Supporting Information

140 H/D-Isotopomers identified by long-range NMR Hyperfine Shifts in Ruthenium(III)-ammine complexes. Hyperconjugation in Ru-NH_3 bonding.

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S1. Spectrum Simulation

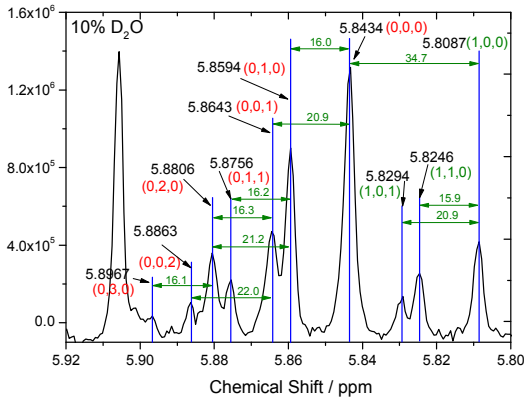


Figure S1(a). 950 MHz spectrum of **I** in water showing resonances due to the minor impurity in which in one of the equatorial ammines in replaced by a water molecule. The relative intensities allow the assignment of three line indices (i,j,k), which refer to the number of deuterons in (i) the axial ammine, (j) the equatorial positions *cis* to the water molecule, and (k) *trans* to the water molecule.

This substitution of one ammonia by water in the impurity leads to a Cp proton up-field shift in the fully protonated species by 132.5 ppb, to 5.8434 ppm. Outer sphere solvation in strong donor solvents leads to up-field shifts (Fig 5(b)). Water is a weaker σ-base than ammonia, but the

presence of an uncoordinated lone-pair makes it a stronger π-donor than ammonia, so that the observed shift supports the assertion that it is the characteristics of the Ru-L π interactions that are critical in determining the Cp hypefine shifts.

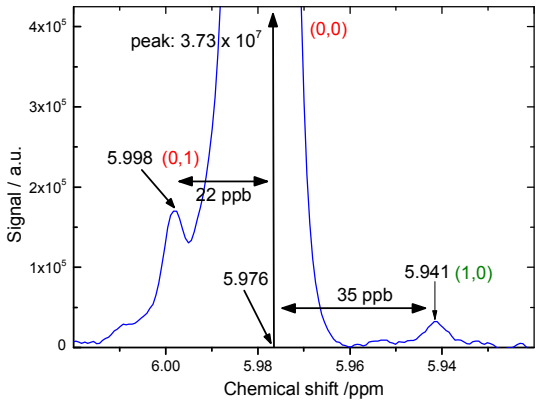


Figure S1(b). As in Figure S1(a) but showing the isotopomeric satellites on the H-15 resonance of **I** due to the natural abundance of deuterium.

S2. Pulsed EPR Spectrum and Simulation

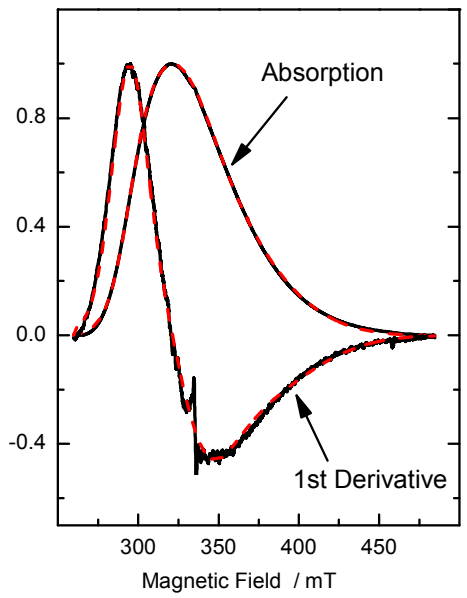


Figure:S2. W-band (93.903067 GHz) echo-detected EPR spectrum (black, absorption) and its numerical derivative (black) measured at T = 7.5 K of **I** in d^6-acetone 20% / d^6-EtOH 80% (2.5 mg in 250μL). The sharp impurity at 335.54 mT is at g = 1.9995. The EPR simulation (red dashed) was calculated with Easyspin, and fitted to the experimental spectrum using a least-squares Newton-gauss Levenberg-Marquart algorithm implemented with a home-written MatLab programme. The simulation parameters are g = [2.2537, 2.0315, 1.7565], with a linewidth L = [7007, 11453, 21498] MHz.

S3. Ammine Resonances and Cp Hyperfine Shifts in various Solvents at 500 MHz

Solvent	Cp(δ_h)	δ(ax)	δ(eq)	δ(ax-eq)
Nitromethane	1.9490	206.4	128.6	77.8
Acetonitrile	1.0564	181.5	137.9	43.6
Acetone	0.4340	165.8	148.8	1 7.0
H_2O	0.6430	170.3	147.9	22.4
D_2O	0.8050	177.3*	148.5*	28.8
Dimethylformamide	-0.6590	133.6	167.3	-33.7
Dimethylsulfoxide	-1.0641	120.1	174.6	-54.5

*No diamagnetic reference is available in D_2O, so these values are relative to TMS. Their difference in the fifth column is unaffected.

These values are plotted in Figure 5(a) and 5(b) of the main text.

Typical linewidths are ~1500 Hz (at 500 MHz)

<u>For reference</u>: ^{1}H NMR (aq)

$Ru(ND_3)_6^{3+}$ $(CF_3SO_3)_3$ in 95D5H; δ = 160.5ppm (at 950MHz; 298K)

$Ru(NH_3)_6^{3+}$ $(CF_3SO_3)_3$ 95H5D; δ = 157.1ppm (at 950MHz; 298K)

Resolution enhancement (exponential line-broadening function of -500 and a Gaussian function of 0.05) enabled several distinct axial and equatorial isotopic resonances to be identified (Figure S3.1) separated by ~ 640 ppb and ~ 500 ppb respectively. In dry d^6-acetone (no exchange) where only a single Cp resonance is observed, the ammine resonances are narrower (FWHM ~ 950 Hz) than in undried d^6-acetone containing residual H_2O / D_2O (FWHM ~ 1500 Hz).

Note the resemblance of the equatorial isotopomer structure, near 147 ppm, to that in the Cp ^{13}C spectrum having the same isotopic composition (see Figure S4.1 below).

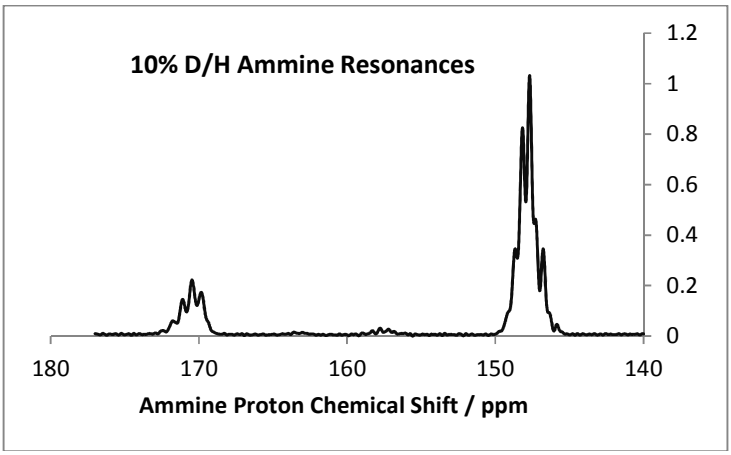


Figure S3.1 Isotopic structure in water at 950 MHz under resolution enhancement

S4. Cp C13 Isotopomer Resonances

Figure S4.1 shows the 13C spectrum in the Cp region in acetone solution containing ~ 10%D.

The structure is very similar to that in the Cp proton spectrum. Where the proton spectrum at 300 K shows equatorial and axial deuteration shifts of 19.7 and –36.2 ppb, and a linewidth of ~ 12.4 ppb; the equivalent intervals in the ^{13}C spectrum are 41.0 and –67.9 ppb, with a linewidth of 17.4 ppb. The spectrum is fitted to a deuterium content of 10.1%.

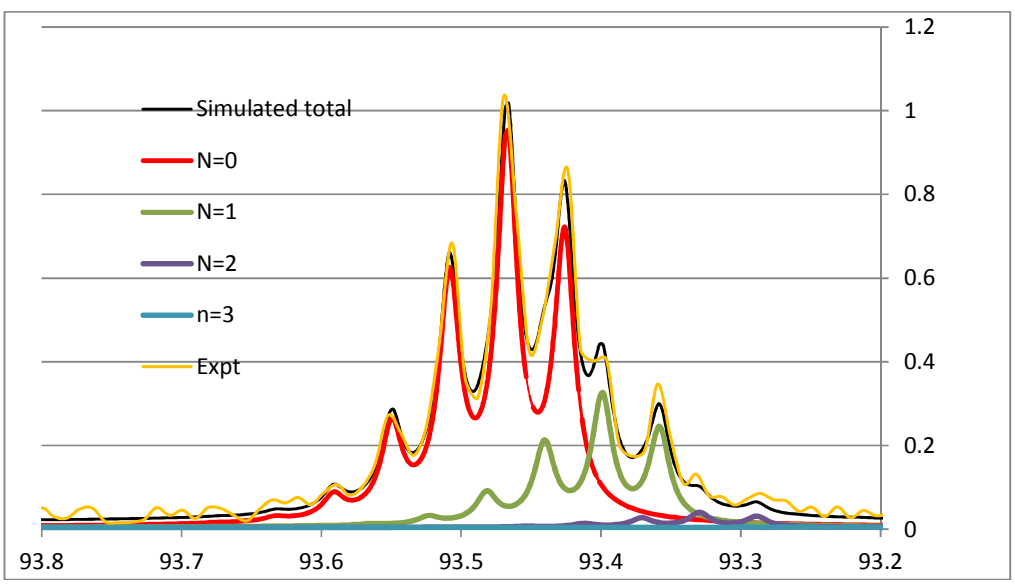


Figure S4.1 Cp ^{13}C spectrum of **I** at 125.7 MHz in Acetone

S5. Linewidth Data. No structural data is available for **II**. We therefore assume the bond angles are the same as in **I**, and only the bond lengths are modified. We estimate these using the Fe-C distance in ferrocene at 101 K, which is 2.052 Å [1], and the Ru-C distance in ruthenocene at 101 K, which is 2.186 Å [2]. The apparent difference in radius of ruthenium and iron in this setting is therefore 13.4 pm. With these assumptions the geometric factor for the axial-dipolar coupling decreases from 6.434 x 10^{27} m^{-3} to 5.518 x 10^{27} m^{-3}, so that the deuteration shifts are expected to decrease by 14.8%. This corresponds well with the experimental reduction of 13.3%.

