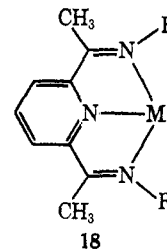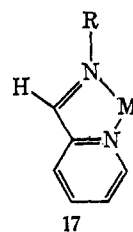16

17   18

of amines and isocyanides parallels the formation of polydentate ligands from the condensation of aldehydes and amines. In the first case the isocyanide provides the carbon donor center while in the Schiff base formation the amine provides the nitrogen donor. Consequently the amine plays the same role in the formation of carbene chelates as the aldehyde does in the formation of polydentate Schiff base ligands. Thus, hydrazine, 2-aminopyridine, and 2,6-diaminopyridine are used to form the chelating ligands in 1, 6, and 8, respectively, while carbonyl compounds—biacetyl, pyridine-2-aldehyde, and 2,6-diacetylpyridine—are used to form the analogous ligands of compounds 16, 17,[17] and 18.[26] Clearly a number of other chelating ligands may be obtained from the amine–isocyanide reaction, but it remains to be seen if such ligands may be constructed

about metals other than palladium and platinum. Ligands such as carbon monoxide and NO^+ which are isoelectronic with isocyanides are known to undergo the addition of nucleophiles such as amines. Consequently, these may also be expected to form related chelating ligands, and at least one parallel exists. The reaction of $Mn(CO)_5Br$ with lithiated amidines produces a chelating ligand analogous to that found in 5b.[27] However, the addition of hydrazine to metal carbonyls generally produces coordinated isocyanate rather than a chelating ligand[28] and so completely parallel behavior is not to be expected.

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On the Kinetic Trans Effect in Square Planar Transition Metal Complexes

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Abstract: It is shown that the trans effect series for square planar d^8 complexes can be related to two spectrochemical parameters. The first one is the octahedral field splitting Dq; the second parameter, τ, accounts for the relative importance of σ and π bonding ($\tau = \pi'/\sigma'$). In the kinetic analysis of the substitution reactions under consideration, the role of the ligand field activation energy (LFAE) has been investigated. The LFAE was considered to be the difference between the ligand field stabilization energy of a trigonal bipyramidal transition state and that of the square planar metal complex. Both energies can be expressed in terms of the relevant spectrochemical parameters. It is found that the experimental trans effect series can be reproduced qualitatively from the predicted variation of the LFAE as a function of Dq and τ. In the same way, predictions can be made on the kinetic cis effect. In this case, however, the limited range of experimental data makes the results less conclusive.

The trans effect has been studied most thoroughly for square planar d^8 systems, especially for Pt(II) complexes. The following series of ligands, A, is shown in order of decreasing rate of substitution of the ligand, T, trans to A: $C_2H_4 \sim CO \sim CN^- > R_3P \sim H^- > CH_3^- > C_6H_5^- > NO_2^- > I^- > SCN^- > Br^- > Cl^- > py > NH_3 > H_2O, OH^-$. The observed rate constants span a range of about five or six orders of magnitude.

In order to rationalize these experimental data, it has been supposed that the Pt–T bond is weakened by the Pt–A interaction.[1] The Pt–T weakening—a purely thermodynamic effect—is usually called the trans influence.[2]

It has been studied rather extensively by measuring Pt–T bond distances, infrared stretching frequencies, and nmr coupling constants.[3] Attempts to understand the trans influence usually invoke the role of the Pt 6s and 6p orbitals in the A–Pt–T bonding.[3–5] Although the bond weakening data could explain part of the rate variations, a more complete understanding of the trans effect requires consideration of the transition state.

Different authors have shown how the energy of the transition state can be affected by the nature of the A

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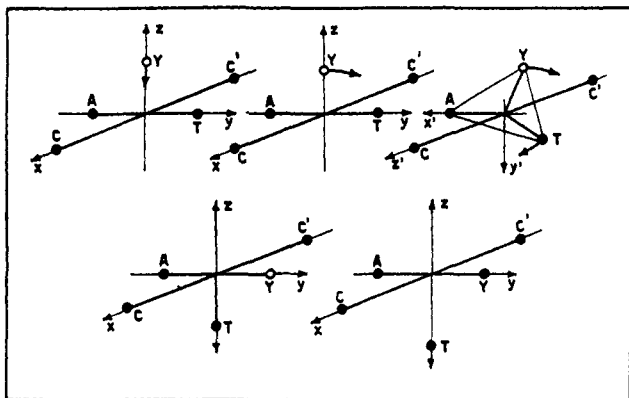(5) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 90, 6669 (1968).

