isotope and Temperature Dependence of Transition-Metal Shielding in Complexes of the Type $M(XY)_6$

Cynthia J. Jameson,[*1a] **Dieter Rehder,**[1b] **and Martin Hoch**[1b]

Contribution from the Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680, and the Institut für Anorganische und Angewandte Chemie der Universität, D-2000 Hamburg 13, Federal Republic of Germany. *Received July 3, 1986*

Abstract: The temperature coefficients of the chemical shift of ^{51}V in carbonyl complexes in solution are reported here. For transition metal nuclei the effects of rovibrational averaging can be obtained from these temperature coefficients without gas-phase studies in the zero-pressure limit. We present a theory for the large temperature coefficients and large isotope shifts observed in transition metal complexes. We use the vibrational analysis of $V(CO)_6^-$ and $Co(CN)_6^{3-}$ to provide dynamic averages of the displacements in the V–C, C–O, Co–C, and C–N bonds as typical examples. The temperature and mass dependencies of these dynamic averages successfully account for the signs and magnitudes of the observed temperature coefficients and isotope shifts. We report observations of a correlation between the temperature coefficients and chemical shifts. This correlation is qualitatively consistent with a simple electrostatic model for shielding. The limitations of the electrostatic model for shielding are discussed.

Transition metal chemical shifts change with temperature, and these changes are large, of the order of 0.1 to 1 ppm/deg.[2-4] The one-bond isotope shifts are also relatively large for transition metal nuclei (about 5–10 ppm/D for deuterium substitution, about 0.3 ppm per ^{13}C).[5] In this paper we report isotope shifts and temperature coefficients of chemical shifts for ^{51}V in a variety of octahedral complexes. We compare the magnitudes of these temperature coefficients with those for ^{59}Co and ^{195}Pt in octahedral complexes. We observe a relationship between the temperature coefficients of ^{51}V shifts and the chemical shifts, which parallels that reported for temperature coefficients $d\sigma_0/dT$ and ^{19}F absolute shielding of fluoromethanes.[6]

The temperature dependence of the chemical shift can be used to characterize the way in which the nuclear shielding changes with bond extension. The mass dependence of the chemical shift, measured as NMR isotope shifts, also depends on the change of nuclear shielding with bond extension. In principle these two can be used together to determine the derivatives of shielding with respect to bond extension. These observations are particularly favorable for transition metal nuclei for the following reasons. In transition metal complexes the change dr_{ML}/dT in the metal–ligand distance r_{ML} is expected to be large since the quadratic force constants for the metal–ligand stretch are small. At the same time the changes $d\sigma/dr_{ML}$ are expected to be large since the paramagnetic term in the shielding is inversely related to the energies of the low-lying states which are magnetic dipole connected to the ground state, and these in turn are very sensitive to changes in the metal–ligand distance. It is desirable to find an interpretation of these observations in a theory which is also consistent with the previously reported temperature and pressure coefficients of the absorption bands in the optical spectrum and the pressure coefficient of shielding in a variety of complexes.

Intrinsic Temperature Dependence of Transition Metal Chemical Shifts from Solution Data

The chemical shift of a nucleus is temperature dependent even in the absence of involvement in conformational, tautomeric, or other chemical equilibria. Part of this temperature dependence is due to intermolecular effects. The rest is intrinsic to the molecule and is a measure of the change in the nuclear shielding with rotation and vibration. For many nuclei, especially for the proton, the effects of intermolecular interaction are the overwhelming factor in the temperature dependence of chemical shifts in the liquid phase.[7] The variation of chemical shift with temperature in liquid-phase samples is dominated by changes in liquid density with temperature, even when the intermolecular coefficient $\sigma_1'(T)$ is only mildly temperature dependent in

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1'(T)\rho_{liq}(T) + ... \tag{1}$$

In such cases it becomes necessary to make measurements in the low-density gas phase and to extrapolate such measurements to zero density according to the virial expansion:

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + ... \tag{2}$$

Only then can the desired $\sigma_0(T) - \sigma_0(300)$ function be obtained, which is usually deshielding with increasing temperature. This intrinsic temperature dependence of the chemical shift of light nuclei such as ^1H, ^{13}C, ^{15}N, and ^{19}F can only be measured in the zero-pressure limit because the temperature shifts due to intermolecular effects are the same magnitude as the desired intrinsic shifts.[7] On the other hand, transition metal nuclei in complexes are surrounded by ligands and are not as exposed as F or H nuclei, so that the intermolecular coefficient $\sigma_1'(T)$ of shielding in the liquid phase is expected to be small. That is,

$$|\sigma_1'(T)\rho_{liq}(T) - \sigma_1'(300)\rho_{liq}(300)| \ll |\sigma_0(T) - \sigma_0(300)| \tag{3}$$

The changes due to expansion of the solvent with increasing temperature are expected to be much smaller than $|\sigma_0(T) - \sigma_0(300)|$. Therefore, it is possible to obtain a good estimate of $\sigma_0(T) - \sigma_0(300)$ for transition metal nuclei *directly* from the chemical shifts observed with increasing temperature in a solution, without going through tedious gas-phase measurements in the zero-pressure limit. While gas-phase measurements may be possible in some cases, such as ^{195}Pt in PtF_6, such experiments are not applicable to ionic complexes such as those considered here. That the inequality expressed in (3) holds for ^{51}V shifts is immediately obvious in a comparison with ^{19}F shifts in the liquid phase. While the ^{51}V nucleus exhibits deshielding with increasing temperature, characteristic of $\sigma_0(T)$, ^{19}F exhibits increased shielding with increasing temperature, characteristic of $\sigma_1\rho_{liq}(T)$.

The typical temperature dependence exhibited by the ^{51}V chemical shift in solution is shown in Figure 1 for the $V(CO)_6^-$ ion in two solutions. The near coincidence of the data from two

---

(1) (a) University of Illinois. (b) University of Hamburg.

(2) Benedek, G. B.; Englman, R.; Armstrong, J. A. *J. Chem. Phys.* **1963**, *39*, 3349–3363.

(3) Brown, T. H.; Cohen, S. M. *J. Chem. Phys.* **1973**, *58*, 395–396.

(4) Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33–83.

(5) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616. Näumann, F.; Rehder, O.; Pank, V. *J. Organomet. Chem.* **1982**, *240*, 363. Hoch, M.; Rehder, D. *Inorg. Chim. Acta* **1986**, *111*, L13.

(6) Jameson, C. J. *Mol. Phys.* **1985**, *54*, 73–79.

(7) Jameson, C. J. *Bull. Magn. Reson.* **1980**, *3*, 3–28.

