CHEMISTRY LETTERS, pp. 503-508, 1974. Published by the Chemical Society of Japan

PROTON MAGNETIC RESONANCE OF METAL AMMINE COMPLEXES. II. THEORETICAL CONSIDERATION OF THE CHEMICAL SHIFTS IN PENTAMMINE COBALT(III) COMPLEXES AND THE RELATION TO COBALT-59 NMR

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The theoretical relation has been established between proton and cobalt-59 chemical shifts in $[Co(NH_3)_5X]$ by assuming that proton shifts come mainly from the paramagnetic anisotropy in Co(III) ion. The relation, coupled with Co-59 shift data, can explain very well proton shifts in these complexes.

In the previous paper,[1] we have reported the proton chemical shifts in $[Co(NH_3)_5X]$ and have shown that these shifts can be interpreted primarily by the paramagnetic anisotropy in the central cobalt(III) ion. Here we wish to present a new theoretical relation between the proton and cobalt-59 chemical shifts, which applies to a series of pentammine cobalt(III) complexes.

Theoretical

We start with Ramsey's expression for chemical shift

$$\sigma(^1H) = \frac{e^2}{2mc^2}\langle 0|\sum_j\{\mathbb{I}(r_j^0)^2 - \mathbb{r}_j^0\mathbb{r}_j^0\}|0\rangle$$
$$-2\sum_n (E_n - E_0)^{-1}\left[\langle 0|\sum_j m_j^0/r_j^{03}|n\rangle\langle n|m_j^0|0\rangle + c.c.\right] \quad (1)$$

All notations have their usual significances and the origin of the co-ordinate system is at the proton under consideration.[1] Equation (1) has been modified by McConnell,[2] in the point dipole approximation, to the form

$$\sigma(^1H) = \frac{\chi}{R^3} - 3\frac{\chi \mathbb{R}\mathbb{R}}{R^5} \quad (2)$$

Here the vector $\mathbb{R}$ is from the atom(s) exerting the dipolar field, in this case the central Co(III) ion, toward the proton in question.

$$\chi = -\frac{1}{2}\frac{e^2}{2m^2c^2}\langle 0|\sum_i\{\mathbb{I}(r_i^2) - \mathbf{r}_i\mathbf{r}_i\}|0\rangle + \sum_n (E_n - E_0)^{-1}\left[\langle 0|\sum_i \mathbf{m}_i|n\rangle\langle n|\sum_i \mathbf{m}_i|0\rangle + \text{c.c.}\right] \quad (3)$$

is the magnetic susceptibility tensor of the Co(III) ion. Note that quantities with and without the superscript 0 refer to the proton and the metal centers, respectively. We will assume that $\chi^d(^{59}Co)$ (the first term of the right side of eq.(3)) is nearly isotropic[3] and consider only the second term, which will be denoted by $\chi^p(^{59}Co)$.

We first calculate $\chi^p(^{59}Co)$ using molecular orbitals of the type

$$\left.\begin{aligned} \Psi_{a1} &= a_{11}d_{z^2} + a_{12}L_{a1} \\ \Psi_{b1} &= b_{11}d_{x^2-y^2} + b_{12}L_{b1} \\ \Psi_{b2} &= d_{xy} \\ \Psi_{ex} &= e_{11}d_{yz} + e_{12}\pi_y \end{aligned}\right\} \quad (4)$$

In the above, the departure of the crystal field from the O_h symmetry is considered to be small.[6] The low-lying excited states contributing significantly to $\chi^p(^{59}Co)$ can be taken as arising from d-d transitions.[3] Under these conditions, we obtain

$$\chi^p_{zz}(^{59}Co) = 16\beta^2(E_{A2} - E_{A1})^{-1}(b_{11} + b_{12}S_{b1})^2 \quad (5)$$

$$\chi^p_{xx}(^{59}Co) = \beta^2(E_E - E_{A1})^{-1}\left[3(e_{11}a_{11} + e_{11}a_{12}S_{eq} + e_{12}a_{11}S_{ex}) + (e_{11}b_{11} + e_{11}b_{12}S_{b1} + e_{12}b_{11}S_{ex})\right]^2 \quad (6)$$

where overlap integrals are defined as

$$\left.\begin{aligned} S_{b1} &= \langle L_{b1}|d_{x^2-y^2}\rangle \\ S_{eq} &= \langle L_{a1}|d_{z^2}\rangle \\ S_{ex} &= \langle \pi_y|d_{yz}\rangle \end{aligned}\right\} \quad (7)$$