Figure 1. Associative substitution reaction Pt(ACC'T) + Y → Pt(ACC'Y) + T. T is the ligand trans to A, C and C' are the ligands cis to A, and Y is the incoming ligand.

ligand. It has been argued that strong σ-bonding between A and the metal 6p orbital favors a low activation energy for the substitution reaction.[4-6] Similarly, ligands possessing empty π* orbitals have been supposed to accommodate the excess electronic charge added to the central metal by the entering ligand, thus lowering the energy of the transition state.[4,6-8] On the basis of simple orbital overlap considerations, it seems possible to rationalize roughly the general trends in the trans effect series.[4]

One might look at the same phenomenon from a different point of view. One of the various contributions to the total activation energy is the ligand field activation energy (LFAE). It is defined as the difference between the ligand field stabilization energy (LFSE) of the transition state and the ligand field stabilization energy of the metal complex entering into the reaction. The LFSE is defined as the one-electron energy gain due to the ligand field splitting; it is the energy stabilization resulting from the. preferential occupation of the lowest d orbitals. The LFAE is obviously only one of the different constituents of the total activation energy; yet, consideration of *only* this constituent has been rather successful in the kinetic study of certain transition metal reactions.[6,9,10] For instance, it has been possible to explain the relative inertness of otherwise comparable complexes by considering only the ligand field part of the activation energy.

Therefore, it seems reasonable to investigate how the LFAE changes for the substitution of the ligand trans to A, as A is varied.

The Reaction Mechanism

It is quite generally accepted that ligand substitution in square planar complexes takes place according to an associative reaction mechanism. Figure 1 can be considered as an approximate representation of the actual reaction path for the Y–T exchange. If so, the transition state cannot be very far from a trigonal bipyramid. The mechanism, represented in Figure 1, explains the stereospecificity of the substitution reactions.

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Temperature studies indicate that the entropy of activation does not vary very significantly in the square planar Pt(II) substitutions. Therefore, a discussion of the reaction rates can be carried out, essentially by looking at the energetics of the system. The steric course of Figure 1 provides a very simple and specific model, which can serve as a basis for energy calculations.

Description of the Orbital Energies

Consider the real d-orbital set $\{z^2,\ xz,\ yz,\ xy,\ x^2 - y^2\}$. Suppose there is only one ligand, A, and let it be situated on the z axis. The matrix elements of the corresponding ligand field Hamiltonian, $\mathcal{K}^z(A)$ or $\mathcal{K}^z$, are given by

$$E(\sigma) = (z^2,\ \mathcal{K}^z\ z^2) = H_{11}{}^z$$

$$E(\pi) = (xz,\ \mathcal{K}^z\ xz) = H_{22}{}^z = (yz,\ \mathcal{K}^z\ yz) = H_{33}{}^z \quad (1)$$

$$E(\delta) = (xy,\ \mathcal{K}^z\ xy) = H_{44}{}^z = (x^2 - y^2,\ \mathcal{K}^z\ x^2 - y^2) = H_{55}{}^z$$

The resulting energy splitting can be described by means of two empirical parameters

$$E'(\sigma) = E(\sigma) - E(\delta)$$

and

$$E'(\pi) = E(\pi) - E(\delta)$$

These two parameters have an immediate chemical significance, being a measure for the strength of the σ and π interactions, respectively.

In the general case, A is not situated on the z axis but on an arbitrary p axis, specified by the polar coordinates θ and φ. The corresponding $H_{ij}{}^p$ matrix will of course not be diagonalized by the orbital set $\{d_i\}$ of eq 1. If a new coordinate system (X,Y,Z) is introduced with the A ligand on the z axis, the (capital) $\{D_i\}$ orbital set is related to the original set by

$$\mathbf{TD} = \mathbf{d} \quad (2)$$

The elements of the real transformation matrix **T** are simple functions of θ and φ.[11] An arbitrary matrix element of $\mathcal{K}^p$ can be written as

$$H_{ij}{}^p = (d_i,\ \mathcal{K}^p\ d_j) = \sum_k \sum_l T_{ik} T_{jl} (D_k,\ \mathcal{K}^p\ D_l) \quad (3)$$