0002-7863/87/1509-2589$01.50/0

Table I. Temperature Dependence of (^{51}V) Chemical Shift in Vanadium Complexes in Solution

$\delta(300)^f$ (ppm)	compound	shift range (ppm)	temp range (K)	temp coeff $d\sigma/dT^h$ (ppm/deg)
−1963	$[V(CO)(PF_3)_5]^{-a}$	−1995/−1957	200/320	−0.32
−1955	$[Et_4N][V(CO)_6]^a$	−1981/−1947	193/323	−0.30
−1954	$[Na(diglyme)_2][V(CO)_6]^a$	−1960/−1941	280/340	−0.31
−1906	$[V(CO)_5CNCH_2CO_2Et]^{-b}$	−1931/−1902	210/320	−0.26
−1855	$[V(CO)_5P(p\text{-}C_6H_4F)_3]^{-a}$	−1838/−1805	193/323	−0.36
−1853	$[V(CO)_5PPhMe_2]^{-a}$	−1881/−1849	213/313	−0.32
−1708	*cis*-$[V(CO)_4(PPhMe_2)_2]^{-a}$	−1741/−1702	213/313	−0.39
−1533	$\eta^5\text{-}C_5H_5V(CO)_4{}^a$	−1598/−1514	193/330	−0.61
−1322	$\eta^5\text{-}C_5H_5V(CO)_3P(p\text{-}C_6H_4F)_3{}^a$	−1396/−1300	193/330	−0.70
−519	$\eta^5\text{-}C_5H_5V(CO)_3NC_5H_5{}^c$	−604/−520	229/302	−1.17
-107^g	$\eta^5\text{-}C_5H_5V(CO)_3THF^e$	−180/−117	250/293	−1.5 ± 0.3
−1385	$V(NO)(CO)_3\text{-}o\text{-}C_6H_4(AsMe_2)_2{}^e$	−1415/−1385	240/300	−0.50
-1303^g	$V(NO)(CO)_3PhP(CH_2CH_2PPH_2)_2{}^e$	−1331/−1317	240/270	−0.47
+282	$[V(NO)_2(THF)_4]Br^d$	+276/+313	290/320	−1.23

[a] Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33–83. [b] Ihmels, K.; Rehder, D. *Organometallics* **1985**, *4*, 1340–1347. [c] Hoch, M.; Rehder, D. *J. Organomet. Chem.* **1985**, *288*, C25–C29. [d] Näumann, F.; Rehder, D. *Inorg. Chem. Acta* **1984**, *84*, 117–123. [e] This work. [f] ^{51}V chemical shift at 300 K, relative to liquid $VOCl_3$. Chemical shifts are defined according to IUPAC convention. δ is negative upfield, that is, $\delta = \sigma(VOCl_3) - \sigma$. [g] Extrapolated. [h] ^{51}V resonance frequency increases with increasing temperature.

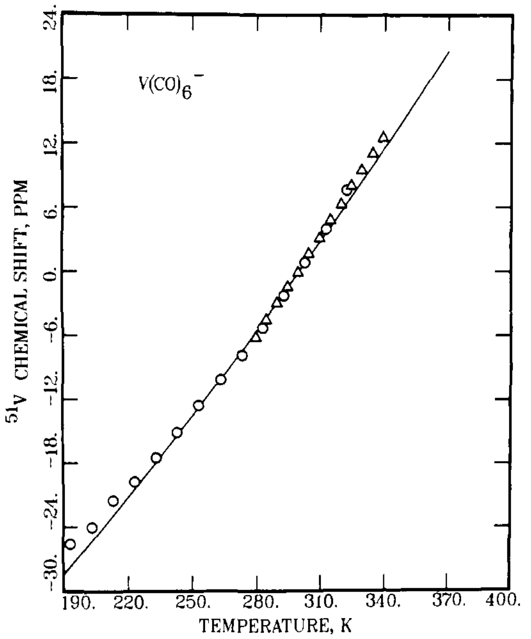

Figure 1. The observed temperature dependence of ^{51}V chemical shift in (Δ) $Na(diglyme)_2{}^+V(CO)_6{}^-$ (280–340 K) and in (○) $(Et_4N)^+V(CO)_6{}^-$ (193–323 K) compared with the calculated temperature dependence according to $\sigma_0(T) - \sigma_0(300\text{ K}) = 6[-2.1 \times 10^3\{\langle\Delta r_{VC}\rangle^T - \langle\Delta r_{VC}\rangle^{300}\} - 8 \times 10^2\{\langle\Delta R_{CO}\rangle^T - \langle\Delta R_{CO}\rangle^{300}\}]$.

solutions involving different cations also indicates that only a very small part of the observed temperature dependence of the ^{51}V chemical shift is due to intermolecular effects. The temperature coefficients for ^{51}V chemical shifts in several carbonyl complexes are given in Table I. These are comparable to those previously reported for ^{59}Co (1.42 to 3.04 ppm/deg)[2] and for ^{195}Pt (0.35 to 0.85 ppm/deg).[3] All are the same sign, i.e., deshielding with increasing temperature. When the temperature dependence of the transition metal chemical shift is studied over a wide range of temperatures, the nonlinear behavior observed in ^{59}Co, ^{195}Pt, and ^{51}V chemical shifts in solution[2-4] is similar to that of ^{19}F in the zero-pressure limit gas phase; that is, the magnitude of the temperature coefficient is somewhat greater at higher temperatures.

Interpretation of Temperature Coefficients of the Chemical Shift and the Isotope Shift

The previous approach to the temperature coefficient of the shielding in Co complexes was based on the notion that as the temperature is changed the statistical occupancy of the ground vibrational levels changes and the *effective* separation between the ground and the excited states is thus changed.[2] The vibration-dependent part of the ligand field splitting parameter Δ was taken to be

$$\delta_{vib}(T) \simeq \sum_j[(\omega_{0j}{}^2 - \omega_{exj}{}^2)/2\omega_{0j}{}^2]h\omega_{0j}\{1/2 + [\exp(h\omega_{0j}/kT) - 1]^{-1}\} \quad (4)$$

such that

$$\sigma = \sigma^d + \sigma^p[1 + \delta_{vib}(T)/\Delta]$$

At first glance this appears to be reasonable. However, in this model, a temperature coefficient depends on the excited electronic state having vibrational frequencies $\omega_{0j} > \omega_{exj}$ different from the ground state. If $\omega_{0j} > \omega_{exj}$, then the lower vibrational frequencies associated with the heavier isotopomers would change the average energy separation in the correct direction to explain the signs of observed NMR isotope shifts. However, this theory would also predict that the isotope shift would be independent of the remoteness of substitution since in eq 4 only the vibrational frequencies of the whole molecule matter, not the location of the observed nucleus relative to the substituted atom. On the contrary, the observation of a strong dependence of the isotope shift on the remoteness of the substitution site from the observed nucleus indicates that NMR isotope shifts in transition metal complexes cannot be properly explained by this theory.

