Theoretical Study of Proton Chemical Shifts Induced by the Paramagnetic Anisotropy of Cobaltic Ion

Yoshiaki NAKASHIMA, Ushio SAKAGUCHI,* and Hayami YONEDA*
Department of Physics, Faculty of Education, Wakayama University, Wakayama 640
**Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730*

(Received November 25, 1974)

A new theoretical relation between proton and cobalt-59 chemical shifts in cobalt(III) compounds has been established on the assumption that the proton shift comes primarily from the anisotropy of the second-order paramagnetism of the central cobalt(III) ion. The additivity observed for cobalt-59 chemical shifts in solution is explained and applied to the problem of proton shifts. The relation between ^{1}H and ^{59}Co chemical shifts, coupled with this additivity, allows one to calculate the chemical shift of a proton under the influence of the paramagnetic anisotropy of a cobalt ion.

In previous papers,[1,2] we have reported the chemical shifts of ammine protons of a series of pentaammine cobalt(III) complexes. The shifts have been interpreted as arising primarily from the paramagnetic anisotropy of the central cobalt ions.

In this paper a more rigorous and convenient method of calculating the PMR shifts for cobalt(III) ammines is given. This new result can explain quantitatively the ammine proton chemical shifts. It has already been applied to α-aminocarboxylato cobalt(III) compounds.[3]

The core of the present theory is the use of cobalt-59 chemical shift data. First we establish a relation between the proton chemical shift and the paramagnetic susceptibility tensor of a cobaltic ion using the formulation of Ramsey[4] and McConnell.[5] Next the paramagnetic susceptibility of the central cobalt ion will be shown to be directly proportional to the chemical shift of the cobalt-59 nucleus. Thus, PMR shifts can be obtained from data on cobalt-59 chemical shifts which have been documented for the vast majority of cobaltic complexes. Finally, an additivity of cobalt-59 shifts will be used to show that proton shifts can be calculated very easily.

Theory

Chemical Shift Induced by Paramagnetic Anisotropy. We start with Ramsey's expression for the chemical shift[4]

$$\begin{aligned}\sigma(^1\mathrm{H}) = {} & (e^2/2mc^2)\langle 0|\sum_j\{1(r_j^0)^2-r_j^0r_j^0\}/(r_j^0)^3|0\rangle \\ & -2\sum_n(E_n-E_0)^{-1}[\langle 0|\sum_j m_j^0/(r_j^0)^3|n\rangle \\ & \times\langle n|\sum_j m_j^0|0\rangle+\mathrm{c.c.}]\end{aligned} \tag{1}$$

All notations have their usual significance[1,2] and c.c. denotes the complex conjugate. The origin of the coordinate system is at the proton under consideration. Equation (1) has been simplified by McConnell,[5] using the point dipole approximation, to the form

$$\sigma(^1\mathrm{H}) = \left(\frac{1}{R^3}-\frac{3\boldsymbol{R}\cdot\boldsymbol{R}}{R^5}\right)\chi \tag{2}$$

Here, the vector $\boldsymbol{R}$ is from the atom exerting the dipole field, in the present case the central cobalt(III) ion, to the proton in question. The magnetic susceptibility tensor of the cobalt(III) ion may be written:

$$\begin{aligned}\chi = {} & -(1/2)(e^2/2mc^2)\langle 0|\sum_i\{1(r_i)^2-r_ir_i\}|0\rangle \\ & +\sum_n(E_n-E_0)^{-1}[\langle 0|\sum_i m_i|n\rangle\langle n|\sum_i m_i|0\rangle+\mathrm{c.c.}]\end{aligned} \tag{3}$$

Note that quantities with the superscript 0 refer to the proton and those without 0 to the metal center. We assume that the first term of the right-hand side of Eq. (3) is nearly isotropic and constant over a wide variety of cobaltic complexes and consider only the second term which we denote by $\chi^\mathrm{p}(^{59}\mathrm{Co})$. The validity of this assumption has been discussed extensively[2,6] and has been well established for many cobalt compounds.[6] With this assumption, we need to treat only the paramagnetic term in proton chemical shift. Thus, we obtain

$$\sigma^\mathrm{p}(^1\mathrm{H}) = \left(\frac{1}{R^3}-\frac{3\boldsymbol{R}\cdot\boldsymbol{R}}{R^5}\right)\chi^\mathrm{p}(^{59}\mathrm{Co}) \tag{4}$$