Since $(D_k,\ \mathcal{K}^p\ D_l) = (d_k,\ \mathcal{K}^z\ d_l)$, and since the $\{d_i\}$-set is diagonal under $\mathcal{K}^z$, it follows that

$$H_{ij}{}^p = \sum_{m=1}^{5} T_{im} T_{jm} H_{mm}{}^z \quad (4)$$

If several ligands are present, the $H_{ij}{}^p$-matrix can be constructed for each ligand separately. In what follows, it will be assumed that the simultaneous effect of different ligands will be adequately described by the simple addition of the $H_{ij}{}^p$ matrices. Actually, this hypothesis is the common underlying assumption of ligand field theory, the angular overlap model,[11,12] or any other perturbation approach.[13,14] Although the metal–ligand interactions are certainly not strictly

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additive, the present procedure allows for a large input of empirical information—two parameters per ligand—while maintaining a simple formalism, which is very well suited for comparative purposes.

Experimental data on the value of $E'(\sigma)$ and $E'(\pi)$ can in principle be derived most readily from the spectra of the linear ML_2 compounds, but, of course, also other compounds, such as the square planar ML_4 or the octahedral $trans$-$ML_2L'_4$ complexes, can be analyzed in terms of $E'(\sigma)$ and $E'(\pi)$.

The ratio

$$\tau = \frac{E'(\pi)}{E'(\sigma)} = \frac{E(\pi) - E(\delta)}{E(\sigma) - E(\delta)} \qquad (5)$$

is a measure for the relative importance of σ and π interactions in a given metal–ligand bond. The available experimental information suggests that the value of τ is situated roughly between 0.2 and 0.5 for a wide variety of ligands and metals.[10,12,15]

If six equal ligands, each characterized by $E'(\sigma)$ and $E'(\pi)$, are placed octahedrally around a central ion, only two distinct d levels are observed. It follows from the matrix additivity assumption that the octahedral splitting Δ (or $10(Dq)$ in crystal field theory) is given by

$$\Delta = 3E'(\sigma) - 4E'(\pi) \qquad (6)$$

Direct experimental data are more readily available for Δ than for either $E'(\sigma)$ or $E'(\pi)$ separately. Indeed, the spectrochemical series provides us with an ordering of the ligands, based on their relative values of Δ.

Instead of characterizing a given ligand by $E'(\sigma)$ and $E'(\pi)$, it is sometimes advantageous to use Δ and τ. It is easily verified that

$$
\begin{aligned}
E'(\sigma) &= \frac{\Delta}{3 - 4\tau} \\
E'(\pi) &= \frac{\Delta}{3 - 4\tau}\tau
\end{aligned}
\qquad (7)
$$

Δ specifies the spectrochemical strength of the ligand, while τ specifies the bonding type, by which this spectrochemical strength is achieved.

Analytical Expressions for the LFSE

Figure 2 shows the d-orbital correlation diagram for the simple exchange of an A ligand with another A ligand. The reaction path is then of course symmetrical; both at the left and at the right hand side, the energy level scheme corresponds to the square planar MA_4 complex. The central part of Figure 2 shows the approximate orbital energies of the trigonal bipyramid. It has been supposed that all metal–ligand distances are identical and that they remain the same at any point of the reaction path. It is unlikely that the deviations of this picture would affect the results significantly.

The primed and unprimed coordinate systems, defined in Figure 1, are chosen in such a way, that the usual real d-orbital sets $\{d_i\}$ and $\{d_i'\}$ diagonalize the ligand field Hamiltonians with fourfold and threefold symmetry, respectively. The precise relative position of the five d orbitals depends on the values of Δ_A and τ_A. Yet, even if the parameters are varied over a rather

(15) C. W. De Kock and D. M. Gruen, *J. Chem. Phys.*, **44**, 4387 (1966).
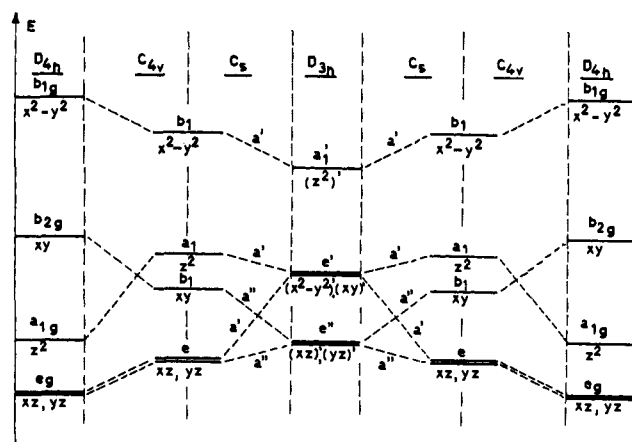

Figure 2. d-Orbital correlation diagram for the ligand exchange $MA_4 + A \rightleftharpoons MA_3A_2 \rightleftharpoons MA_4 + A$. The primed ($D_{3h}$) and unprimed ($D_{4h}$, C_{4v}) coordinate systems are defined in Figure 1.

wide range, the relative order of the d orbitals remains the same. In any case $d_{x^2-y^2}$ and d'_{z^2} remain the most energetic orbitals in the square plane and the trigonal bipyramid, respectively.