The temperature coefficient of the chemical shift and the isotope shift are intimately connected in that they are both measures of the shielding sensitivity to changes in bond lengths and bond angles. A theory which has been successful in interpreting both the intrinsic temperature dependence and the isotope shifts in NMR is based on the expansion of the nuclear shielding as a function of powers of the displacement coordinates, which may be normal coordinates or internal coordinates.[8,9] We choose internal coordinates so as to have mass-independent derivatives of shielding with respect to displacements. We write for a diatomic molecule[8]

$$\sigma_0(T) = \sigma_e + (\partial\sigma/\partial\Delta r)_e\langle\Delta r\rangle + 1/2(\partial^2\sigma/\partial\Delta r^2)_e\langle(\Delta r)^2\rangle + \ldots \quad (5)$$

where the derivatives of the nuclear shielding are evaluated at the equilibrium bond length. For a diatomic molecule[9]

$$\langle\Delta r\rangle_{vib} \simeq (3a/2)\langle(\Delta r)^2\rangle$$

in which a is the Morse parameter. Thus the intrinsic temperature-dependent chemical shift is

---

(8) Jameson, C. J.; Osten, H. J. *J. Chem. Phys.* **1984**, *81*, 4915–4921, 4288–4292, 4293–4299, 4300–4305. Jameson, C. J. *Ibid.* **1977**, *66*, 4977–4982.

(9) Jameson, C. J.; Osten, H. J. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 1–78.

$$\sigma_0(T) - \sigma_0(300) \simeq \{(\partial\sigma/\partial\Delta r)_e + (1/3a)(\partial^2\sigma/\partial\Delta r^2)_e\}\{\langle\Delta r\rangle^T - \langle\Delta r\rangle^{300}\}_{\mathrm{vib}} + (\partial\sigma/\partial\Delta r)_e\{\langle\Delta r\rangle^{\mathrm{T}} - \langle\Delta r\rangle^{300}\}_{\mathrm{rot}} \quad (6)$$

and the isotope shift is

$$^1\Delta = \sigma - \sigma^* \simeq \{(\partial\sigma/\partial\Delta r)_e + (1/3a)(\partial^2\sigma/\partial\Delta r^2)_e\}\{\langle\Delta r\rangle - \langle\Delta r\rangle^*\} \quad (7)$$

where $\langle\Delta r\rangle^*$ is for the heavy isotopomer.

In M(CO)$_6$, the M chemical shift does not depend on Δr_{MC} alone but also on ΔR_{CO},m $\Delta\alpha_{\mathrm{CMC}}$, and $\Delta\beta_{\mathrm{MCO}}$. Still, the largest change in M shielding should be reflected by $(\partial\sigma^{\mathrm{M}}/\partial\Delta r_{\mathrm{MC}})_e\cdot\langle\Delta r_{\mathrm{MC}}\rangle$. We expect the other derivatives such as $(\partial\sigma^{\mathrm{M}}/\partial\Delta R_{\mathrm{CO}})_e$ to be much less important. Furthermore we shall neglect terms in the second derivatives of the shielding. With these assumptions we can interpret the M shielding changes by the same equations as for an M–C diatomic molecule, except that the right-hand sides of eq 6 and 7 should be summed over all the bonds to M. For M(CO)$_6$ all the M–C bonds are equivalent so that the right-hand sides of eq 6 and 7 can simply be multiplied by 6. $^1\Delta/6$ is then the isotope shift per ^{13}C substitution in M(CO)$_6$. Thus,

$$^1\Delta = \sigma - \sigma^* \approx 6(\partial\sigma/\partial\Delta r)_e\{\langle\Delta r\rangle - \langle\Delta r\rangle^*\} + \ldots \quad (8)$$

Since the mean bond displacements in V(CO)$_6^-$ have been obtained in the previous paper,[10] the shielding sensitivity to changes in bond length can be estimated. Using the observed additive isotope shift in V(CO)$_6^-$, $^1\Delta^{51}\mathrm{V}(^{13/12}\mathrm{C})/6 = -0.27 \pm 0.03$ ppm per ^{13}C,[5] and $\langle\Delta r\rangle_{\mathrm{V^{12}C}} - \langle\Delta r\rangle_{\mathrm{V^{13}C}} = 1.27 \times 10^{-4}$ Å, we obtain:

$$(\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e \approx -(2.1 \pm 0.2) \times 10^3 \text{ ppm/Å} \quad (9)$$

The two-bond isotope shift has also been reported to be additive: $^2\Delta^{51}\mathrm{V}(^{18/16}\mathrm{O})/6 = -0.10 \pm 0.02$ ppm per ^{18}O substitution.[5] We find this as a sum of two terms due to the small change in the V–C bond length and the larger change in the C–O bond length upon ^{18}O substitution:

$$^2\Delta/6 \approx (\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e[\langle\Delta r_{\mathrm{VC}}\rangle_{^{16}\mathrm{O}} - \langle\Delta r_{\mathrm{VC}}\rangle_{^{18}\mathrm{O}}] + (\partial\sigma^{\mathrm{V}}/\partial\Delta R_{\mathrm{CO}})_e[\langle\Delta R_{\mathrm{CO}}\rangle_{^{16}\mathrm{O}} - \langle\Delta R_{\mathrm{CO}}\rangle_{^{18}\mathrm{O}}] \quad (10)$$

Using the respective oxygen mass dependence of Δr_{VC} and ΔR_{CO} already calculated in the previous paper,[10] we obtain

$$-0.10 \pm 0.02 \text{ ppm} \approx -2.1 \times 10^3 \times 6 \times 10^{-6} + (\partial\sigma^{\mathrm{V}}/\partial\Delta R_{\mathrm{CO}})_e 1.06 \times 10^{-4} \quad (11)$$

We note that the first term on the right (due to the slight change in the V–C bond length) is –0.013 ppm, which is of the same order of magnitude as the quoted error in $^2\Delta$. We therefore can neglect this term and find $(\partial\sigma^{\mathrm{V}}/\partial\Delta R_{\mathrm{CO}})_e \simeq -900$ ppm/Å. If we include the first term we would obtain −800 ppm/Å; therefore we report this derivative as

$$(\partial\sigma^{\mathrm{V}}/\partial\Delta R_{\mathrm{CO}})_e \simeq -800 \pm 100 \text{ ppm/Å} \quad (12)$$

This change in ^{51}V shielding due to extension of the remote C–O bond is indeed smaller than the -2.1×10^3 ppm/Å value for $(\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})$. Now we can use the derivatives we have estimated in order to see if they are consistent with the observed temperature dependence:

$$[(\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e]\{\langle\Delta r_{\mathrm{VC}}\rangle^T - \langle\Delta r_{\mathrm{VC}}\rangle^{300}\}_{\mathrm{vib}} + (\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e\{\langle\Delta r_{\mathrm{VC}}\rangle^T - \langle\Delta r_{\mathrm{VC}}\rangle^{300}\}_{\mathrm{rot}} + (\partial\sigma^{\mathrm{V}}/\partial\Delta R_{\mathrm{CO}})_e\{\langle\Delta R_{\mathrm{CO}}\rangle^T - \langle\Delta R_{\mathrm{CO}}\rangle^{300}\} \simeq \tfrac{1}{6}[\sigma_0(T) - \sigma_0(300)] \quad (13)$$