Table S5. NMR parameters in d_6-acetone at 500 MHz and T = 298 K

	α^2 / %	D-shift (eq) /ppb	T_1 /ms	FWHM /Hz
$[Cp(CO)_2Fe(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$, **I**	0.47	20.20	125	4.23 [a]
$[Cp(CO)_2Ru(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$, **II**	< 0.4*	17.51	171	1.58 [a]
$[Cp(dppe)Fe(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$	2.8	n/a	17.4	25

* the charge transfer transition is obscured, and too high in energy to identify any smaller values. [a] at 950 MHz

The values of α^2 in Table S5 show that carbonyl ligands stabilize the low oxidation state ruthenium donor in **II** against the oxidation implicit in the intermetallic charge transfer more effectively than in the iron analogue **I**. This is a familiar feature of first and second row organo-transition-metal elements.

The decrease in linewidth between **I** and **II** appears to be too large to be attributed to the increased distance between the Cp protons and a point dipole on the Ru(III) centre, because the rate of dipole-dipole relaxation scales as r^{-6}.

S6. Derivation of Expressions for the Hyperfine Shift

The basis functions are chosen to diagonalize the main components of the Hamiltonian, i.e. the ligand field and the spin-orbit interactions. A residual Hamiltonian H_1 describes perturbations operating within this basis and includes interactions of the electronic and nuclear moments with the vacuum flux density $\mathbf{B}_0$ (loosely referred to as the field strength in vacuum) as well as the electron-nuclear hyperfine interactions. For a single nucleus with $I = \frac{1}{2}$ and gyromagnetic ratio γ_I (in units of radians s^{-1} T^{-1}), characterised by the spin angular momentum operator $\mathbf{I}$,

$$H_1 = -\boldsymbol{\mu} \cdot \mathbf{B}_0 - \hbar\gamma_I \mathbf{B}_0 \cdot \mathbf{I} + \hbar\gamma_I \mathbf{A} \cdot \mathbf{I} \qquad \{1\}$$

Here the terms are arranged in order of decreasing magnitude and the small diamagnetic screening corrections that determine the local flux density are ignored. We employ the notation of Kurland and McGarvey,[3] but use SI units. The electronic magnetic moment operator is $\boldsymbol{\mu} = -\beta(\mathbf{L} + g_e\mathbf{S})$, where $\beta = |\mu_B|$ is the absolute value of the Bohr Magneton. Note the opposite signs of electronic magnetic moment and the angular momenta. The magnetic field at the nucleus (i.e. the hyperfine field) due to the electronic moments is represented by $\mathbf{A} = \mathbf{A}_F + \mathbf{A}_D + \mathbf{A}_L$. Its three components $\mathbf{A}_F, \mathbf{A}_D$ and $\mathbf{A}_L$ are a Fermi contact term, spin-dipolar, and electron orbital contributions:

$$\begin{aligned}
\mathbf{A}_F &= \frac{2\mu_0}{3} g_e \beta \sum_i \delta(r_i)\mathbf{s}_i \\
\mathbf{A}_D &= \frac{\mu_0 g_e \beta}{4\pi} \sum_i \left[3(\mathbf{s}_i \cdot \mathbf{r}_i)\mathbf{r}_i - r_i^2 \mathbf{s}_i\right] r_i^{-5} \qquad \{2\} \\
\mathbf{A}_L &= \frac{\mu_0 \beta}{2\pi} \sum_i r_i^{-3} \mathbf{l}_i
\end{aligned}$$

{The units of these fields are in Tesla because: $\beta \equiv$ Am^2, μ_0 $\equiv$ $JA^{-2}m^{-1}$ $\equiv$ NA^{-2}, r_i^{-3} $\equiv$ m^{-3} and their product has units $NA^{-1}m^{-1}$ $\equiv$ Tesla.} In these expressions $\mathbf{r}_i$ is the vector between the *i*th

electron and the nucleus. The Dirac delta function $\delta(r_i)$ has the dimensions of a volume density (at the nucleus), i.e. m^{-3}.

S6.1 Bases

The $^2T_{2g}$ ground state of the low-spin octahedral $Ru^{3+}(d^5)$ ion is split by the spin-orbit interaction $\left(\zeta \sim 1000\,\text{cm}^{-1}\right)$ into two sets of levels which, in O* double-group representations, are an E'' Kramers doublet ground state and an excited U' quartet. Their separation is $\frac{3}{2}\zeta \approx 1500\,\text{cm}^{-1}$ which means that the thermal population of the U' state is negligible at ambient temperature (~0.2%). With symmetry-determined coupling constants, the electronic wavefunctions are found to be:

$$
\begin{aligned}
\left|E''\alpha''\right\rangle &= \frac{1}{\sqrt{3}}\left|T_2 0,\ \alpha'\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}\left|T_2 1,\ \beta'\right\rangle \\
\left|E''\beta''\right\rangle &= -\frac{1}{\sqrt{3}}\left|T_2 0,\ \beta'\right\rangle + \frac{\sqrt{2}}{\sqrt{3}}\left|T_2 -1,\ \alpha'\right\rangle \\
\left|U'\kappa\right\rangle &= -\frac{1}{\sqrt{3}}\left|T_2 -1,\ \alpha'\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}\left|T_2 0,\ \beta'\right\rangle \\
\left|U'\nu\right\rangle &= -\frac{1}{\sqrt{3}}\left|T_2 1,\ \beta'\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}\left|T_2 0,\ \alpha'\right\rangle \\
\left|U'\lambda\right\rangle &= \left|T_2 -1,\ \beta'\right\rangle \\
\left|U'\mu\right\rangle &= \left|T_2 1,\ \alpha'\right\rangle
\end{aligned}
\qquad \{3\}
$$

where α' and β' are spin functions with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ respectively. We adopt a contracted notation in which the ground state components are labelled by $i = \alpha, \beta$ and those of the excited state quartet by $j = \kappa, \lambda, \mu, \nu$. In the cyano-bridged Ruthenium pentammine complexes the tetragonal component of the ligand field introduces a first order splitting of the U' quartet and also leads to the mixing of α with ν and β with κ. The treatment that follows is restricted to

properties that can be derived by using these six basis states. We begin by analysing the octahedral case, adding the effect of the tetragonal field later, as a perturbation.

S6.2. Second Order Corrections to the Hamiltonian

First-order corrections to the ground state wavefunction will have the form,

$$\sum_j \frac{H_{ij}}{\Delta\varepsilon_{ij}}$$

in which $\Delta\varepsilon_{ij} = (\varepsilon_i - \varepsilon_j)$ is, as implied by the notation, *negative*, and the sum over j means all excited states. Correcting the zeroth-order function $|i_0\rangle$ for the perturbation introduced by the external magnetic field:

$$H_{ij} = -\langle i_0 | \mathbf{B}_0 \cdot \boldsymbol{\mu} | j \rangle$$
$$|i\rangle = |i_0\rangle - \sum_j \frac{\langle i_0 | \mathbf{B}_0 \cdot \boldsymbol{\mu} | j \rangle}{\Delta\varepsilon_{ij}}$$

Using these functions together with {1} gives the energy of the *i*th Kramers component:

$$\begin{aligned}
\varepsilon_i &= \langle i | H_1 | i \rangle \\
&= -\langle i_0 | \mathbf{B_0} \cdot \boldsymbol{\mu} | i_0 \rangle - \hbar\gamma_I \mathbf{B_0} \cdot \mathbf{I} + \hbar\gamma_I \langle i_0 | \mathbf{A} \cdot \mathbf{I} | i_0 \rangle \\
&\quad + 2\sum_j \frac{\hbar\gamma_I \langle i_0 | \mathbf{B_0} \cdot \boldsymbol{\mu} | j \rangle \langle j | \mathbf{B_0} \cdot \boldsymbol{\mu} | i_0 \rangle}{\Delta\varepsilon_{ij}} \\
&\quad - 2\sum_j \frac{\hbar\gamma_I \langle i_0 | \mathbf{B_0} \cdot \boldsymbol{\mu} | j \rangle \langle j | \mathbf{A} \cdot \mathbf{I} | i_0 \rangle}{\Delta\varepsilon_{ij}}
\end{aligned} \qquad \{4\}$$

S6.3. The Nuclear Transition Energy

The energy of the nuclear transition in electronic state $|i\rangle$ is given by the difference in the value of eqn {4} with $\mathbf{I} = -\frac{1}{2}$ and $\mathbf{I} = +\frac{1}{2}$:

$$\delta\varepsilon_i = \hbar\gamma_I \left\{ \mathbf{B_0} \cdot \mathbf{h}_0 - \langle i|\mathbf{A} \cdot \mathbf{h}_0|i\rangle + 2\sum_j \frac{\langle i|\mathbf{B_0} \cdot \boldsymbol{\mu}|j\rangle\langle j|\mathbf{A} \cdot \mathbf{h}_0|i\rangle}{\Delta\varepsilon_{ij}} \right\} \qquad \{5\}$$

where $\mathbf{h}_0$ is a unit vector parallel to the external field, and the small normalization difference between $|i\rangle$ and $|i_0\rangle$ has been ignored. The sign of $\langle i|\mathbf{A}_A \cdot \mathbf{h}_0|i\rangle$ is that of the coupling constant times the angular momentum operator, when $i = \alpha$ (which as we will see later is the more populated Kramers component), the effect of the second term in {5} is to increase the energy of the nuclear spin transition when the coupling constant is positive. An NMR experiment at fixed frequency resonance therefore require a lower field, leading to a resonance at a more positive chemical shift (δ).

S6.4. Thermal Population Averaging

Provided that the electron spin relaxation time (~10^{-12} s) is very short compared to the period of the nuclear Larmor frequency (~2 x10^{-9} s), the effective fields that determine the nuclear hyperfine interaction energies are obtained by averaging those associated with each of the Kramers doublet states. The nuclear transition energy is therefore obtained by weighting its value in each Kramers state (as given by {5}) with the thermal population of that state, which is, in turn, determined by the energies in {4}.