For the d^8 system under consideration, only the highest d orbital is empty. Therefore, in the particular case of the A–A exchange, the LFSE is simply given by twice the energy of that orbital.

Using the notation of eq 1–4, the energy of $d_{x^2-y^2}$ in D_{4h} is

$$E(x^2 - y^2) = \sum_{p=1}^{4} H_{55}{}^p$$

and the energy of d'_{z^2} in D_{3h} is

$$E(z^{2\prime}) = \sum_{p=1}^{5} H_{11}{}^p$$

where p runs over the four (or five) ligand positions. With respect to the d-orbital baricenter, the ligand field stabilization energies are then easily calculated from eq 7 to be $(2/5)[(11 - 8\tau_A)/(3 - 4\tau_A)]\Delta_A$ for the square plane and $(1/2)[(7 - 8\tau_A)/(3 - 4\tau_A)]\Delta_A$ for the trigonal bipyramid. These energies take a slightly simpler form if they are expressed as a function of Δ_A and $E'(\sigma_A)$ or σ_A' for short; they become $2\sigma_A' + 4/5\Delta_A$ and $1/2\sigma_A' + \Delta_A$, respectively.

In the general case of the reactions

$$MACC'T + Y \longrightarrow MACC'Y + T$$
$$MACC'T + Y \longrightarrow MAYC'T + C$$
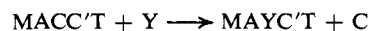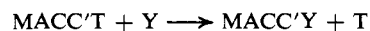
similar correlation diagrams can be derived. The diagrams will of course no longer by symmetrical and the degeneracies of Figure 2 will be removed. The orbital basis set $\{d_i\} = \{z^2, xz, yz, xy, x^2 - y^2\}$ will not diagonalize the general Hamiltonian $\mathcal{H} = \Sigma_p \mathcal{H}^p(L_p)$, when L_p no longer equals A for any p, but when it stands for A, C, C', T, or Y.

Instead of solving numerically the five by five matrix problems for a set of specific examples, it is more illuminating to analyze the relevant matrices from a slightly different point of view. The A–A exchange in

$$MA_4 + A \longrightarrow MA_5 \longrightarrow MA_4 + A$$

can be described at any point of the reaction path by a Hamiltonian of the type $\Sigma_p \mathcal{H}^p(A)$. The Y–T or Y–C

exchange is described by $\sum_p \mathcal{JC}^p(L_p)$. The $MA_4 + A \rightarrow MA_5 \rightarrow MA_4 + A$ reaction can now be considered to provide a set of zero-order situations, and a perturbation Hamiltonian

$$\mathcal{JC}' = \sum_p [\mathcal{JC}^p(L_p) - \mathcal{JC}^p(A)]$$

can be introduced, accounting for the difference in the nature of the ligands. Since $\{d_i\}$ diagonalizes $\sum_p \mathcal{JC}^p(A)$, the diagonal elements of $\sum_p \mathcal{JC}^p(L_p)$ in the $\{d_i\}$ basis set can be regarded as the first order corrected energies of the different orbitals. Similarly, the second-order perturbations can easily be derived from the off-diagonal matrix elements.

The ligand field stabilization energies are obtained in their most convenient form, if they are expressed as a function of the parameters Δ_L and σ_L'. The first-order energies, $LFSE^{(1)}$, are found to be, for the square plane (sp) and the trigonal bipyramid (tb), respectively

$$LFSE^{(1)}{}_{sp} = \frac{1}{10}\sum_L (5\sigma_L' + 2\Delta_L) \qquad (8)$$

$$LFSE^{(1)}{}_{tb} = \frac{1}{10}\left[\sum_{L_{eq}}(-5\sigma_L' + 2\Delta_L) + 2\sum_{L_{ax}}(5\sigma_L' + \Delta_L)\right] \qquad (9)$$

where the summation over L_{eq} and L_{ax} runs over the three equatorial and the two axial ligands only.