For the temperature range 190 to 340 K, the observed total shielding change is −40 ppm, whereas eq 13 gives

$$\sigma_0(340\text{ K}) - \sigma_0(190\text{ K}) \approx -41.2 - 2.8 - 0.3 = -44.3\text{ppm} \quad (14)$$

We note that for the V–C bond the rotational contribution to the shielding change with temperature is small compared to that due to vibration, i.e., −2.8 ppm compared to −41.2 ppm. This is due to the small rotational contribution (7%) to the mean bond extension with temperature in this molecule. We also note that the contribution to the temperature coefficient of the ^{51}V shielding coming from the CO bond extension is negligible, which supports our contention that $(\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e$ is primarily responsible for the temperature coefficient. Thus, we find that the observed isotope shift and temperature coefficient of the ^{51}V chemical shift in V(CO)$_6^-$ can be interpreted within the same theoretical framework, with a value of $(\partial\sigma^{\mathrm{V}}/\partial\Delta r_{\mathrm{VC}})_e \simeq -2.1 \times 10^3$ ppm/Å.

Using the shielding derivatives obtained from isotope shifts, we have plotted the calculated function $\sigma_0(T) - \sigma_0(300)$ vs. temperature in Figure 1. The curvature is in the same direction as that found for $\sigma(T) - \sigma(300)$ of ^{59}Co in Co(NH$_3$)$_6^{3+}$ and of ^{145}Pt in Pt(R$_3$P)$_2$Cl$_2$,[2,3] and also found in the $\sigma_0(T) - \sigma_0(300)$ of ^{19}F in the zero-pressure limit in gaseous fluoromethanes and fluoroethenes.[11,12] The observed nonlinear temperature dependence of the chemical shift of the transition metal nucleus is due to the nonlinear behavior of $\langle\Delta r\rangle^T$ and $\langle(\Delta r)^2\rangle^T$, such as shown in the previous paper.[10] The curvature in these bond displacement functions is less at higher temperatures, just as they are for C–F bonds[11,12] and for Pt–Cl bonds,[13] which is entirely consistent with the commonly observed more nearly linear behavior of $\sigma_0(T) - \sigma_0(300)$ at higher temperatures.[2,3]

We can apply the same procedure to the ^{59}Co shielding in the Co(CN)$_6^{3-}$ complex. The observed isotope shifts are additive:[14]

$$^1\Delta^{59}\mathrm{Co}(^{13/12}\mathrm{C})/6 = -0.914 \pm 0.004 \text{ ppm per } ^{13}\mathrm{C}$$

$$^2\Delta^{59}\mathrm{Co}(^{15/14}\mathrm{N})/6 = -0.197 \pm 0.007 \text{ ppm per } ^{15}\mathrm{N}$$

From $^1\Delta$ we can obtain,

$$(\partial\sigma^{\mathrm{Co}}/\partial\Delta r_{\mathrm{CoC}})\mathrm{e} \simeq -0.914/(1.22 \times 10^{-4}\text{ Å}) = -7.5 \times 10^3 \text{ ppm Å}^{-1} \quad (15)$$

From $^2\Delta$ we can use an equation similar to eq 10 to obtain

$$(\partial\sigma^{\mathrm{Co}}/\partial\Delta R_{\mathrm{CN}}): \quad {}^2\Delta^{59}\mathrm{Co}(^{15/14}\mathrm{N})/6 \approx (\partial\sigma^{\mathrm{Co}}/\partial\Delta r_{\mathrm{CoC}})_e[\langle\Delta r_{\mathrm{CoC}}\rangle_{^{14}\mathrm{N}} - \langle\Delta r_{\mathrm{CoC}}\rangle_{^{15}\mathrm{N}}] + (\partial\sigma^{\mathrm{Co}}/\partial\Delta R_{\mathrm{CN}})_e[\langle\Delta R_{\mathrm{CN}}\rangle_{^{14}\mathrm{N}} - \langle\Delta R_{\mathrm{CN}}\rangle_{^{15}\mathrm{N}}] \quad (16)$$

Using the calculated nitrogen mass dependence of $\langle\Delta r_{\mathrm{CoC}}\rangle$ and $\langle\Delta R_{\mathrm{CN}}\rangle$ which we found in the previous paper,[10] we get

$$(\partial\sigma^{\mathrm{Co}}/\partial\Delta R_{\mathrm{CN}})_e \simeq -2.3 \times 10^3 \text{ ppm Å}^{-1} \quad (17)$$

We can use these derivatives to calculate the temperature dependence of the ^{59}Co shift in Co(CN)$_6^{3-}$:

$$(\partial\sigma^{\mathrm{Co}}/\partial\Delta r_{\mathrm{CoC}})_e\{\langle\Delta r_{\mathrm{CoC}}\rangle^T - \langle\Delta r_{\mathrm{CoC}}\rangle^{300}\}_{\mathrm{vib}} + (\partial\sigma^{\mathrm{Co}}/\partial\Delta r_{\mathrm{CoC}})_e\{\langle\Delta r_{\mathrm{CoC}}\rangle^T - \langle\Delta r_{\mathrm{CoC}}\rangle^{300}\}_{\mathrm{rot}} + (\partial\sigma_{\mathrm{Co}}/\partial\Delta R_{\mathrm{CN}})_e\{\langle\Delta R_{\mathrm{CN}}\rangle^T - \langle\Delta R_{\mathrm{CN}}\rangle^{300}\} \approx \tfrac{1}{6}[\sigma_0(T) - \sigma_0(300)] \quad (18)$$

For the temperature range 280 to 360 K the numerical values of the three terms in eq 18 are respectively

$$\sigma_0(360) - \sigma_0(280) = -95.2 - 5.0 - 0.3 = -100.5 \text{ ppm} \quad (19)$$

Note that the contributions to the temperature coefficient of the ^{59}Co shift coming from rotation and remote bond extension are again much smaller than that due to vibration. For ^{59}Co shift in this complex, Benedek et al. reported a temperature coefficient of −1.38 ± 0.01 ppm/deg between 280 and 360 K,[2] which gives a total change of −110 ppm to be compared with our −100.5 ppm.

One of the largest isotope shifts which has been observed is the deuterium-induced ^{59}Co shift in Co(NH$_3$)$_6^{3+}$ ion which is −5.2 ppm per D.[16] We have previously calculated $\langle\Delta r_{\mathrm{NH}}\rangle - \langle r_{\mathrm{ND}}\rangle$

---

(10) Jameson, C. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(11) Jameson, C. J.; Osten, H. J. *Mol. Phys.* **1985**, *55*, 383–395.

(12) Jameson, C. J.; Osten, H.J. *J. Chem. Phys.* **1985**, *83*, 5425–5433.

(13) Jameson, C. J.; Jameson, A. K. *J. Chem. Phys.* **1986**, *85*, 5484–5492.

(14) Lauterbur, P. C. *J. Chem. Phys.* **1965**, *42*, 799.