The following treatment is less general than that of Kurland and McGarvey[3] because it assumes that the temperature is low enough to exclude any population of the U' excited states. This is easily justified because the fraction of the population in these states at ambient temperature is

~4*exp(-1500/200) = 2.2 x 10^{-3} or 0.2% and can be safely ignored. When the Zeeman energies are small compared to kT, the partition function is to a good approximation equal to 2, so that,

$$\langle \delta\varepsilon \rangle = \tfrac{1}{2}\hbar\gamma_I \sum_{i=\alpha,\beta} \left[\begin{array}{l} \left\{ 1 - (kT)^{-1}\left(-\langle i|\mathbf{B_0}\cdot\boldsymbol{\mu}|i\rangle \right) \right\} \\ \left\{ \mathbf{B_0}\cdot\mathbf{h}_0 - \langle i|\mathbf{A}\cdot\mathbf{h}_0|i\rangle + 2\sum_j \dfrac{\langle j|\mathbf{B_0}\cdot\boldsymbol{\mu}|i\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle}{\Delta\varepsilon_{ij}} \right\} \end{array} \right] \qquad \{6\}$$

The factor in the first curly bracket represents the population of each Kramers state, and that in the second the resonance energy in that state. Terms that include the nuclear moments do not significantly affect the populations and are omitted from the first bracket. Similarly the second-order electronic Zeeman interaction cannot influence the relative energy of the Kramers states and is therefore omitted from the temperature dependent part.

To simplify {6} we note that $\langle \beta|\boldsymbol{\mu}\cdot\mathbf{B_0}|\beta\rangle = -\langle \alpha|\boldsymbol{\mu}\cdot\mathbf{B_0}|\alpha\rangle$, $\langle \beta|\mathbf{A}\cdot\mathbf{h}_0|\beta\rangle = -\langle \beta|\mathbf{A}\cdot\mathbf{h}_0|\beta\rangle$. It follows that products in {6} that are linear in these quantities will be absent from the summation over *i*. On the other hand for every element $\langle \alpha|\boldsymbol{\mu}\cdot\mathbf{B_0}|j\rangle$ or $\langle \alpha|\mathbf{A}\cdot\mathbf{h}_0|j\rangle$ there exists an element $\langle \beta|\boldsymbol{\mu}\cdot\mathbf{B_0}|j'\rangle$ or $\langle \beta|\mathbf{A}\cdot\mathbf{h}_0|j'\rangle$ of the same sign and magnitude, so that products linear in these elements do not vanish.

{These conclusions follow from the coupling coefficients. The angular momentum operators transform as T_1 so it is straightforward to show that for the *z* components: $\langle \alpha|T_1 0|\alpha\rangle = -\langle \beta|T_1 0|\beta\rangle = \left(1/\sqrt{3}\right)\langle E''\|T_1\|E''\rangle$; $\langle \beta|T_1 0|\kappa\rangle = \langle \alpha|T_1 0|\mu\rangle = -\left(1/\sqrt{3}\right)\langle E''\|T_1\|U'\rangle$; and symmetry requires a similar relationship in the orthogonal directions.}

Eqn {6} can be reduced to two parts, one inversely proportional to the temperature and the other independent of it:

$$\langle \delta\varepsilon \rangle = \tfrac{1}{2}\hbar\gamma_I \sum_{i=\alpha,\beta} \left[\begin{array}{l} \left\{ \mathbf{B_0}\cdot\mathbf{h}_0 + 2\sum_j \dfrac{\langle j|\mathbf{B_0}\cdot\boldsymbol{\mu}|i\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle}{\Delta\varepsilon_{ij}} \right\} \\ -(kT)^{-1}\left\{ \langle i|\mathbf{B_0}\cdot\boldsymbol{\mu}|i\rangle\langle i|\mathbf{A}\cdot\mathbf{h}_0|i\rangle \right\} \end{array} \right] \qquad \{7\}$$

The hyperfine shift in the resonant frequency, δ_h relative to, and also normalized with respect to, the diamagnetic nuclear transition energy, is found by subtracting $\hbar\gamma_I \mathbf{B}_0$ from the right hand side of Eqn{7} and then dividing by it to give:

$$\delta_h = \tfrac{1}{2}\sum_{i=\alpha,\beta}\left[\left\{2\sum_j \frac{\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|j\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle}{\Delta\varepsilon_{ij}}\right\} - (kT)^{-1}\left\{\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|i\rangle\langle i|\mathbf{A}\cdot\mathbf{h}_0|i\rangle\right\}\right] \qquad \{8\}$$

S6.5. Reconciliation with Kurland and McGarvey[3]

Kurland and McGarvey (in their footnote {1}) define the hyperfine shift as $\Delta\mathbf{B}_0/\mathbf{B_0}$ where $\Delta\mathbf{B}_0 = (\mathbf{B}_0 - \mathbf{B}_0^0)$ and $\mathbf{B_0^0}$ is the diamagnetic resonance field. This is also the definition used to obtain {8} from {7}. $\Delta\mathbf{B}_0/\mathbf{B_0}$ is therefore *negative* for a downfield shift, so that the corresponding chemical shift δ_h attributable to the hyperfine interaction, according to conventional definition, is *positive*. We should therefore expect opposite signs in the expressions for δ in Eqn {8} and for $\Delta\mathbf{B}_0/\mathbf{B_0}$ in Eqn {11} of K and G, which is indeed the case. Using the definitions of K and M Eqns.{10,11} $q = 2$, $\exp(-\varepsilon_\Gamma/kT) = 1$ and $Q_{\Gamma\Gamma'} = \Delta\varepsilon_{ij}^{-1}$, Eqn{8} seen to be identical to K and M Eqns.{11} when it is realized that the double summation in their Eqn {11b} ensures that every term labelled by *ij* occurs twice.

The terms on the right side of {8} should be dimensionless, a condition that is satisfied because the magnetic moment matrix elements have units of JTesla^{-1} and the hyperfine field operators have units of Tesla, and every term has a denominator in units of energy.

The first temperature independent term in {8} gives the interaction energy of the second-order contribution to the electronic moment (that is induced in both Kramers components) with the nuclear moment, via the hyperfine field operators. The second term represents the interaction

energy of the nuclear moment with the hyperfine field arising from the population-induced average moment in the unperturbed ground-state.

The Angular Average in Solution

Up to this point it has been assumed that the molecule has a fixed orientation relative to the external field. Note however that each term in Eqn {8} contains the product of the projection of two molecule-based vectors onto the external field direction. As a result we can make a rotational average for the three Cartesian directions within the molecule. This leads to the factor of 1/3 in each case. Eqn {8} therefore can be written in the form:

$$\langle \delta_h \rangle = \tfrac{1}{3} \sum_{k=x,y,z} \tfrac{1}{2} \sum_{i=\alpha,\beta} \left[2\sum_j \frac{\langle i|\hat{\mu}_k|j\rangle\langle j|\hat{A}_k|i\rangle}{\Delta\varepsilon_{ij}} - (kT)^{-1}\left\{\langle i|\hat{\mu}_k|i\rangle\langle i|\hat{A}_k|i\rangle\right\} \right] \qquad \{9\}$$

and is identical to that given by Kurland and McGarvey in their eqn {12}, apart from its overall sign, as expected from our discussion in the previous section.

The Contact Shift

Substituting the Fermi contact part of Eqn {2} into {9} gives:

$$\delta_c = \frac{\mu_0 g_e \beta}{9} \sum_{k=x,y,z} \sum_{i=\alpha,\beta} \left[\begin{array}{l} 2\sum_j \dfrac{\langle i|\hat{\mu}_k|j\rangle\langle j|\sum_n \delta(r_n)\hat{s}_k|i\rangle}{\Delta\varepsilon_{ij}} \\ -(kT)^{-1}\left\{\langle i|\hat{\mu}_k|i\rangle\langle i|\sum_n \delta(r_n)\hat{s}_k|i\rangle\right\} \end{array} \right] \qquad \{10\}$$

where $\delta(r_n)$ is the Dirac delta function for the *n*th electron at the nucleus, and $\hat{s}_k$ is the *k*th component of the spin angular momentum operator for that electron. The sum is over all electrons that have any amplitude at the nucleus.

The Spin Density Operator

Following K and M we assume that $\sum_n \delta(r_n)\hat{s}_k \propto \hat{S}_k$, where $\hat{S}_k$ is evaluated at the metal centre. (Since $\hat{s}_k$ returns the value $\pm\frac{1}{2}$, the conventional definition of the "spin density" is actually $\rho_s(r_n) = 2\sum_n \delta(r_n)\hat{s}_k$). To relate the two a coupling factor K_i is defined, which conveys the extent to which those molecular orbitals associated with metal-centred spin-angular momentum introduce spin-density at the ligand nucleus. This factor therefore reflects the extent of delocalization of the spin as well as the effects of spin-polarisation in those orbitals (i.e. 1*s*) with non-zero amplitude at the nucleus. For example in evaluating the z-component of the contact shift for a nucleus on the z-axis, we will require matrix elements such as:

$$\begin{aligned}
\langle E''\alpha''|\sum_n \delta(r_n)\hat{s}_z|E''\alpha''\rangle &= \langle E''\alpha''|\hat{\sigma}_z|E''\alpha''\rangle \\
&= \left\langle \frac{1}{\sqrt{3}}|T_2 0,\ \alpha'\rangle - \frac{\sqrt{2}}{\sqrt{3}}|T_2 1,\ \beta'\rangle \middle| \sum_n \delta(r_n)\hat{s}_z \middle| \frac{1}{\sqrt{3}}|T_2 0,\ \alpha'\rangle - \frac{\sqrt{2}}{\sqrt{3}}|T_2 1,\ \beta'\rangle \right\rangle \\
&= \frac{1}{3}\langle T_2 0,\ \alpha'|\sum_n \delta(r_n)\hat{s}_z|T_2 0,\ \alpha'\rangle + \frac{2}{3}\langle |T_2 1,\ \beta'\rangle|\sum_n \delta(r_n)\hat{s}_z||T_2 1,\ \beta'\rangle\rangle \\
&= \frac{1}{3}.\frac{1}{2}.K_0 - \frac{2}{3}.\frac{1}{2}.K_1 = \frac{1}{6}(K_0 - 2K_1)
\end{aligned}$$

in which $K_m = \langle T_2 m(0)|T_2 m(0)\rangle$ determines the density at the nucleus that is attributable to the spin in the $T_2 m$ m.o. Here we have used the orthogonality of the spatial functions and the fact that the spin-density operator only operates on the spin part. The matrix elements of this operator can then be tabulated, as follows:

Spin density matrix, $\hat{\sigma}_z$. (N.B. for comparison with the conventional definition of spin-density these quantities should be multiplied by 2).