The second-order corrections to the ligand field stabilization energy, of the general type $H_{ij}^2/\Delta E$, are given by

$$LFSE^{(2)}{}_{sp} = \frac{3}{4}\frac{(\sigma_A' - \sigma_C' + \sigma_T' - \sigma_{C'}')^2}{4\sigma_A'} \qquad (10)$$

$$LFSE^{(2)}{}_{tb} = \frac{3}{4} \times$$
$$\frac{(\sigma_1'{}^2 + \sigma_2'{}^2 + \sigma_3'{}^2) - \dfrac{(\sigma_1'\sigma_2' + \sigma_2'\sigma_3' + \sigma_3'\sigma_1')}{3}}{\sigma_A' + \dfrac{3}{4}\Delta_A} \qquad (11)$$

where σ_1', σ_2', and σ_3' are the three equatorial ligands of the trigonal bipyramid, i.e., T, A, and Y for the Y–T exchange and C, C', and Y for the Y–C exchange. Equations 10 and 11 obviously reduce to zero if all ligands are equal. In the general case, the second-order corrections can still be expected to be small, since the numerators always contain partly canceling terms.

Kinetic Effects and Spectrochemical Parameters

To first order in perturbation theory, the ligand field activation energy for the Y–T exchange is given by

$$LFAE^{(1)}{}_{Y-T} =$$
$$\left(\sigma_A' + \sigma_T' - \frac{1}{2}\sigma_C' - \frac{1}{2}\sigma_{C'}'\right) + \left(\frac{1}{2}\sigma_Y' - \frac{1}{5}\Delta_Y\right) \qquad (12)$$

The first parenthesized term is a function of the parameters of the initial square planar complex and the second term contains only the parameters of the incoming ligand. A similar expression can of course be derived for the Y–C substitution

$$LFAE^{(1)}{}_{Y-C} = \left(-\frac{1}{2}\sigma_A' - \frac{1}{2}\sigma_T' + \sigma_C' + \sigma_{C'}'\right) + \left(\frac{1}{2}\sigma_Y' - \frac{1}{5}\Delta_Y\right) \qquad (13)$$

If all ligands involved are kept the same, except for A, the only variable terms in eq 12 and 13 are (σ_A') and $(-{}^1/_2\sigma_A')$, respectively. Hence, the LFAE of the trans substitution is twice as sensitive to A variations as the LFAE of the cis substitution; moreover, the effects are in the opposite sense.

It is not surprising that σ' turns out to be the only determining parameter. Indeed, neither $d_{z^2-y^2}$ in the square plane nor d'_{z^2} in the trigonal bipyramid are affected by π bonding. The ligand field activation energies will of course be modified somewhat by the incorporation of the second-order contributions. But since the latter are small, it seems reasonable to suppose that the main trends can be derived from eq 12 and 13.

In eq 7, it was shown that $\sigma' = \Delta/(3 - 4\tau)$. Therefore, if τ is a constant within a given series of ligands, eq 12 predicts a linear increase of the ligand field activation energy as a function of Δ. If A is a strong field generator in the spectrochemical series, the ligand field contribution to the activation energy will be large, and the associated trans effect will be small. To the extent that the trans effect is determined solely by the LFAE, a constant value of τ would lead one to expect the spectrochemical series to be just the opposite of the trans effect series.

Although τ will probably not vary too drastically for ligands of a given type, say the halogens, it is certainly *not* a constant within the whole set of ligands under consideration; small values of τ can be expected for ligands which are nearly pure σ bonders, such as H^- or CH_3^-, or for ligands with strong π back-bonding ability, such as C_2H_4, CO, CN^-, or R_3P. These ligands will have a smaller LFAE—and a larger trans effect—than would be expected on the basis of their spectrochemical strength alone.

The actual trans effect series looks very much as if indeed it resulted from the interplay of the parameters τ and Δ. The strongest trans directors are precisely those ligands characterized by small values of τ. Otherwise, there is an overall tendency for the trans effect to decrease, as the ligand field strength increases.

The agreement is of course only qualitative, and the absolute values obtained from eq 12 and 13 would certainly not be very meaningful. In the first place, the matrix additivity model, applied on the limited d-orbital basis set, carries its own inherent inaccuracy. Another obvious source of quantitative error is the assumption that all distances remain the same in going from the square plane to the transition state. The actual reaction will take place by readapting the interatomic distances so as to minimize the energy at any point of the reaction path.