(15) Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458–463.

Table II. Shielding Sensitivity to Bond Extension

compound	derivative, ppm $Å^{-1}$
$V(CO)_6^-$	$(\partial\sigma^V/\partial\Delta r_{VC})_e \approx -2 \times 10^3$
	$(\partial\sigma^V/\partial\Delta R_{CO})_e \approx -8 \times 10^2$
$Co(CN)_6^{3-}$	$(\partial\sigma^{Co}/\partial\Delta r_{CoC})_e \approx -8 \times 10^3$
	$(\partial\sigma^{Co}/\partial\Delta R_{CN})_e \approx -2 \times 10^3$
$Co(NH_3)_6^{3+}$	$(\partial\sigma^{Co}/\partial\Delta R_{NH})_e \approx -9 \times 10^2$

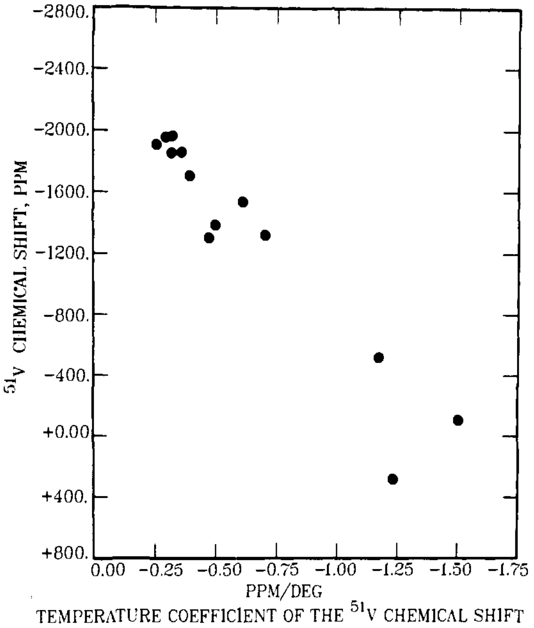

Figure 2. Temperature coefficients of the ^{51}V chemical shift for the carbonyl complexes listed in Table I. The chemical shifts are in ppm relative to $VOCl_3$(l).

= 5.56 × 10^{-3} Å in NH_3 and ND_3.[17] Thus, we can estimate $(\partial\sigma^{Co}/\partial\Delta r_{NH})_e \simeq -5.2$ ppm/5.56 × 10^{-3} Å = −935 ppm $Å^{-1}$. This value is not all unusual compared to −800 and −2300 ppm $Å^{-1}$ that we have found for the change in transition metal shielding transmitted through two bonds. Our results are summarized in Table II.

Correlations of $d\sigma_0/dT$ with Chemical Shifts

Observations. For purposes of comparison of the temperature dependence of ^{51}V shielding in several compounds, the average $d\sigma/dT$ values in the temperature ranges shown are given in Table I and plotted in Figure 2. The ordinate in Figure 2 is in terms of chemical shifts relative to $VOCl_3$(l) reference. The absolute σ^p for ^{51}V in $V(CO)_6^-$ ion has been estimated to be −5800 ppm;[18] however, this is subject to the errors in the determination of γ_0, which has yet to be carried out for ^{51}V to the precision that is now available for ^{59}Co.[19] The correlation of the temperature coefficients with the shielding of ^{51}V in Figure 2 is similar to that reported previously for ^{19}F in fluoromethanes.[6] The magnitude of $d\sigma_0/dT$ increases with decrease in shielding for both nuclei. While ^{19}F values varied from −0.001 to −0.01 ppm/deg over a 300-ppm range of chemical shifts, ^{51}V values range from −0.3 to −1.5 ppm/deg in a 2500-ppm range of chemical shifts. Nevertheless, the trends are the same.

The correlation observed in Figure 2 is between the chemical shift (or σ) which is largely an electronic property and a quantity ($d\sigma_0/dT$) which includes electronic factors ($(\partial\sigma/\partial\Delta r)_e$) and dynamic factors ($\langle\Delta r\rangle^T$, $\langle(\Delta r)^2\rangle^T$). The temperature coefficient of the mean bond displacement is not drastically different for the same bond in closely related molecules. For example, $d\langle\Delta r\rangle^T/dT$ at 300 K is 4.05 to 4.25 × 10^{-6} Å/deg in the halomethanes through the series CF_4, ..., $CFCl_3$, ..., CF_3I.[11] V–C and Co–C bond lengths have similar temperature coefficients, as shown in the preceding paper.[10] The relatively small variation in the dynamic factors from one carbonyl compound to another allows the correlation between the two electronic quantities $(\partial\sigma/\partial r)_e$ and σ to be observed.

It has been postulated that the observed correlation of $(\partial\sigma/\partial r)_e$ and σ in ^{19}F is based on the larger changes upon bond extension in the paramagnetic contribution to shielding compared to the diamagnetic contribution.[6,9] For example, the parallel component which is entirely diamagnetic (by symmetry) in HF is not very sensitive to bond extension; $(\partial\sigma_{\parallel}^F/\partial\Delta r)_e = -3.7$ ppm/Å in HF. On the other hand, the perpendicular component, which includes both diamagnetic and paramagnetic terms, changes drastically; $(\partial\sigma_{\perp}^F/\partial\Delta r)_e = -662$ ppm/Å.[9] Theoretical calculations of the change in the diamagnetic shielding term upon bond extension all yield relatively small values.[20] Thus, it is reasonable to look to the paramagnetic term in seeking an explanation for the observed correlation in Figure 2.

Shielding Dependence on Metal–Ligand Distance in an Electrostatic Model. There have been some ab initio calculations of transition metal shielding, in particular, of Mn in $Mn(CO)_5X$ complexes.[21] These results support an important assumption that has usually been made in qualitative models of transition metal shielding, namely, that there are negligible changes in the diamagnetic shielding from the free atom value when compared to the changes in the paramagnetic shielding. Furthermore, these calculations show that the paramagnetic term is dominated (99%) by d orbitals of Mn. Therefore, we shall consider our results in terms of only the paramagnetic terms σ^p with a semiquantiative model involving only d orbitals. The latest form of this model is that of Bramley et al. which combines the influences of ligand position in the nephelauxetic series and the spectrochemical series:[19]

$$\sigma^p = -k(\langle r_{3d}^{-3}\rangle/\beta)\left\{\beta \sum_{\alpha=x,y,z} \frac{|\langle a^1A_{1g}|\tilde{\mathbf{L}}_z|a^1T_{1g}(z)\rangle|^2}{\Delta E(a^1T_{1g}(\alpha))}\right\} \quad (20)$$