Next, we consider the chemical shift tensor for cobalt-59 nucleus, $\sigma(^{59}Co)$. Since $\sigma^d(^{59}Co)$ (the so-called "diamagnetic term") has been shown both theoretically and experimentally[3] to be constant when varying the ligand X in $[Co(NH_3)_5X]$,

we attribute the chemical shift variation to the paramagnetic term, $\sigma^{P}(^{59}Co)$. Almost the same calculation as used to derive $\chi^{P}_{ii}(^{59}Co)$ leads us to

$$\sigma^{P}_{zz}(^{59}Co) = -32\beta^2\langle r^{-3}\rangle_{3d}(E_{A2}-E_{A1})^{-1}b_{11}(b_{11}+b_{12}S_{b1}) \quad (8)$$

$$\sigma^{P}_{xx}(^{59}Co) = -2\beta^2\langle r^{-3}\rangle_{3d}(E_E-E_{A1})^{-1}(3e_{11}a_{11}+e_{11}b_{11}) \times\left[3(e_{11}a_{11}+e_{11}a_{12}S_{eq}+e_{12}a_{11}S_{ex})+(e_{11}b_{11}+e_{11}b_{12}S_{b1}+e_{12}b_{11}S_{ex})\right] \quad (9)$$

Here $\langle r^{-3}\rangle_{3d}$ means the average of r^{-3} over a metal 3d wavefunction.

To a first approximation, we will neglect all overlap integrals. The relation between the principal values of the susceptibility and the chemical shift tensors is given, in this approximation, by

$$\chi^{P}_{zz}(^{59}Co) = -\frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{zz}(^{59}Co) \quad (10)$$

$$\chi^{P}_{xx}(^{59}Co) = -\frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{xx}(^{59}Co) \quad (11)$$

Substituting eqs.(10) and (11) into eq.(2), we obtain for trans (to ligand X) ammine protons

$$\left.\begin{aligned}\sigma^{P}_{zz}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{zz}(^{59}Co)(3\cos^2\theta-1)/R^3\\ \sigma^{P}_{xx}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{xx}(^{59}Co)(3\sin^2\theta\cos^2\phi-1)/R^3\\ \sigma^{P}_{yy}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{xx}(^{59}Co)(3\sin^2\theta\sin^2\phi-1)/R^3\end{aligned}\right\} \quad (12)$$

Similarly, for cis ammine protons

$$\left.\begin{aligned}\sigma^{P}_{zz}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{zz}(^{59}Co)(3\sin^2\theta'\sin^2\phi'-1)/R^3\\ \sigma^{P}_{xx}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{xx}(^{59}Co)(3\cos^2\theta'-1)/R^3\\ \sigma^{P}_{yy}(^1H) &= \frac{1}{2}\langle r^{-3}\rangle^{-1}_{3d}\,\sigma^{P}_{xx}(^{59}Co)(3\sin^2\theta'\cos^2\phi'-1)/R^3\end{aligned}\right\} \quad (13)$$

As to the definitions of θ, ϕ, θ', and ϕ', see Fig. 1.

After taking the NH_3-rotation about Co-N bond axes into consideration, the proton chemical shift in solution can be obtained as

$$\sigma^{P}_{t}(^1H) = \frac{1}{6}\langle r^{-3}\rangle^{-1}_{3d}\left[\sigma^{P}_{zz}(^{59}Co)-\sigma^{P}_{xx}(^{59}Co)\right](3\cos^2\theta-1)/R^3 \quad (14)$$

$$\sigma^{P}_{c}(^1H) = \frac{-1}{12}\langle r^{-3}\rangle^{-1}_{3d}\left[\sigma^{P}_{zz}(^{59}Co)-\sigma^{P}_{xx}(^{59}Co)\right](3\cos^2\theta'-1)/R^3 \quad (15)$$

In the above, the subscripts t and c refer to trans and cis ammine protons, respectively. The following equation applies to complexes of C_{4v} symmetry

$$\sigma^{P}(^{59}Co) = \frac{1}{3}\left[2\sigma^{P}_{xx}(^{59}Co) + \sigma^{P}_{zz}(^{59}Co) \right] \tag{16}$$

Thus, eqs. (14) and (15) are reduced to

$$\sigma^{P}_{t}(^{1}H) = \frac{1}{4}\langle r^{-3}\rangle^{-1}_{3d}\left[\sigma^{P}_{zz}(^{59}Co) - \sigma^{P}(^{59}Co) \right](3\cos^{2}\theta - 1)/R^{3} \tag{17}$$

$$\sigma^{P}_{c}(^{1}H) = \frac{-1}{8}\langle r^{-3}\rangle^{-1}_{3d}\left[\sigma^{P}_{zz}(^{59}Co) - \sigma^{P}(^{59}Co) \right](3\cos^{2}\theta' - 1)/R^{3} \tag{18}$$

Equations (17) and (18) establish the relation between the proton and the cobalt-59 chemical shifts of $[Co(NH_3)_5X]$ in solution. Since $\sigma^{P}_{zz}(^{59}Co)$ can be considered to be constant over a series of complexes,[3] the above result indicates that the proton chemical shifts in these complexes should be directly proportional to the cobalt-59 chemical shifts.