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	$\frac{1}{6}(K_0-2K_1)$	0	0	$-\frac{\sqrt{2}}{6}(K_0+K_1)$	0	0
$E''\beta''$	0	$-\frac{1}{6}(K_0-2K_1)$	$-\frac{\sqrt{2}}{6}(K_0+K_1)$	0	0	0
$U'\kappa$	0	$-\frac{\sqrt{2}}{6}(K_0+K_1)$	$-\frac{1}{6}(2K_0-K_1)$	0	0	0
$U'\nu$	$-\frac{\sqrt{2}}{6}(K_0+K_1)$	0	0	$\frac{1}{6}(2K_0-K_1)$	0	0
$U'\lambda$	0	0	0	0	$-\frac{1}{2}K_1$	0
$U'\mu$	0	0	0	0	0	$\frac{1}{2}K_1$

Spin Density matrix, $\hat{\sigma}_x$.

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	0	$-\frac{1}{6}K_0$	$-\frac{\sqrt{2}}{6}K_0$	0	0	$-\frac{1}{\sqrt{6}}K_1$
$E''\beta''$	$-\frac{1}{6}K_0$	0	0	$\frac{\sqrt{2}}{6}K_0$	$+\frac{1}{\sqrt{6}}K_1$	0
$U'\kappa$	$-\frac{\sqrt{2}}{6}K_0$	0	0	$\frac{2}{6}K_0$	$-\frac{1}{2\sqrt{3}}K_1$	0
$U'\nu$	0	$\frac{\sqrt{2}}{6}K_0$	$\frac{2}{6}K_0$	0	0	$-\frac{1}{2\sqrt{3}}K_1$
$U'\lambda$	0	$+\frac{1}{\sqrt{6}}K_1$	$-\frac{1}{2\sqrt{3}}K_1$	0	0	0
$U'\mu$	$-\frac{1}{\sqrt{6}}K_1$	0	0	$-\frac{1}{2\sqrt{3}}K_1$	0	0

The matrix elements of the magnetic moment operators $\hat{\mu}_k$ are also required, and can be obtained by using the t_{2g}^5 wavefunctions tabulated by Griffith (Table A24).[4] For those with α spin, these are:

$$\left|T_2 1, a\right\rangle = -\left|1^+ - 1^2 \zeta_1^2\right\rangle$$
$$\left|T_2 0, a\right\rangle = -\left|1^2 - 1^2 \zeta_1^+\right\rangle$$
$$\left|T_2 -1, a\right\rangle = \left|1^2 - 1^+ \zeta_1^2\right\rangle$$

where $\zeta_1 = i\zeta = \frac{1}{\sqrt{2}}\left\{\left|22\right\rangle - \left|2-2\right\rangle\right\} = d_{xy}$.

Bringing the above functions into matching order, for any one-electron operator $\hat{O}$ we have

$$\left\langle T_2 1\middle|\hat{O}\middle|T_2 0\right\rangle = -\left\langle \zeta_1\middle|\hat{O}\middle|1\right\rangle; \quad \left\langle T_2 -1\middle|\hat{O}\middle|T_2 0\right\rangle = \left\langle \zeta_1\middle|\hat{O}\middle|-1\right\rangle$$

The matrix elements of $\hat{L}_x = \frac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$, are required so we note that:

$$\left\langle T_2 1\middle|\hat{L}_+\middle|T_2 0\right\rangle = -\left\langle \zeta_1\middle|\hat{L}_+\middle|1\right\rangle = -\tfrac{1}{\sqrt{2}}\left\langle 2\middle|\hat{L}_+\middle|1\right\rangle$$
$$\left\langle T_2 -1\middle|\hat{L}_-\middle|T_2 0\right\rangle = \left\langle \zeta_1\middle|\hat{L}_-\middle|-1\right\rangle = -\tfrac{1}{\sqrt{2}}\left\langle -2\middle|\hat{L}_-\middle|-1\right\rangle$$

However:
$$\hat{L}_+\left|21\right\rangle = \hbar\sqrt{(2-1)(2+1+1)}\left(\left|22\right\rangle\right) = 2\hbar$$
$$\hat{L}_-\left|2-1\right\rangle = \hbar\sqrt{(2-1)(2+1+1)}\left(\left|2-2\right\rangle\right) = 2\hbar$$

so that
$$\left\langle T_2 1\middle|\hat{L}_+\middle|T_2 0\right\rangle = -\sqrt{2}\hbar = \left\langle T_2 -1\middle|\hat{L}_-\middle|T_2 0\right\rangle$$
$$\left\langle T_2 1\middle|\hat{L}_x\middle|T_2 0\right\rangle = -\tfrac{1}{\sqrt{2}}\hbar = \left\langle T_2 -1\middle|\hat{L}_x\middle|T_2 0\right\rangle$$

and also:
$$\left\langle T_2 0\middle|\hat{L}_z\middle|T_2 0\right\rangle = 0; \quad \left\langle T_2 \pm 1\middle|\hat{L}_z\middle|T_2 \pm 1\right\rangle = \mp\hbar$$
$$\left\langle \alpha\middle|2\hat{S}_z\middle|\alpha\right\rangle = \hbar; \ \left\langle \beta\middle|2\hat{S}_z\middle|\beta\right\rangle = -\hbar$$
$$\left\langle \alpha\middle|2\hat{S}_x\middle|\beta\right\rangle = \left\langle \beta\middle|2\hat{S}_x\middle|\alpha\right\rangle = \hbar$$

in which $g_e = 2$ has been used. The magnetic moment matrices are:

$\hat{\mu}_z = -\beta\left(\hat{L}_z + 2\hat{S}_z\right)$; in units of β:

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	$+1$	0	0	$\sqrt{2}$	0	0
$E''\beta''$	0	-1	$\sqrt{2}$	0	0	0
$U'\kappa$	0	$\sqrt{2}$	0	0	0	0
$U'\nu$	$\sqrt{2}$	0	0	0	0	0
$U'\lambda$	0	0	0	0	0	0
$U'\mu$	0	0	0	0	0	0

$\hat{\mu}_x = -\beta\left(\hat{L}_x + 2\hat{S}_x\right)$; in units of β.

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	0	$+1$	$\frac{1}{\sqrt{2}}$	0	0	$\frac{\sqrt{3}}{\sqrt{2}}$
$E''\beta''$	$+1$	0	0	$-\frac{1}{\sqrt{2}}$	$-\frac{\sqrt{3}}{\sqrt{2}}$	0
$U'\kappa$	$\frac{1}{\sqrt{2}}$	0	0	0	0	0
$U'\nu$	0	$-\frac{1}{\sqrt{2}}$	0	0	0	0
$U'\lambda$	0	$-\frac{\sqrt{3}}{\sqrt{2}}$	0	0	0	0
$U'\mu$	$\frac{\sqrt{3}}{\sqrt{2}}$	0	0	0	0	0

These matrix elements agree with those of K and M on page 297.

The first and second order terms in the bracket in Eqn.{10} are dealt with separately. Summing over the Kramers index *i*, for the vector components of the first order term; we have: $\frac{\beta}{3}\left(K_0 - 2K_1\right)$ for the *z* component and $-\frac{\beta}{3}K_0$ for the *x* component. Since the *y* component must have the same magnitude as the *x* component, the first order term is:

$$\sum_{k=x,y,z}\sum_{i=\alpha,\beta} -(kT)^{-1}\left\{\langle i|\hat{\mu}_k|i\rangle\langle i|\sum_n \delta(r_n)\hat{s}_k|i\rangle\right\} = \frac{\beta}{3kT}(K_0 + 2K_1)$$

For the numerator in the second order term, the z component is $-\frac{2\beta}{3}(K_0 + K_1)$, and the x component is $-\frac{\beta}{3}K_0 - K_1$. So the sum over k is $-\frac{4\beta}{3}(K_0 + 2K_1)$ and Eqn {10} becomes:

$$\delta_c = \frac{\mu_0 g_e \beta^2 \left(\frac{1}{3}K_0 + \frac{2}{3}K_1\right)}{9}\left[-\frac{8}{\Delta\varepsilon_{ij}} + \frac{1}{kT}\right] = \frac{\mu_0 g_e \beta^2 \left(\frac{1}{3}K_0 + \frac{2}{3}K_1\right)}{9}\left[\frac{16}{3\zeta} + \frac{1}{kT}\right] \quad \{11\}$$

in which we have used the fact that $\Delta\varepsilon_{ij}$ is intrinsically negative and equal to $\frac{3}{2}\zeta$. Multiplying top and bottom by 3 gives

$$\delta_c = \frac{\mu_0 g_e \beta^2 \left(\frac{1}{3}K_0 + \frac{2}{3}K_1\right)}{27}\left[\frac{16}{\zeta} + \frac{3}{kT}\right] \quad \{12\}$$

which resembles Eqn {2} of Waysbort and Navon,[5] except that the whole expression has the opposite sign, which is expected because of our use of the chemical shift δ_c rather than $\Delta H / H$. Notice that for $\zeta = 1000\,\mathrm{cm}^{-1}$ and $T = 298K$ the temperature dependent and temperature independent contributions in {12} are almost identical and have the same sign. The absolute sign is determined by the coupling coefficients K_0 and K_1.

We now consider the perturbation of these shifts as a result of the influence of the tetragonal field perturbation. It will be helpful to use a dimensionless tetragonal field parameter, $v/\zeta = x$.