where k is a product of fundamental constants $\mu_0 e^2/(12\pi m_e^2)$, β is the nephelauxetic ratio, and the prefix a in a^1A_{1g} and a^1T_{1g} indicates that this is the lowest term of the symmetry type. The parametric d^q model, as it is called, uses optical spectra to define empirical parameters Δ, B, and C (B and C are Racah parameters); the transition energies are found by diagonalization of the appropriate matrices for the d^n configuration assuming an intermediate field (not necessarily the strong field limit) for the complex. The eigenvectors found in the energy diagonalization are used to calculate the **L** matrix elements for the complex. This model includes only d electrons and also neglects any covalency effects in evaluating the **L** matrix elements. The energy term corresponding to the first cubic absorption band ($a^1A_{1g} \rightarrow a^1T_{1g}$) denoted by $\Delta E(a^1T_{1g})$ in eq 20 is predominantly determined by the field strength Δ. It is found by Bramley et al. in applying this model to d^6 cobalt complexes, that the quantity $(\langle r^{-3}\rangle_{3d}/\beta)$ is a constant. That is, $\langle r^{-3}\rangle_{3d}$ for the complex varies with B for the complex in such a way that a plot of $\gamma_0(1 - \sigma^{Co})$ for octahedral complexes vs. the quantity in curly brackets in eq 20 gives a straight line with intercept $\gamma_0(1 - \sigma^d)$ and slope related to $\langle r_{3d}^{-2}\rangle$ in the complex scaled by β. This plot shows considerably less scatter than any others previously proposed and includes ligand atoms from different rows of the periodic table. Knowing $\gamma_0(^{59}Co)$ from the intercept and using $\sigma^d = 0.0022$ (the free atom value) leads to paramagnetic shielding values $\sigma^p = -0.0227$ for $Co(H_2O)_6^{3+}$ and −0.0076 for the $Co(CN)_6^{3-}$ ion.[19]

Keeping in mind the limitations of this electrostatic model for shielding, we can use eq 20 to examine the r dependence of σ^p. The factors involved can be written as foollows:

---

(16) Bendall, M. R.; Doddrell, D. M. *Aust. J. Chem.* **1978**, *31*, 1141–1143. Russell, J. G.; Bryant, R. G.; Kreevoy, M. M. *Inorg. Chem.* **1984**, *23*, 4565–4567.

(17) Osten, H. J.; Jameson, C. J. *J. Chem. Phys.* **1985**, *82*, 4595–4606.

(18) Juranic, N. *Inorg. Chem.* **1985**, *24*, 1599–1601.

(19) Bramley, R.; Brorson, M.; Sargeson, A. M.; Schäffer, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 2780–2787.

(20) Amos, R. D. *Mol. Phys.* **1980**, *39*, 1–14. *Chem. Phys. Lett.* **1979**, *68*, 536–539.

(21) Kanda, K.; Nakatsuji, H.; Endo, K.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5888–5892.

$$\sigma^{\mathrm{p}} \approx -k'(\beta L/\Delta E) \tag{21}$$

where k' includes the fundamental constants and $\langle r^{-3}\rangle_{3\mathrm{d}}/\beta$, L stands for $|\langle a^1\mathrm{A}_{1g}|\mathrm{L}_z|a^1\mathrm{T}_{1g}(z)\rangle|^2$, and ΔE^{-1} stands for $\sum_{\alpha=x,y}\Delta E^{-1}(a^1\mathrm{T}_{1g}(\alpha) - a^1\mathrm{A}_{1g})$. All three factors depend on the metal–ligand distance, so that we may write,

$$\frac{1}{\sigma^{\mathrm{p}}}\frac{\partial\sigma^{\mathrm{p}}}{\partial r} = -\frac{1}{\Delta E}\frac{\partial \Delta E}{\partial r} + \frac{1}{\beta}\frac{\partial\beta}{\mathrm{d}r} + \frac{1}{L}\frac{\partial L}{\partial r} \tag{22}$$

In eq 22 and $(\partial\Delta E/\partial r)$ term is the dominant one. This is supported by the linear relationship found in cobalt complexes between the gyromagnetic ratio of ^{59}Co measured in Co(III) complexes and the wavelength of the $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{T}_{1g}$ transition in these complexes, both change with temperature such that $\mathrm{d}\gamma/\mathrm{d}\lambda$ is approximately constant.[22] In the limiting case in which the ligands are point charges (ze) and $\Delta/B = \infty$, $\Delta E = (5/3)ze^2\langle r^4\rangle_{3\mathrm{d}}r^{-5}$. Therefore, let us assume that for intermediate ligand fields ΔE varies as r^{-n} in the vicinity of r_{e}, the equilibrium metal–ligand distance. If we make the further drastic assumptions that $\beta \propto r^m$ and $L \propto r^l$ in the vicinity of r_{e}, then these allow us to write

$$\left(\frac{\partial\sigma^{\mathrm{p}}}{\partial r}\right)_{\mathrm{e}} \approx \frac{(n+m+l)}{r_{\mathrm{e}}}\sigma_{\mathrm{e}}^{\mathrm{p}} \tag{23}$$

and

$$\left(\frac{\partial^2\sigma^{\mathrm{p}}}{\partial r^2}\right)_{\mathrm{e}} \approx \frac{(n+m+l-1)}{r_{\mathrm{e}}}\left(\frac{\partial\sigma^{\mathrm{p}}}{\partial r}\right)_{\mathrm{e}} \tag{24}$$

If we neglect the r dependence of σ^{d}, then $(\partial\sigma/\partial r) \approx (\partial\sigma^{\mathrm{p}}/\partial r)$, and we can write the temperature dependence of the shielding (eq 7) as

$$\sigma_0(T) - \sigma_0(300) \approx [(n+m+l)\sigma^{\mathrm{p}}]6[\langle\Delta r\rangle^{\mathrm{T}} - \langle\Delta r\rangle^{300}]/r_{\mathrm{e}} \tag{25}$$

In this simple electrostatic model of shielding, values of $(n + m + l)$ between 5 and 6 can be assumed, based on the following related experiments. The dependence of ΔE on the metal–ligand distance in some octahedral complexes has been determined experimentally by Drickamer.[23] V^{3+}, Ni^{2+}, Ni^{3+}, Cr^{3+}, and Ti^{3+} ions are present substitutionally in Al^{3+} sites having octahedral symmetry in $\mathrm{Al_2O_3}$. Because the lattice is very rigid with high cohesive energy, the effects of pressure can be translated directly into a uniform change in the metal–O distance as obtained from compressibility data. The dependence of ΔE on pressure (up to 60 kbars) for all these metal ions fall on *the same* r_{MO}^{-5} curve.[23] Thus, $(1/\Delta E)(\partial\Delta E/\partial r) = (-n/r)$, where $n = 5$ for these ions. In other systems, deviations of high-pressure optical experiments from the r^{-5} law have been attributed to local relaxation and higher local compressibility near the foreign ion.

The dependence of β on the metal–ligand distance in octahedral complexes has been studied by measuring the pressure dependence of the second and third optical transitions which depend on B and C. B has been found to decrease with increasing pressure in all cases. For example, for pressures of 1, 50×10^3, and 100×10^3 atm, $\Delta r/r_0$ in several complexes changed from 0 to −0.01 to −0.016,[24] while $\Delta B/B_0$ changed from 0 to −0.023 to −0.035.[25] If we assume the form $\beta \propto r^m$, then these data translate to $0 < m \lesssim 1$.