Relation to ^{59}Co Chemical Shifts. The chemical shift of a cobalt-59 nucleus can be calculated from

$$\sigma(^{59}\mathrm{Co}) = \sigma^\mathrm{d}(^{59}\mathrm{Co}) + \sigma^\mathrm{p}(^{59}\mathrm{Co}) \tag{5}$$

where

$$\begin{aligned}\sigma^\mathrm{p}(^{59}\mathrm{Co}) = {} & -2\sum_n(E_n-E_0)^{-1}[\langle 0|\sum_j m_j/r_j{}^3|n\rangle \\ & \times\langle n|\sum_j m_j|0\rangle+\mathrm{c.c.}]\end{aligned} \tag{6}$$

For the reasons mentioned above, we need to consider only the term $\sigma^\mathrm{p}(^{59}\mathrm{Co})$. We use a simple molecular orbital theory, which takes into account the covalency and the anisotropy in chemical shift. The wavefunctions used here are assumed to be well approximated by those appropriate in a crystal field of $\mathrm{O_h}$ symmetry, irrespective of the real symmetry of the complex in question. Thus, the theory is similar, in some respects, to that which Yamatera[7] used to explain the absorption spectra of diamagnetic cobalt compounds. This we call the $\mathrm{O_h}$ approximation.

The excited state that contributes most to $\sigma_\mathrm{p}(^{59}\mathrm{Co})$ is the $^1\mathrm{T_{1g}}$ state, which corresponds to the first absorption band in cobaltic complexes. In the $\mathrm{O_h}$ approximation, it will suffice to investigate the zz component as an example. It is a straightforward matter to show that Eq. (6) can be reduced to

$$\begin{aligned}\sigma_\mathrm{zz}^\mathrm{p}(^{59}\mathrm{Co}) = {} & -4(E_\mathrm{E}-E_0)^{-1}[\langle\Psi_{\mathrm{t2g(z)}}|m_\mathrm{z}/r^3|\Psi_{\mathrm{eg(z)}}\rangle \\ & \times\langle\Psi_{\mathrm{eg(z)}}|m_\mathrm{z}|\Psi_{\mathrm{t2g(z)}}\rangle+\mathrm{c.c.}]\end{aligned} \tag{7}$$

for a cobalt(III) ion in a crystal field of $\mathrm{O_h}$ symmetry. Here, E_E and E_0 are the energies of the excited state

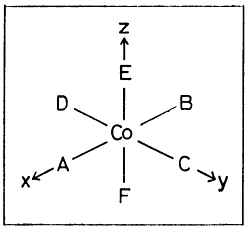


Fig. 1. The coordinate system for a complex [Co(ABCDEF)]. A, B, ⋯, F stand for ligand molecules.

$^1T_{1g}$ and the ground state $^1A_{1g}$, respectively. Covalency effects can be taken into account by using the molecular orbitals of the form

$$\Psi_{\mathrm{eg(z)}} = c_{\mathrm{M1}}3\mathrm{d}_{\mathrm{x^2-y^2}} + c_{\mathrm{L1}}\Phi_{\mathrm{L1}} \tag{8}$$

$$\Psi_{\mathrm{t2g(z)}} = c_{\mathrm{M2}}3\mathrm{d}_{\mathrm{xy}} + c_{\mathrm{L2}}\Phi_{\mathrm{L2}} \tag{9}$$

Here, the ligand molecular orbitals are defined by linear combinations of atomic orbitals:

$$\Phi_{\mathrm{L1}} = (\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}-\sigma_{\mathrm{C}}-\sigma_{\mathrm{D}})/2 \tag{10}$$

$$\Phi_{\mathrm{L2}} = (\pi_{\mathrm{A}}+\pi_{\mathrm{B}}-\pi_{\mathrm{C}}-\pi_{\mathrm{D}})/2 \tag{11}$$