The Tetragonal Field Perturbation. With $\nu/\zeta = x$, (ν is positive when $\varepsilon_{xy} > \varepsilon_{xz,yz}$)

	$\lvert E''\alpha''\rangle$	$\lvert E''\beta''\rangle$	$\lvert U'\kappa\rangle$	$\lvert U'\nu\rangle$	$\lvert U'\lambda\rangle$	$\lvert U'\mu\rangle$
$\lvert E''\alpha''\rangle$	0	0	0	$+\frac{1}{\sqrt{2}}x$	0	0
$\lvert E''\beta''\rangle$	0	0	$-\frac{1}{\sqrt{2}}x$	0	0	0
$\lvert U'\kappa\rangle$	0	$-\frac{1}{\sqrt{2}}x$	$\frac{1}{2}(3-x)$	0	0	0
$\lvert U'\nu\rangle$	$+\frac{1}{\sqrt{2}}x$	0	0	$\frac{1}{2}(3-x)$	0	0
$\lvert U'\lambda\rangle$	0	0	0	0	$\frac{1}{2}(3+x)$	0
$\lvert U'\mu\rangle$	0	0	0	0	0	$\frac{1}{2}(3+x)$

As a result of which we may write:

$$\lvert E''\alpha''\rangle \to \lvert E''\alpha''\rangle - \frac{\sqrt{2}x}{(3-x)}\lvert U'\nu\rangle;\ \lvert E''\beta''\rangle \to \lvert E''\beta''\rangle + \frac{\sqrt{2}x}{(3-x)}\lvert U'\kappa\rangle$$

$$\lvert U'\nu\rangle \to \lvert U'\nu\rangle + \frac{\sqrt{2}x}{(3-x)}\lvert E''\alpha''\rangle;\ \lvert U'\kappa\rangle \to \lvert U'\kappa\rangle - \frac{\sqrt{2}x}{(3-x)}\lvert E''\beta''\rangle$$

Defining $s = \dfrac{x}{(3-x)}$, the magnetic moment matrix elements become;

$$\langle E''\alpha''\lvert\hat{\mu}_z\rvert E''\alpha''\rangle \to \langle E''\alpha''\lvert\hat{\mu}_z\rvert E''\alpha''\rangle - \frac{2\sqrt{2}x}{(3-x)}\langle E''\alpha''\lvert\hat{\mu}_z\rvert U'\nu\rangle = \beta(1-4s)$$

$$\langle E''\beta''\lvert\hat{\mu}_z\rvert E''\alpha''\rangle \to \langle E''\beta''\lvert\hat{\mu}_z\rvert E''\alpha''\rangle + \frac{2\sqrt{2}x}{(3-x)}\langle E''\beta''\lvert\hat{\mu}_z\rvert U'\kappa\rangle = -\beta(1-4s)$$

$$\langle E''\alpha''\lvert\hat{\mu}_x\rvert E''\beta''\rangle \to \langle E''\alpha''\lvert\hat{\mu}_x\rvert E''\beta''\rangle + \frac{\sqrt{2}x}{(3-x)}\langle E''\alpha''\lvert\hat{\mu}_x\rvert U'\kappa\rangle - \frac{\sqrt{2}x}{(3-x)}\langle E''\beta''\lvert\hat{\mu}_x\rvert U'\nu\rangle$$
$$= \beta(1+2s)$$

$$\langle E''\alpha''\lvert\hat{\mu}_z\rvert U'\nu\rangle \to \langle E''\alpha''\lvert\hat{\mu}_z\rvert U'\nu\rangle - \frac{\sqrt{2}x}{(3-x)}\langle U'\nu\lvert\hat{\mu}_z\rvert U'\nu\rangle + \frac{\sqrt{2}x}{(3-x)}\langle E''\alpha''\lvert\hat{\mu}_z\rvert E''\alpha''\rangle$$
$$= \sqrt{2}\beta(1+s) = \langle E''\beta''\lvert\hat{\mu}_z\rvert U'\kappa\rangle$$

$$\langle E''\alpha''\lvert\hat{\mu}_x\rvert U'k\rangle \to \langle E''\alpha''\lvert\hat{\mu}_x\rvert U'k\rangle - \frac{\sqrt{2}x}{(3-x)}\langle E''\alpha''\lvert\hat{\mu}_x\rvert E''\beta''\rangle$$
$$= \beta\left(\frac{1}{\sqrt{2}} - \sqrt{2}s\right)$$

$$\langle E''\beta''|\hat{\mu}_x|U'\nu\rangle \to \langle E''\beta''|\hat{\mu}_x|U'\nu\rangle + \frac{\sqrt{2}x}{(3-x)}\langle E''\alpha''|\hat{\mu}_x|E''\beta''\rangle$$

$$= -\beta\left(\frac{1}{\sqrt{2}} - \sqrt{2}s\right)$$

$$\langle E''\alpha''|\hat{\mu}_x|U'\mu\rangle \to \langle E''\alpha''|\hat{\mu}_x|U'\mu\rangle = \beta\left(\frac{\sqrt{3}}{\sqrt{2}}\right)$$

$$\langle E''\beta''|\hat{\mu}_x|U'\lambda\rangle \to \langle E''\beta''|\hat{\mu}_x|U'\lambda\rangle = -\beta\left(\frac{\sqrt{3}}{\sqrt{2}}\right)$$

So that we may rewrite the magnetic moment matrices in the perturbed basis as:

(a) $\hat{\mu}_z = -\beta\left(\hat{L}_z + 2\hat{S}_z\right)$**;** units of β, where $s = \frac{x}{(3-x)}$

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	$+1-4s$	0	0	$\sqrt{2}(1+s)$	0	0
$E''\beta''$	0	$-1+4s$	$\sqrt{2}(1+s)$	0	0	0
$U'\kappa$	0	$\sqrt{2}(1+s)$	0	0	0	0
$U'\nu$	$\sqrt{2}(1+s)$	0	0	0	0	0
$U'\lambda$	0	0	0	0	0	0
$U'\mu$	0	0	0	0	0	0

(b) $\hat{\mu}_x = -\beta\left(\hat{L}_x + 2\hat{S}_x\right)$**;** units of β, where $s = \frac{x}{(3-x)}$

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	0	$+1+2s$	$\frac{1}{\sqrt{2}} - \sqrt{2}s$	0	0	$\frac{\sqrt{3}}{\sqrt{2}}$
$E''\beta''$	$+1+2s$	0	0	$-\frac{1}{\sqrt{2}} + \sqrt{2}s$	$-\frac{\sqrt{3}}{\sqrt{2}}$	0
$U'\kappa$	$\frac{1}{\sqrt{2}} - \sqrt{2}s$	0	0	0	0	0
$U'\nu$	0	$-\frac{1}{\sqrt{2}} + \sqrt{2}s$	0	0	0	0
$U'\lambda$	0	$-\frac{\sqrt{3}}{\sqrt{2}}$	0	0	0	0
$U'\mu$	$\frac{\sqrt{3}}{\sqrt{2}}$	0	0	0	0	0

and applying the same methodology to the spin density matrices.

(c) Perturbed Spin density, $\hat{\sigma}_z$.

$$
\begin{array}{c|cccccc}
 & E''\alpha'' & E''\beta'' & U'\kappa & U'\nu & U'\lambda & U'\mu \\
\hline
E''\alpha'' & A & 0 & 0 & -B & 0 & 0 \\
E''\beta'' & 0 & -A & -B & 0 & 0 & 0 \\
U'\kappa & 0 & -B & -C & 0 & 0 & 0 \\
U'\nu & -B & 0 & 0 & C & 0 & 0 \\
U'\lambda & 0 & 0 & 0 & 0 & -D & 0 \\
U'\mu & 0 & 0 & 0 & 0 & 0 & D
\end{array}
\quad \text{where:} \quad
\begin{aligned}
A &= \frac{1}{6}\left(K_0(1+4s) - 2K_1(1-2s)\right) \\
B &= \frac{\sqrt{2}}{6}\left(K_0(1+s) + K_1(1+s)\right) \\
C &= \frac{1}{6}\left(2K_0(1-2s) - K_1(1+4s)\right) \\
D &= \frac{1}{2}K
\end{aligned}
$$

(d) Perturbed Spin density, $\hat{\sigma}_x$.

$$
\begin{array}{c|cccccc}
 & E''\alpha'' & E''\beta'' & U'\kappa & U'\nu & U'\lambda & U'\mu \\
\hline
E''\alpha'' & 0 & -A & -B & 0 & 0 & -D \\
E''\beta'' & -A & 0 & 0 & B & D & 0 \\
U'\kappa & -B & 0 & 0 & C & -E & 0 \\
U'\nu & 0 & B & C & 0 & 0 & -E \\
U'\lambda & 0 & D & -E & 0 & 0 & 0 \\
U'\mu & -D & 0 & 0 & -E & 0 & 0
\end{array}
\quad \text{where:} \quad
\begin{aligned}
A &= \frac{1}{6}K_0(1+4s) \\
B &= \frac{\sqrt{2}}{6}K_0(1+s) \\
C &= \frac{2}{6}K_0(1-2s) \\
D &= \frac{1}{\sqrt{6}}K_1(1-s) \\
E &= \frac{1}{2\sqrt{3}}K_1(1+2s)
\end{aligned}
$$

from which we can deduce that the first order term in Eqn {10} is:

$$
\sum_{k=x,y,z}\sum_{i=\alpha,\beta} -(kT)^{-1}\left\{\langle i|\hat{\mu}_k|i\rangle\langle i|\sum_n \delta(r_n)\hat{s}_k|i\rangle\right\} = \frac{\beta}{3kT}\left\{(K_0+2K_1)+12s(K_0-K_1)\right\} \qquad \{13\}
$$

and the second order term is:

$$
\sum_{k=x,y,z}\sum_{i=\alpha,\beta}\left[2\sum_j \frac{\langle i|\hat{\mu}_k|j\rangle\langle j|\sum_n \delta(r_n)\hat{s}_k|i\rangle}{\Delta\varepsilon_{ij}} = -\beta\frac{8}{3}\frac{\left(K_0+2K_1+\frac{s}{2}\{K_0-K_1\}\right)}{\Delta\varepsilon_{ij}}\right] \qquad \{14\}
$$

Substituting {14} and {15} in {11}gives:

$$\delta_c = \frac{\mu_0 g_e \beta^2}{9}\left[\left(\tfrac{1}{3}K_0 + \tfrac{2}{3}K_1\right)\left\{\frac{16}{3\zeta} + \frac{1}{kT}\right\} + s\left(K_0 - K_1\right)\left\{\frac{8}{9\zeta} + \frac{4}{kT}\right\}\right] \qquad \{15\}$$

In deriving {15} we have assumed that the tetragonal field is sufficiently small so that a single denominator $\Delta\varepsilon_{ij} = -3\zeta/2$ can be used in the summation of the various excited states in {14}, that are in reality split by this perturbation.