The number of detailed kinetic data on the cis effect is far more limited. It is beyond doubt, however, that the cis effect is much smaller than the trans effect. From a comparison of eq 12 and 13, it appears that the activation energies vary twice as much for a trans substitution as for a cis substitution. In terms of reaction

rate constants, this means that a range of 10^5 to 10^6 for the trans effect would correspond to a range of about $10^{2.5}$ to 10^3 for the cis effect.

The inverse order of the cis and trans effect is less well confirmed by experiment. Although one of the earliest generalizations[16,17] derived from the experimental data was indeed such an inverse order, there are by now definite counterexamples.

Conclusions

Although it is obvious that the present considerations do not explain the whole set of detailed experimental data on the trans and cis effects, the general trend seems rather well reproduced. Invoking the role of the ligand field activation energy apparently provides a way, by itself, to explain the main features of the experimental

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data. It seems certain that the LFAE plays an important role in the kinetic study of the square planar Pt(II) reactions.

This is not to imply that the trans influence and the role of 6s and 6p orbitals can be neglected. Indeed, these factors are known to be important in the phenomena under consideration.[3,4] From the present approach, however, it is impossible to estimate the relative importance of the ligand field activation energies and the other effects.

Finally, it is well to stress that eq 12 and 13 should not be used to study the influence of the leaving or incoming ligands. Indeed in these reactions, the bond energy will contribute an additional, very important variable to the total activation energy.

Calculation of Lanthanide Induced Shifts from Molecular Structure[1]

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Abstract: The nmr spectra of $Eu(dpm)_3(py)_2$ in CS_2 at ambient temperature and $Eu(dpm)_3(3\text{-pic})_2$ in CS_2 at low temperature ($-105°$) were studied and the lanthanide induced shifts for all protons, including those of the chelate, were calculated using the complete pseudocontact shift equation. The low temperature spectrum of $Eu(dpm)_3(3\text{-pic})_2$ shows peaks from both free and complexed ligands. Comparison of the integrated areas of the chelate peaks and the coordinated 3-pic peaks show that the species present is the 1:2 adduct. The magnetic anisotropies from a least-square fit of the data agree with single crystal anisotropy data, and their temperature dependence is in fair agreement with Bleaney's theoretical predictions. The results show that lanthanide induced shifts, at least for this type of complex, cannot be explained on the basis of a single term equation which assumes that the principal magnetic axis passes through the donor atom. They can be understood in terms of the more complete two-term equation.

In the original paper reporting the ability of $Eu(dpm)_3(py)_2$[2] to induce large dipolar shifts in the nmr spectrum of Lewis base substrates, Hinckley[3] quoted the general equation derived for dipolar shifts by La Mar, Horrocks, and Allen.[4] Recent theoretical work[5,6] has shown that the dipolar shift equation can be written in terms of molecular susceptibility anisotropies instead of g tensor anisotropies, so that the most general equation for dipolar shifts would be[7]

$$\frac{\Delta\nu}{\nu_0} = D_1\left(\frac{3\cos^2\theta - 1}{r^3}\right) + D_2\left(\frac{\sin^2\theta \cos 2\Omega}{r^3}\right) \quad (1)$$

In this equation $\Delta\nu$ is the dipolar shift, ν_0 is the probe frequency, r is the length of a vector which joins the metal atom and the nucleus being examined, θ is the angle this vector makes with the z magnetic axis, Ω is the angle which the projection of r into the xy plane makes with the x magnetic axis, and D_1 and D_2 are functions of the magnetic anisotropy of the complex. For the case where $1/\tau_m \ll (ZAE)$, D_1 and D_2 can be expressed as

$$D_1 = \frac{1}{3N}(\chi_z - \chi_x/2 - \chi_y/2) \quad (2)$$

$$D_2 = \frac{1}{2N}(\chi_x - \chi_y) \quad (3)$$

where τ_m is the solution tumbling correlation time, (ZAE) is the Zeeman anisotropy energy, N is the Avogadro number and χ_x, χ_y, and χ_z are the principal molecular magnetic susceptibilities.[8] For molecules with threefold or higher symmetry $\chi_x - \chi_y = 0$ so that

(1) This paper is abstracted from a dissertation submitted to the Graduate Division of the University of Hawaii by R. D. in partial fulfillment of the requirements for the Doctor of Philosophy Degree in Chemistry.
(2) Key: dpm = dipivalomethanato or 2,2,6,6-tetramethylheptane-3,5-dionato ion; py = pyridine.
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