The dependence of the quantity L in eq 21 on the metal–ligand distance r in octahedral complexes has not been directly determined. However, Bramley et al. have calculated L as a function of $\beta/\Delta E$ for 11 orthoaxial Co complexes.[19] We have fitted their values of L and $(\beta/\Delta E)$ and found that for these complexes $L \propto (\beta/\Delta E)^{0.036}$. Thus, we take the r dependence of L to be $L \propto r^l$ where $l = 0.036$ $(n + m)$, clearly negligible compared to $n + m$. Thus, in the electrostatic model of shielding $(n + m + l)$ in eq 23 − 25 is between 5 and 6.

Table III. ^{51}V Isotope Shifts Induced by ^{12}CO/^{13}CO Substitution

δ^a (ppm)	compound	$^1\Delta^{51}\mathrm{V}(^{13/12}\mathrm{C})$ (ppm per $^{13}\mathrm{C}^b$)
−1955	$[\mathrm{V(CO)}_{6-n}(^{13}\mathrm{CO})_n]^-$	$-0.27(3)^c$
−1533	η^5-$\mathrm{C_5H_5V(CO)}_{4-n}(^{13}\mathrm{CO})_n$	$-0.46(2)^c$
−1489	η^5-$\mathrm{C_5Me_5V(CO)}_{4-n}(^{13}\mathrm{CO})_n$	−0.42
−1485	η^7-$\mathrm{C_7H_7V(CO)}_{3-n}(^{13}\mathrm{CO})_n$	−0.38

[a] ^{51}V chemical shift (for the lightest isotopomer) at 300 K, ppm relative to $\mathrm{VOCl_3(l)}$. [b] The isotope shifts, indicated for $\Delta n = 1$, are linear throughout within the limits of error (the estimated error is given in parentheses). All measurements have been carried out at 94.54 MHz. [c] Hoch, M.; Rehder, D. *Inorg. Chim. Acta* **1986**, *111*, L13.

Applications and Limitations of the Electrostatic Model. The d^q model is considerably less sophisticated than the ab initio coupled Hartree–Fock shielding model so we should expect only *qualitative* agreement with experiment. Nevertheless, eq 25 is useful for our purposes. From this equation, it is immedately obvious that $\mathrm{d}\sigma_0/\mathrm{d}T$ should be negative (since σ^{p} is negative) and should correlate with values of σ^{p} in related compounds, provided that the dynamic averages inside the curly brackets are roughly constant for the complexes being compared. Thus, although the terms $(n + m + l)$, r_{e}, and $(\mathrm{d}/\mathrm{d}T)\langle\Delta r\rangle^T$ are all changing slightly in the series of vanadium complexes from $\mathrm{V(CO)_6}^-$ to $\mathrm{CpV(CO)_3THF}$, the general correlation with σ^{p} itself as expressed in eq 25 should be apparent: the most deshielded ^{51}V environments (largest σ^{p}) exhibit the greatest temperature coefficients. This is indeed the trend observed in Figure 2. The sign of $\mathrm{d}\sigma_0/\mathrm{d}T$ and the general correlation of $\mathrm{d}\sigma_0/\mathrm{d}T$ with the chemical shift is correctly predicted by this model.

By substituting eq 23 and 24 into eq 8 we predict that the isotope shift $^1\Delta$ should also correlate with σ^{p}. That is, the magnitude of the isotope shift should increase with decreased shielding in a series of related molecules when the dynamic averages $(\langle\Delta r\rangle - \langle\Delta r\rangle^*)$ vary only slowly in the series. To verify this we compare the ^{13}C-induced ^{51}V isotope shifts in several carbonyl complexes in Table III. The magnitudes of the isotope shifts do roughly correlate with shielding in the same way as the temperature coefficients of shielding. This trend has been pointed out previously in other systems.[6,9]

There are important limitations in this model for $(\partial\sigma/\partial r)_{\mathrm{e}}$. It is a parametric model which ignores the covalent bonding in the complex except as the covalency information is implicitly contained in the empirical parameters Δ and B. Note that covalent bonding can change the value of L relative to that calculated by the d^q model, as is known from magnetic susceptibility measurements.[26] The direct proportionality between $(\partial\sigma/\partial r)_{\mathrm{e}}$ and σ^{p} resulting from the electrostatic nature of the model is too restrictive. If indeed we can write $(\partial\sigma/\partial\Delta r)_{\mathrm{e}}$ so simply as $[(n + m + l)/r_{\mathrm{e}}]\sigma^{\mathrm{p}}$, then with $r_{\mathrm{e}} = 1.89$ Å[27] and $\sigma^{\mathrm{p}} = -0.0076$[19] for $\mathrm{Co(CN)_6}^{3-}$ ion, eq 23 would lead to $(\partial\sigma/\partial\Delta r_{\mathrm{Co-C}})_{\mathrm{e}} \simeq -2.0 \times 10^4$ ppm Å^{-1}. (We had obtained -8×10^3 ppm Å^{-1} from the $^{13/12}$C-induced isotope shift and temperature coefficients.) Similarly, for $\mathrm{Co(NH_3)_6}^{3+}$ ion in which $\sigma^{\mathrm{p}} = -0.015\,82$,[19] eq 25 leads to $(\partial\sigma^{\mathrm{Co}}/\partial\Delta r_{\mathrm{Co-N}})_{\mathrm{e}} \approx -4.2 \times 10^4$ ppm Å^{-1}. We believe these values predicted by the electrostatic model to be *too large*.

It may be tempting to use eq 25 as a basis for estimating *absolute shielding* by extrapolating values of $\mathrm{d}\sigma_0/\mathrm{d}T$ in several series of related complexes to a common point of zero σ^{p}.[3] However, this would be an unwarranted use of a very simple model and could lead to an incorrect absolute shielding scale. In the case of ^{51}V the intercept (zero $\mathrm{d}\sigma_0/\mathrm{d}T$) in the vicinity of $\delta \approx -2500$ ppm relative to $\mathrm{VOCl_3(l)}$ would lead to $\sigma^{\mathrm{p}}(\mathrm{V(CO)_6}^-) \approx -500$ ppm. If this is correct then $\sigma^{\mathrm{p}}(\mathrm{CpV(CO)_3THF})$ would be ≈ -2500 ppm and the temperature coefficients calculated by eq 25 using identical dynamic factors for both molecules would be −0.3 and −1.5 ppm/deg, respectively. These values are in excellent agreement

---

(22) Juranic, N. *J. Chem. Phys.* **1981**, *74*, 3690–3693.

(23) Drickamer, H. G. *Solid State Phys.* **1965**, *17*, 1–133.

(24) Parsons, R. W.; Drickamer, H. G. *J. Chem. Phys.* **1958**, *29*, 930–937.