Because the unpaired spin associated with the $T_2 0$ wavefunction is localized in the d_{xy} orbital, any density communicated through a bridge on the z axis to the remote proton,, should be negligible, and with $K_0 = 0$ equation {15} simplifies to:

$$\delta_c = \frac{\mu_0 g_e \beta^2}{9}\left[\tfrac{2}{3}K_1\left\{\frac{16}{3\zeta} + \frac{1}{kT}\right\} - sK_1\left\{\frac{8}{9\zeta} + \frac{4}{kT}\right\}\right] \qquad \{16\}$$

Eqn {15} can also be used to predict the effect of the contact shift of the axial and equatorial ammine protons. Eqn {16} is suitable for the axial case. The density in *xz* (or *yz*) is half of that associated with that in a $T_2 \pm 1$ function, so for the equatorial case the K_0 contribution is retained, but the replacement $K_1 \rightarrow K_1/2$ is used in order to account for the contribution from the $T_2 \pm 1$ in the e.g. the *x* direction. It also seems reasonable to assume that, for the ammine ligands, the axial and equatorial overlap integrals and MO coefficients are effectively identical, in which case $K_1 = K_0 = K$ so that the contact shift for the equatorial ammines is given by:

$$\delta_c(eq) = \frac{\mu_0 g_e \beta^2}{9}\left[\left(\tfrac{2}{3}K\right)\left\{\frac{16}{3\zeta} + \frac{1}{kT}\right\} + \tfrac{1}{2}sK\left\{\frac{8}{9\zeta} + \frac{4}{kT}\right\}\right] \qquad \{16a\}$$

Note that for axial ligands positive values of *s* in Eqn {16} lead to a reduction of δ_c relative to octahedral case, and this is consistent with the concentration of spin in the d_{xy} orbital, and a reduction in the density in the $d_{xz,yz}$ orbitals, from which spin can propagate across the bridge.

For the equatorial ammines the contact shift (Eqn 16a) occurs in the opposite direction, for a given value of *s*, and is of half the magnitude.

The Pseudo-Contact Shift

Following K and M Eqn{16} for a molecule fixed in orientation, the dipolar component of the hyperfine field parallel to $\mathbf{B}_0$ is given by:

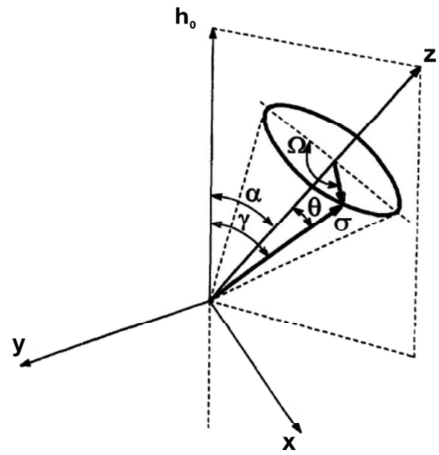
$$\mathbf{A}_D \cdot \mathbf{h}_0 = \left(\frac{\mu_0}{4\pi}\right)\frac{1}{r^3}\left[\boldsymbol{\mu}\cdot\mathbf{h}_0 - 3(\boldsymbol{\mu}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\right] \qquad \{17\}$$

where *r* is the distance between the origin of the electronic magnetic moment (taken as a point) and the nucleus, in the direction of the unit vector $\boldsymbol{\sigma}$. In the diagram below, $\mathbf{h}_0 \cdot \boldsymbol{\sigma} = \cos\gamma$, the molecular *z* axis is parallel to the unit vector and makes an angle α to $\mathbf{h}_0$, $\mathbf{x}$ is a unit vector is perpendicular to $\mathbf{h}_0$ in the $\mathbf{h}_0\mathbf{z}$ plane, and $\mathbf{y}$ is a unit vector perpendicular to this plane. We can use this choice of *x* and *y* axes because $\mu_y \cdot \mathbf{h}_0 = 0$, and in axial symmetry $\mu_x = \mu_y$ so that any angular average is invariant to a rotation about *z*.

We now write the components of $\boldsymbol{\mu}$ as $\vec{\mu}_z = \mu_z\mathbf{z}$ and $\vec{\mu}_x = \mu_x\mathbf{x}$ where μ_x and μ_y are used generically to indicate the *magnitude* of a matrix element of a component of the magnetic moment operator.

$$\begin{aligned}
\boldsymbol{\mu}\cdot\mathbf{h}_0 &= \mu_z\mathbf{z}\cdot\mathbf{h}_0 + \mu_x\mathbf{x}\cdot\mathbf{h}_0 \\
A_z\mathbf{z}\cdot\mathbf{h}_0 &= \left(\frac{\mu_0}{4\pi}\right)\frac{\mu_z}{r^3}\left[\mathbf{z}\cdot\mathbf{h}_0 - 3(\mathbf{z}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\right] \qquad \{18) \\
A_x\mathbf{x}\cdot\mathbf{h}_0 &= \left(\frac{\mu_0}{4\pi}\right)\frac{\mu_x}{r^3}\left[\mathbf{x}\cdot\mathbf{h}_0 - 3(\mathbf{x}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\right]
\end{aligned}$$

Now $\mathbf{z}\cdot\boldsymbol{\sigma} = \cos\theta$, $\mathbf{x}\cdot\boldsymbol{\sigma} = -\sin\theta\cos\Omega$, $\mathbf{z}\cdot\mathbf{h}_0 = \cos\alpha$, $\mathbf{x}\cdot\mathbf{h}_0 = -\sin\alpha$ and $\mathbf{h_0}\cdot\boldsymbol{\sigma} = \cos\gamma = (\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos\Omega)$.



.

In Eqn {8} the quantities of interest are products of the form $\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|j\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle$ and have the units of energy. We therefore define $E_{ij}=\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|j\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle$. It is the sum over the various components of E_{ij} for which an angular average is required, so explicitly:

$$
\begin{aligned}
E_{ij} &= \langle i|\mu_z\mathbf{z}\cdot\mathbf{h}_0|j\rangle\langle j|A_z\mathbf{z}\cdot\mathbf{h}_0|i\rangle+\langle i|\mu_x\mathbf{x}\cdot\mathbf{h}_0|j\rangle\langle j|A_x\mathbf{x}\cdot\mathbf{h}_0|i\rangle \\
&= \left(\frac{\mu_0}{4\pi}\right)\frac{1}{r^3}\left[\mu_z^2\cos\alpha\{\mathbf{z}\cdot\mathbf{h}_0-3(\mathbf{z}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\}-\mu_x^2\sin\alpha\{\mathbf{x}\cdot\mathbf{h}_0-3(\mathbf{x}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\}\right] \\
&= \left(\frac{\mu_0}{4\pi}\right)\frac{1}{r^3}\left[\{\mu_z^2\cos^2\alpha+\mu_x^2\sin^2\alpha\}-3\{\mu_z^2\cos\alpha(\mathbf{z}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})-\mu_x^2\sin\alpha(\mathbf{x}\cdot\boldsymbol{\sigma})(\mathbf{h}_0\cdot\boldsymbol{\sigma})\}\right] \\
&= \left(\frac{\mu_0}{4\pi}\right)\frac{1}{r^3}\left[\{\mu_z^2\cos^2\alpha+\mu_x^2\sin^2\alpha\}-3\{\mu_z^2\cos\alpha\cos\theta(\mathbf{h}_0\cdot\boldsymbol{\sigma})+\mu_x^2\sin\alpha\sin\theta\cos\Omega(\mathbf{h}_0\cdot\boldsymbol{\sigma})\}\right] \\
&= \left(\frac{\mu_0}{4\pi}\right)\frac{1}{r^3}\left[\begin{array}{l}\{\mu_z^2\cos^2\alpha+\mu_x^2\sin^2\alpha\}-3\{(\cos\alpha\cos\theta+\sin\alpha\sin\theta\cos\Omega)\} \\ \{\mu_z^2\cos\alpha\cos\theta+\mu_x^2\sin\alpha\sin\theta\cos\Omega\}\end{array}\right]
\end{aligned}
$$

In which we have used Eqn {18}, and which can be simplified to:

$$
E_{ij}=-\frac{\mu_0}{4\pi\, r^3}\left[\begin{array}{l}\mu_z^2\cos^2\alpha\left(3\cos^2\theta-1\right) \\ +\mu_x^2\sin^2\alpha\left(3\sin^2\theta\cos^2\Omega-1\right) \\ +\frac{3}{4}\left(\mu_z^2+\mu_x^2\right)\sin 2\alpha\sin 2\theta\cos\Omega\end{array}\right] \qquad \{19\}
$$

This is the solid-state result, which must then be averaged over all possible orientations of the molecular axes relative to the external field. This is done in two stages. The first is an average over all orientations of the x and y axes, i.e. with respect to the angle Ω, and the second over all orientations of z with respect to the external field, i.e. with respect to α.

We first require the integrals: $\frac{1}{2\pi}\int_0^{2\pi}\cos\Omega\,\mathrm{d}\Omega = 0, \qquad \frac{1}{2\pi}\int_0^{2\pi}\cos^2\Omega\,\mathrm{d}\Omega = \frac{1}{2}$

So that {34} is reduced to:

$$E_{ij} = -\frac{\mu_0}{4\pi\, r^3}\begin{bmatrix}\mu_z^2\cos^2\alpha\left(3\cos^2\theta - 1\right) \\ +\,\mu_x^2\sin^2\alpha\left(\frac{3}{2}\sin^2\theta - 1\right)\end{bmatrix}$$

We also need: $\frac{1}{2}\int_0^{\pi}\cos^2\alpha\sin\alpha\,\mathrm{d}\alpha = \frac{1}{3}, \qquad \frac{1}{2}\int_0^{\pi}\left(1-\cos^2\alpha\right)\sin\alpha\,\mathrm{d}\alpha = \frac{2}{3}$

The result, which is well known, is:

$$E_{ij} = -\frac{\mu_0}{12\pi\, r^3}\left[\left(\mu_z^2 - \mu_x^2\right)\left(3\cos^2\theta - 1\right)\right] \qquad \{20\}$$

When this expression is substituted into Eqn {8} we obtain:

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)}{3\,r^3}\cdot\frac{1}{2}\sum_{i=\alpha,\beta}\left\{\frac{\left\{\langle i|\mu_z|i\rangle^2 - \langle i|\mu_x|i\rangle^2\right\}}{kT} - 2\sum_j\frac{\left\{\langle i|\mu_z|j\rangle^2 - \langle i|\mu_x|j\rangle^2\right\}}{\Delta\varepsilon_{ij}}\right\}$$