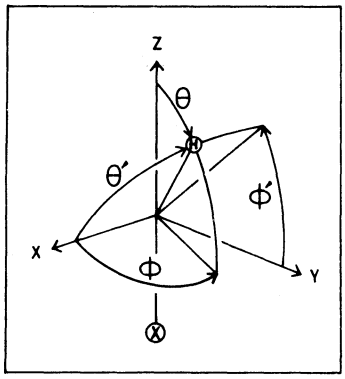

Fig. 1. The co-ordinate system.

Comparison with Experiments

The geometrical factors necessary for the calculation of eqs.(17) and (18) can be estimated by the following procedure. By taking the Co-N and N-H distances as 2.0Å(3.78a.u.) and 1.0Å (1.89a.u.), respectively,[4] we obtain R = 4.77a.u.(2.52Å) and $\theta = 22.0^{\circ}$, $\theta' = 2?.0^{\circ}$. The value of $\langle r^{-3}\rangle_{3d}$ is estimated from eq.(8) using the data for $[Co(NH_3)_6]^{3+}$; $E_{A2} - E_{A1}$ (in this case $E_{T1g} - E_{A1g}$) = 2.10×10^{4} cm^{-1},[5] $\sigma^{P}_{zz}(^{59}Co) = -1.91\times10^{-2}$,[3] b_{11} = 0.924, b_{12} = - 0.61, and S_{b1} = 0.2.[6] Substitution of these values into eq.(8) yields the value of 5.77a.u. for $\langle r^{-3}\rangle_{3d}$. As stated earlier, $\sigma^{P}_{zz}(^{59}Co)$ can be taken as -1.91×10^{-2} for all complexes we are dealing with. Fujiwara and coworkers have measured the cobalt-59 chemical shifts in pentammine complexes. Their values are; X($\sigma^{P}(^{59}Co)$ in 10^{-2}) = CN^{-}(-1.77), NO_2^{-}(-1.85), NH_3(-1.91), H_2O(-2.00) OH^{-}(-2.01), Cl^{-}(-1.98), and Br^{-}(-1.93).[7]

Substituting the values obtained just above into eqs.(17) and (18), we can calculate $\sigma^{P}_{t}(^{1}H)$ and $\sigma^{P}_{c}(^{1}H)$. The calculated proton chemical shifts are illustrated in Fig. 2, together with the observed shift values. The agreement between the calculated and the observed values is remarkably good for complexes with X =H_2O,

OH^-, Cl^-, and Br^-. For X = CN^- and NO_2^-, the agreement is also good. In view of the roughness of the approximations used, these agreement may be fortuitous but it is quite satisfying that we could obtain correct orders of magnitude for chemical shifts. Therefore, it can be concluded that the proton chemical shift behavior in pentammine cobalt(III) complexes can be ascribed to the anisotropy in the second-order paramagnetism of the central cobalt(III) ion. The discrepancies, though small, left behind after these calculations may be found in the disregard of the possible variation of the Co-N distances, the neglect of all overlap integrals, or the point dipole approximation itself. Solvent effects may have some contribution.[8]

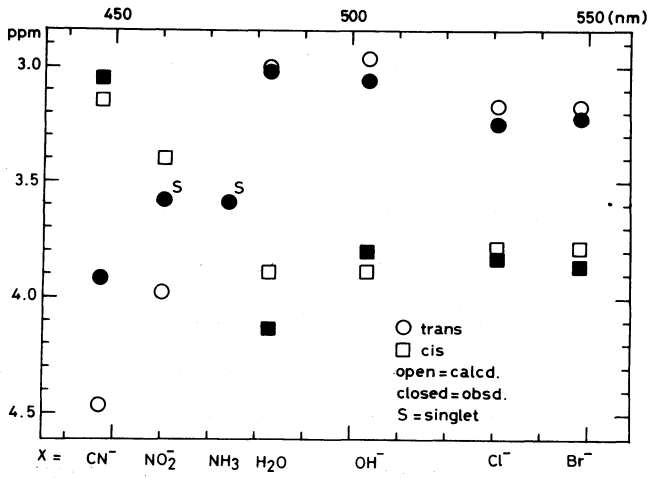

Fig. 2. Comparison of the calculated shift values with the observed values. Shifts[1] are from DSS internal standard and the abscissa is the reciprocal of the excitation energy $E_E - E_{A1}$.

Finally, it is worth pointing out that the similar procedure to that used above will probably explain the main features of the proton chemical shifts in some hydride complexes of platinum, e.g., $[PtHL(PEt_3)_2]$, since a linear relationship has been observed between the hydride proton and the platinum-195 chemical shifts.[9]

The authors are much indebted to Prof. S. Fujiwara ans Drs. A. Yamasaki and F. Yajima at Tokyo University. One of the authors(Y. N.) thanks the Ministry of Education for the financial assistance of a Grant for Scientific Research.

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(Received March 23, 1974)