(25) Zahner, J. C.; Drickamer, H. G. *J. Chem. Phys.* **1961**, *35*, 1483–1496.

(26) Stevens, K. W. H. *Proc. R. Soc. London, Ser. A* **1953**, *219*, 542–555.

(27) Curry, N. A.; Runciman, W. A. *Acta Crystallogr.* **1959**, *12*, 674.

with experiment. However, this agreement can only be fortuitous. The value $\sigma^p \approx -500$ ppm for $V(CO)_6^-$ appears to be too small. The absolute shielding for ^{51}V is not yet known although there are two estimates of σ^p for $^{51}V(CO)_6^-$: −5800 ppm (Juranic[18]) and −5993 ppm (Nakano[28]).[29]

There are two important conditions that are not fulfilled in the region of extrapolation. While $(\partial\sigma/\partial r)_e$ may be dominated by $(\partial\sigma^p/\partial r)_e$ when σ^p is a large negative contribution, this is not likely to hold when $\sigma^p \sim 0$. While the observed $\mathrm{d}\sigma/\mathrm{d}T$ in solution may be dominated by $\mathrm{d}\sigma_0/\mathrm{d}T$ when the latter is large compared to intermolecular effects $\sigma_1'(\mathrm{d}\rho_{\mathrm{liq}}/\mathrm{d}T)$, this is not likely to hold in the vicinity of $\mathrm{d}\sigma_0/\mathrm{d}T \sim 0$. While the empirical correlation in Figure 2 is deceptively linear, as the electrostatic model predicts, the empirical correlation observed for ^{19}F in fluoromethanes is decidedly curved, approaching $\mathrm{d}\sigma_0/\mathrm{d}T = 0$ asymptotically with F in CH_3F molecule at that extreme end ($\sigma^p \sim 0$).[6] Although all observations indicate that $(\partial\sigma/\partial r)$ and σ^p are related, the true relationship cannot be as simple as the strict proportionality between $(\partial\sigma/\partial r)$ and σ^p which results from the assumptions of the electrostatic model for shielding.

Conclusions

The magnitude of the temperature coefficients of the chemical shifts are much larger for transition metal nuclei than for others (^{19}F, ^{15}N, ^{13}C, ^{31}P). Thus, the effects of intermolecular interactions, while not small in the absolute sense, are small enough to be neglected compared to the total temperature coefficient. Therefore, for transition metal nuclei it is possible to obtain the effects of rovibrational averaging on nuclear shielding in complexes in solution, without zero-pressure limit gas-phase studies.

We have presented a theory which accounts for the observed temperature coefficients of nuclear shielding for transition metal nuclei in complexes in solution and the relatively large isotope shifts which are induced by substitution of ligand atoms. As typical examples, the vibrational analysis of $V(CO)_6^-$ and $Co(CN)_6^{3-}$ provide dynamic averages of the bond displacements V–C, C–O, Co–C, and C–N, in terms of anharmonic force constants, taking into account Morse stretching anharmonicity as well as nonbonded interactions. These dynamic averages are temperature and mass dependent in a way which successfully accounts for the observed NMR shifts with temperature and isotopic substitution in these complexes. The conclusions for these two typical cases provide a general explanation for temperature coefficients and isotope shifts of transition metal nuclei in their complexes.

We have observed a correlation between the temperature coefficients and the chemical shifts. This correlation is qualitatively consistent with the simple electrostatic model for shielding which was originally proposed in the 1960s and recently refined by Bramley et al. While the electrostatic model for shielding is very successful in correlating chemical shifts of a wide variety of transition metal complexes and also in correlating the temperature coefficients of the chemical shifts with the chemical shifts themselves, the exact form of the predicted dependence of transition metal shielding on the metal–ligand distance is probably incorrect.

Acknowledgment. This research was supported in part by the National Science Foundation (CHE85-05725) and the Fonds der Chemischen Industrie, F.R.G.

---

[28] Nakano, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 661–665.

[29] These estimates are not independent since both values are based on Nakano's value for VO_4^-. The latter method gives σ^p values for Mn in $Mn(CO)_5X$ that are considerably different from the ab initio calculations, so the ^{51}V estimates may be seriously flawed.

Benzobisdithiazole (BBDT): An Electron Spin Resonance Study

Elmar Dormann,*[†] Michael J. Nowak, Keith A. Williams, Richard O. Angus, Jr., and Fred Wudl*

Contribution from the Institute for Polymers and Organic Solids, Department of Physics, University of California, Santa Barbara, California 93106. *Received July 7, 1986*

Abstract: We report on ESR properties of the title compound in different oxidation states in solution and in the solid state. Comparative studies of the ESR properties of the deuterated derivatives of BBDT and benzodithiazole (BDT) in conjunction with extended Hückel molecular orbital calculations are also reported. It is shown that BBDT forms a diradical which exists as an oligomer in solution and in the solid state. The radical cation exhibits the expected hyperfine spectrum whereas the diradical does not; explanations for these observations are presented.

In a recent paper we described preliminary findings on our research on the novel title compound[1] which was prepared as part of a program to design molecules which would be stable, neutral diradicals[2] with the intent to generate neutral organic metals. However, we also realized that these molecules may fit a variant along the lines of the McConnell hypothesis where we let the neutral donor be the triplet and the acceptor be the *radical ion derived from the donor*. This modification would allow us to generate homomolecular stacks which could give rise to *ferromagnetic organic metals* (FOM). The McConnell–Breslow and our approaches are sketched in Figure 1.

As can be seen from the figure, our FOM (Figure 1d) has two important differences from one version of the McConnell idea (Figure 1b): (a) the stoichiometry is D_2A (A = monovalent, closed-shell counteranion), rather than simple charge-transfer complex "DA", and (b) degeneracy; i.e., the species on the left of the double-headed arrow are identical with those on the right (a dictate of the spin conservation rules and a consequence of point a). The proposed FOM evolved naturally from extensive research on organic metals and superconductors[3,4] [e.g., $(TMTSF)_2X$]. The crux of our FOM is the design of a stable donor diradical which should have a triplet ground state and should not have a driving force toward dimerization (polymerization). We concluded that the functional group best suited to fulfill these requirements would

---

[†] Visiting Scientist from the Physikalisches Institut und Bayreuther Institut für Makromolekül-Forschung (BIMF), Universität Bayreuth, POB 10 12 51, D-8580 Bayreuth, Federal Republic of Germany.

[1] Williams, K. A.; Nowak, M. J.; Dormann, E.; Wudl, F. *Synth. Met.* **1986**, *14*, 233. See also: Wolmershäuser, G.; Schnauber, M.; Wilhelm, T.; Sutcliffe, L. H. *Ibid.* **1986**, *14*, 239.

[2] Wudl, F. *Pure Appl. Chem.* **1982**, *54*, 1051.

[3] Bechgaard, K.; Jerome, D. *Sci. Am.* **1982**, *247*, 52.

[4] Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227 and references therein.

0002-7863/87/1509-2594$01.50/0