The sum over the two Kramers states yields two terms of equal magnitude so this expression is simply:

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)}{3\,r^3}\cdot\left\{\frac{\left\{\langle i|\mu_z|i\rangle^2 - \langle i|\mu_x|i\rangle^2\right\}}{kT} - 2\sum_j\frac{\left\{\langle i|\mu_z|j\rangle^2 - \langle i|\mu_x|j\rangle^2\right\}}{\Delta\varepsilon_{ij}}\right\} \qquad \{21\}$$

It is conventional in a Spin Hamiltonian to take S as a dummy angular momentum quantum number for a ground state with 2S+1 components and to use $\beta\, g_{kk}$ to indicate the proportionality

between the magnetic moment and the eigenvalues of the angular momentum operator. In this form $\langle i|\mu_z|i\rangle^2 = \beta^2 g_{zz}^2 \langle i|\hat{s}_z|i\rangle^2 = \frac{1}{4}\beta^2 g_{zz}^2$ (when $S = ½$) and the first term in {21} is:

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)}{12\,r^3}\cdot\frac{\beta^2\left\{g_{zz}^2 - g_{xx}^2\right\}}{kT} = \frac{\mu_0}{4\pi}\frac{\beta^2}{12kT}\left\{g_{zz}^2 - g_{xx}^2\right\}\frac{1}{r^3}\left(3\cos^2\theta - 1\right)$$

The second part of this equation is rearranged to make clear that it is identical to Bertini {2.18}[6] (when $S = ½$). It is also the same as K and M Eqn {20} (after allowing for inclusion of the factor $\mu_0/4\pi$ due to our use of the SI convention). In what follows it {21} will be evaluated using explicit values of the angular momentum matrix elements.

The Ru(III)-centred contribution to the Pseudo-Contact Shift

In {21} it is assumed that $\Delta\varepsilon_{ij} = -\frac{3}{2}\zeta$ for all excited states, i.e. the tetragonal field splitting of the Kramers quartet is ignored. In general $s << 1$ so terms in s^2 are ignored.

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2}{3\,r^3}\cdot\left\{-\frac{12s}{kT} + \frac{4}{3\zeta}6s\right\} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2}{3\,r^3}\cdot\left\{-\frac{12s}{kT} + \frac{8s}{\zeta}\right\} \quad \{22\}$$

The Bridge centred contribution to the Pseudo-Contact Shift

Here we follow K and M, in assuming that in a typical term $\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|j\rangle\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle$ the matrix element $\langle i|\boldsymbol{\mu}\cdot\mathbf{h}_0|j\rangle$ is associated with the average value of the moment induced by the external field, and that its value will thus well approximated by the ruthenium centred contribution. However, in so far as the molecular orbitals extend over the cyanide bridge, there is a contribution to the element $\langle j|\mathbf{A}\cdot\mathbf{h}_0|i\rangle$ associated with atomic orbitals centred on the bridge (and even on the donor metal), for which the angular momentum operators need to be evaluated locally. Only those bridge orbitals that matching the symmetry of $T_2 \pm 1$ components of the metal-centred bases need to be considered, and we assume (along with K and M) that a covalency coefficient f represents the appropriate contribution on a bridging atom. We then find modified magnetic moment matrices, as follows:

(a) $\mu_z(L) = -\beta\left(\hat{L}_z(L) + 2\hat{S}_z(L)\right)$ Units βf^2:

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	$\frac{4}{3}(1-2s)$	0	0	$\frac{2\sqrt{2}}{3}(1+s)$	0	0
$E''\beta''$	0	$-\frac{4}{3}(1-2s)$	$\frac{2\sqrt{2}}{3}(1+s)$	0	0	0
$U'\kappa$	0	$\frac{2\sqrt{2}}{3}(1+s)$	$-\frac{2}{3}(1+4s)$	0	0	0
$U'\nu$	$\frac{2\sqrt{2}}{3}(1+s)$	0	0	$\frac{2}{3}(1+4s)$	0	0
$U'\lambda$	0	0	0	0	0	0
$U'\mu$	0	0	0	0	0	0

(a) $\mu_x(L) = -\beta\left(\hat{L}_x(L) + 2\hat{S}_x(L)\right)$ Units βf^2 :

	$E''\alpha''$	$E''\beta''$	$U'\kappa$	$U'\nu$	$U'\lambda$	$U'\mu$
$E''\alpha''$	0	0	0	0	0	$\frac{\sqrt{2}}{\sqrt{3}}(1-s)$
$E''\beta''$	0	0	0	0	$-\frac{\sqrt{2}}{\sqrt{3}}(1-s)$	0
$U'\kappa$	0	0	0	0	0	0
$U'\nu$	0	0	0	0	0	0
$U'\lambda$	0	$-\frac{\sqrt{2}}{\sqrt{3}}(1-s)$	0	0	0	0
$U'\mu$	$\frac{\sqrt{2}}{\sqrt{3}}(1-s)$	0	0	0	0	0

In which terms in s^2 have been ignored.

$$\delta_{pc}(L) = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2 f^2}{3\,r(L)^3}\cdot\left\{\frac{4(1-6s)}{3kT} - 2\cdot\left(-\frac{2}{3\zeta}\right)\frac{(1+14s)}{3}\right\} \qquad \{23\}$$

Summarising all these results:

Contact Shift (cf. Eqn{17}:

$$\delta_c(ax) = \frac{\mu_0 g_e \beta^2 K_1}{9}\left[\frac{2}{9}\left(\frac{16-4s}{\zeta} + \frac{3-18s}{kT}\right)\right]$$

$$\delta_c(eq) = \frac{\mu_0 g_e \beta^2 K_1}{9}\left[\frac{2}{9}\left(\frac{16+2s}{\zeta} + \frac{3+9s}{kT}\right)\right]$$

Pseudo-Contact Shift(Metal):

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2}{3\,r^3}\cdot\left\{-\frac{12s}{kT} + \frac{8s}{\zeta}\right\}$$

Pseudo-Contact Shift(Bridge):

$$\delta_{pc}(L) = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2 f^2}{3\,r(L)^3}\cdot\left\{\frac{4(1-6s)}{3kT} + \frac{4(1+14s)}{9\zeta}\right\}$$

Notice that when $s = 0$ the metal-centred pseudo contact term vanishes. However this is not true of the contribution from the bridge, within which the angular momentum is intrinsically anisotropic.

In the limit that $x = v/\zeta << 1$, we may write $x \approx 3s$ and the above expressions become:

Contact Shift (cf. Eqn{11}:

$$\delta_c(ax) = \frac{\mu_0 g_e \beta^2 K_1}{9}\left[2\left(\frac{16}{9\zeta} + \frac{1}{3kT} - \frac{4x}{27\zeta} - \frac{2x}{3kT}\right)\right]$$

$$\delta_c(eq) = \frac{\mu_0 g_e \beta^2 K_1}{9}\left[2\left(\frac{16}{9\zeta} + \frac{1}{3kT} + \frac{2x}{27\zeta} + \frac{x}{3kT}\right)\right] \qquad \{24a\}$$

Pseudo-Contact Shift(Metal):

$$\delta_{pc} = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2}{3\,r^3}\cdot\left\{\frac{8x}{3\zeta} - \frac{4x}{kT}\right\} \qquad \{24b\}$$

Pseudo-Contact Shift(Bridge):

$$\delta_{pc}(L) = \frac{\mu_0}{4\pi}\frac{\left(3\cos^2\theta - 1\right)\beta^2 f^2}{r(L)^3}\cdot\frac{4}{9}\left\{\frac{1}{3\zeta} + \frac{1}{kT} + \frac{14x}{9\zeta} - \frac{2x}{kT}\right\} \qquad \{24c\}$$

N.B. in the main text the tetragonal field parameter variable x is replaced by t.

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S7. Computational Data

Table S7.1 Geometry Optimisations

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$ C_s symmetry B3LYP/SDD

44	0.069594000	-2.560305000	0.000000000
1	2.604940000	-2.040317000	0.821873000
7	0.096911000	-0.574994000	0.000000000
1	-2.454994000	-1.970471000	0.820791000
7	0.075515000	-2.617242000	2.177994000
1	-0.481826000	-5.125269000	0.822202000
1	-0.806568000	-2.954541000	-2.583737000
6	0.072545000	0.624150000	0.000000000
26	-0.079267000	2.491893000	0.000000000
6	-1.334304000	2.514215000	-1.321031000
8	-2.126349000	2.502016000	-2.170682000
6	-1.334304000	2.514215000	1.321031000
8	-2.126349000	2.502016000	2.170682000
1	2.542121000	2.314817000	1.363056000
6	1.933402000	2.937838000	-0.722108000
6	1.036723000	3.970898000	-1.165366000
6	0.455863000	4.595265000	0.000000000
6	1.036723000	3.970898000	1.165366000
6	1.933402000	2.937838000	0.722108000
1	2.542121000	2.314817000	-1.363056000
1	0.844028000	4.249436000	-2.194298000
1	-0.233816000	5.429899000	0.000000000
1	0.844028000	4.249436000	2.194298000
7	-2.112352000	-2.484405000	0.000000000
1	-2.454994000	-1.970471000	-0.820791000
1	-2.580308000	-3.399391000	0.000000000
7	0.011323000	-4.752485000	0.000000000
1	-0.481826000	-5.125269000	-0.822202000
1	0.941821000	-5.189838000	0.000000000
7	2.253195000	-2.545751000	0.000000000
1	2.704041000	-3.469178000	0.000000000
1	2.604940000	-2.040317000	-0.821873000
7	0.075515000	-2.617242000	-2.177994000
1	0.221022000	-1.663447000	-2.531098000
1	0.825083000	-3.203522000	-2.566739000
1	0.825083000	-3.203522000	2.566739000
1	0.221022000	-1.663447000	2.531098000
1	-0.806568000	-2.954541000	2.583737000

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$ No symmetry B3LYP/SDD

44	0.286006000	0.018729000	-0.051774000
1	0.915762000	2.105422000	-1.620579000
7	2.277139000	0.182671000	-0.031827000
1	1.442690000	-2.259460000	0.742881000
7	0.371745000	-0.750094000	-2.087418000
1	-2.287838000	-0.250725000	-1.012362000
1	-0.358431000	0.217395000	2.624956000
6	3.478301000	0.224695000	-0.039049000
26	5.336858000	0.169832000	-0.097200000
6	5.415834000	-1.447252000	0.700541000
8	5.447443000	-2.483345000	1.232005000
6	5.367112000	-0.429730000	-1.799276000
8	5.366612000	-0.800424000	-2.903610000
1	4.704125000	2.845691000	1.002347000
6	6.177252000	1.252087000	1.588602000
6	7.257541000	0.644461000	0.833775000
6	7.234130000	1.183742000	-0.490998000
6	6.139128000	2.132470000	-0.573625000

6	5.520104000	2.193142000	0.722611000
1	5.973575000	1.092590000	2.638916000
1	7.974319000	-0.072925000	1.213391000
1	7.929855000	0.943789000	-1.285284000
1	5.901043000	2.748737000	-1.430153000
7	0.452394000	-1.985051000	0.781888000
1	0.166583000	-2.053316000	1.766872000
1	-0.077550000	-2.703807000	0.271417000
7	-1.895799000	-0.143932000	-0.067230000
1	-2.242537000	-0.940213000	0.484185000
1	-2.337200000	0.694550000	0.335323000
7	0.173577000	2.014590000	-0.915616000
1	-0.718507000	2.237091000	-1.375884000
1	0.344536000	2.754287000	-0.222862000
7	0.219340000	0.779285000	1.987020000
1	1.180259000	0.768122000	2.352381000
1	-0.119417000	1.747005000	2.066210000
1	-0.051514000	-0.122861000	-2.783247000
1	1.360897000	-0.860784000	-2.345938000
1	-0.072973000	-1.669170000	-2.211388000

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CN)Ru(NH_3)_5]^{3+}.5H_2O$ C_s symmetry B3LYP/TZP

44	-0.337746000	-1.708646000	0.000000000
1	2.176699000	-1.658896000	0.842080000
7	-0.018366000	0.303193000	0.000000000
1	-2.722536000	-0.710286000	0.822124000
7	-0.291872000	-1.668811000	2.166935000
1	-1.518869000	-3.965975000	0.809880000
1	-0.866917000	-0.899687000	-2.528585000
6	0.013247000	1.501521000	0.000000000
26	-0.105622000	3.388253000	0.000000000
6	-1.314722000	3.384441000	-1.323543000
8	-2.094542000	3.363514000	-2.194592000
6	-1.314722000	3.384441000	1.323543000
8	-2.094542000	3.363514000	2.194592000
1	2.491755000	3.107620000	1.361276000
6	1.908946000	3.757734000	-0.724454000
6	1.063799000	4.827442000	-1.165036000
6	0.503258000	5.470233000	0.000000000
6	1.063799000	4.827442000	1.165036000
6	1.908946000	3.757734000	0.724454000
1	2.491755000	3.107620000	-1.361276000
1	0.876261000	5.111461000	-2.192687000
1	-0.152894000	6.330339000	0.000000000
1	0.876261000	5.111461000	2.192687000
7	-2.469981000	-1.270137000	0.000000000
1	-2.722536000	-0.710286000	-0.822124000
1	-3.077895000	-2.125842000	0.000000000
7	-0.918718000	-3.767811000	0.000000000
1	-1.518869000	-3.965975000	-0.809880000
1	-0.194054000	-4.527937000	0.000000000
7	1.754159000	-2.082692000	0.000000000
1	2.057868000	-3.085208000	0.000000000
1	2.176699000	-1.658896000	-0.842080000
7	-0.291872000	-1.668811000	-2.166935000
1	0.687089000	-1.495264000	-2.475049000
1	-0.618433000	-2.531437000	-2.616232000
1	-0.618433000	-2.531437000	2.616232000
1	0.687089000	-1.495264000	2.475049000
1	-0.866917000	-0.899687000	2.528585000
8	2.492268000	-1.285004000	2.832861000
8	2.492268000	-1.285004000	-2.832861000
1	2.956197000	-1.972008000	-3.355039000
1	2.828713000	-0.405453000	-3.101047000
1	2.828713000	-0.405453000	3.101047000

1	2.956197000	-1.972008000	3.355039000
8	-4.100951000	-3.572301000	0.000000000
8	3.143330000	-4.526008000	0.000000000
8	0.236569000	-6.282542000	0.000000000
1	-4.609876000	-3.833690000	0.795238000
1	-4.609876000	-3.833690000	-0.795238000
1	3.520622000	-4.951842000	-0.794613000
1	3.520622000	-4.951842000	0.794613000
1	0.319317000	-6.842194000	-0.797673000
1	0.319317000	-6.842194000	0.797673000

Table 7.2 Experimental and calculated structural parameters (Å and °) for $[(\eta^5-C_5H_5)Fe(CO)_2(\mu-CN)Ru(NH_3)_5]^{3+}$

	Exp.	C_s B3LYP/SDD	No sym B3LYP/SDD
Ru-N_{eq} (av 2-5)	2.108(2)	2.18	2.18
Ru-N_{ax} (6)	2.100(2)	2.19	2.19
Ru-N(1)	2.019(2)	1.99	1.99
Fe-C(1)	1.889(3)	1.87	1.86
Fe-C(2)	1.794(3)	1.82	1.81
Fe-C(3)	1.791(4)	1.82	1.81
Fe-C_{cp}(av 4-8)		2.18	2.18
N(1)-C(1)	1.142(4)	1.20	1.20
C(2)-O(1)	1.129(4)	1.16	1.17
C(3)-O(2)	1.135(4)	1.16	1.17
Fe-C(1)-N(1)	177.5	177	176
Ru-N(1)-C(1)	179.6	178	177
C(1)-Fe-C(2)	92.55(14)	94	93
C(1)-Fe-C(3)	93.31(15)	94	93
C(2)-Fe-C(3)	93.31(15)	93	97

Table. 7.3 Calculated spin densities on metal atoms in $[(\eta^5-C_5H_5)Fe(CO)_2(\mu-CN)Ru(NH_3)_5]^{3+}$

Method	Solvent	Ru	Fe
B3LYP/SDD C_s	None	0.62	0.48
B3LYP/SDD Nosym	None	0.88	0.16
BP/TZ2P C_s	None	0.54	0.45
SAOP/TZ2P C_s	None	0.59	0.48
LB94/TZ2P C_s	None	0.49	0.41
B3LYP/TZ2P C_s	None	0.78	0.27
B1PW91	None	0.61	0.47
BP/TZ2P C_s	Water	0.79	0.19
BP/TZ2P Nosym	Water	0.82	0.16
BP/TZ2P C_s	DMF	0.79	0.2
BP/TZ2P C_s	DMSO	0.79	0.2
BP/TZ2P C_s	Nitromethane	0.78	0.2
B3LYP/TZP C_s +5H_2O	Water	0.93	0.05

Table 7.4

Calculation File Number Conditions/Symmetry			#19 Vac Cs SO	#20 Vac No sym SO	#21 Vac Cs ZORA	#22 Vac No sym ZORA	#24 Water Cs SO	#26 Water No Sym SO	#23 Water Cs ZORA	#25 Water No Sym ZORA
g-tensor elements		Ga	2.637	2.835			2.949	3.259		
		Gb	2.211	2.253			2.500	2.644		
		Gc	1.903	1.857			1.819	1.819		
			a(iso)/MHz	a(iso)/MHz	Spin Density	Spin Density	a(iso)/MHz	a(iso)/MHz	Spin Density	Spin Density
Geometrical Numbering		Calculation Numbering								
Ru		1 Ru			0.5359	0.5605			0.7886	0.8207
N1	CN Bridge	3 N			0.0727	0.0723			0.0221	0.0193
C1	CN Bridge	8 C			-0.0302	-0.0289			0.0313	0.0317
Fe		9 Fe			0.4505	0.4212			0.1936	0.1649
C4	Cp ring In-plane	17 C	0.826	2.27	-0.0077	-0.0130	0.284	-0.027	-0.0033	-0.0052
H4	Far from Ru	22 H	0.528	0.737	0.0002	0.0007	0.311	0.403	0.0001	0.0002
C5	Cp ring - off plane	16 C	0.097	-0.305	-0.0033	-0.0130	0.101	-0.062	-0.0009	-0.0053
H5	Intermediate	21 H	0.049	0.742	0.0003	0.0009	0.030	0.413	0.0001	0.0000
C6	Near Ru	15 C	0.475	-0.305	0.0081	0.0243	0.402	1.005	0.0035	0.0111
H6	**Near Ru**	20 H	-0.232	-0.673	-0.0006	-0.0012	-0.187	-0.273	-0.0003	-0.0005
C7	Near Ru	19 C	0.097	2.29	0.0081	-0.0172	0.396	-0.587	0.0035	-0.0070
H7	Near Ru	14 H	-0.232	0.872	-0.0006	0.0014	-0.184	0.380	-0.0003	0.0007
C8	Intermediate	18 C	0.826	-1.56	-0.0033	0.0244	0.102	1.004	-0.0009	0.0104
H8	Intermediate	23 H	0.049	-0.676	0.0003	-0.0010	0.029	-0.288	0.0001	-0.0005
N2	cis parallel to Cs	30 N	-1.103	-1.394	-0.0048	-0.0046	-1.6848	-2.313	-0.0081	-0.0078
N3	cis perpendicular to Cs	33 N	**-1.086**	-1.393	-0.0054	-0.0051	-2.2276	-2.307	-0.0098	-0.0088
N4	cis parallel to Cs	24 N	-1.120	-1.543	-0.0050	-0.0074	-1.6888	-2.416	-0.0082	-0.0117
N5	cis perpendicular to Cs	5 N	-1.086	-1.403	-0.0054	-0.0068	-2.2279	-2.311	-0.0098	-0.0113
N6	Trans	27 N	-2.511	-2.747	-0.0087	-0.0101	-3.3475	-3.657	-0.0131	-0.0155

Average a(iso)/MHz		Average a(iso)/MHz	
Protons		*Protons*	
0.032	0.200	0.000	0.127
Average (Sym+No Sym)/MHz		Average (Sym+No Sym)/MHz	
0.116		0.063	
C-13		*C-13*	
0.464	0.478	0.257	0.267
Average (Sym+No Sym)/MHz		Average (Sym+No Sym)/MHz	
0.471		0.262	
Ratioi C-13/H	**4.05**	Ratioi C-13/H	**4.13**