The subscripts A, B, C, and D stand for ligand molecules or ions, see Fig. 1. In cases where ligand π^* orbitals are important, molecular orbitals (11) should be replaced by

$$\Psi_{\mathrm{t2g(z)}} = c_{\mathrm{M3}}3\mathrm{d}_{\mathrm{xy}} + c_{\mathrm{L3}}\Phi_{\mathrm{L3}} \tag{12}$$

$$\Phi_{\mathrm{L3}} = (\pi^*_{\mathrm{A}}+\pi^*_{\mathrm{B}}-\pi^*_{\mathrm{C}}-\pi^*_{\mathrm{D}})/2 \tag{13}$$

Substitution of Eqs. (8) and (9) into Eq. (7) yields

$$\sigma^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co}) = -32\beta^2\langle r^{-3}\rangle(E_{\mathrm{E}}-E_0)^{-1} \times (c_{\mathrm{M1}}c_{\mathrm{M2}}+c_{\mathrm{M2}}c_{\mathrm{L1}}S_\sigma+c_{\mathrm{M1}}c_{\mathrm{L2}}S_\pi)^2 \tag{14}$$

where we have used the relations

$$\Phi_{\mathrm{L1}} = S_\sigma 3\mathrm{d}_{\mathrm{x^2-y^2}} + S_\sigma' 4\mathrm{d}_{\mathrm{x^2-y^2}} + \cdots \tag{15}$$

$$\Phi_{\mathrm{L2}} = S_\pi 3\mathrm{d}_{\mathrm{xy}} + S_\pi' 4\mathrm{d}_{\mathrm{xy}} + \cdots \tag{16}$$

in which

$$S_\sigma = \langle 3\mathrm{d}_{\mathrm{x^2-y^2}}|\Phi_{\mathrm{L1}}\rangle \tag{17}$$

$$S_\pi = \langle 3\mathrm{d}_{\mathrm{xy}}|\Phi_{\mathrm{L2}}\rangle \tag{18}$$

We have neglected small terms in S_σ^2 and S_π^2, which do not affect the final result (see below). $<r^{-3}>$ is an average of r^{-3} over a metal 3d orbital.

Almost the same calculation leads us to an expression for $\chi^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co})$.

$$\chi^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co}) = 16\beta^2(E_{\mathrm{E}}-E_0)^{-1} \times (c_{\mathrm{M1}}c_{\mathrm{M2}}+c_{\mathrm{M2}}c_{\mathrm{L1}}S_\sigma+c_{\mathrm{M1}}c_{\mathrm{L2}}S_\pi)^2 \tag{19}$$

Thus, we obtain

$$\chi^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co}) = -\sigma^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co})/2\langle r^{-3}\rangle \tag{20}$$

and hence

$$\chi^{\mathrm{p}}(^{59}\mathrm{Co}) = -\sigma^{\mathrm{p}}(^{59}\mathrm{Co})/2\langle r^{-3}\rangle \tag{21}$$

This result is quite general and does not depend on the symmetry of the complex in question. In the previous paper,[2)] we verified the above relation using molecular orbitals appropriate to C_{4v} symmetry and applied it to the calculation of the proton chemical shift of $[\mathrm{CoX(NH_3)_5}]$. From Eqs. (4) and (21), we obtain

$$\sigma^{\mathrm{p}}(^1\mathrm{H}) = -\left(\frac{1}{R^3}-\frac{3\boldsymbol{R}\cdot\boldsymbol{R}}{R^5}\right)\sigma^{\mathrm{p}}(^{59}\mathrm{Co})/2\langle r^{-3}\rangle \tag{22}$$

which establishes the relation between the proton and cobalt-59 chemical shifts.

Additivity of ^{59}Co Chemical Shifts. Since the pioneering work of Proctor and Yu,[8)] the chemical shift of the cobalt-59 nucleus has been the subject of many investigations.[4,6,9–17)] Freeman, Murray, and Richards[14)] and Griffith and Orgel[15)] have noted that the shift is inversely proportional to the energy of the first absorption band in cobalt(III) complexes. Betteridge and Golding[16)] and Fujiwara and coworkers[6)] have pointed out that the covalency between the metal and ligand orbitals should be considered. Recently, it has been reported by Fujiwara *et al.*[17)] that an additivity holds for shift values of a wide variety of cobaltic compounds, namely, the observed shift value in solution can roughly be given by the sum of contributions from each ligand. To this additivity rule we present an interpretation and an extension, which we believe explains all the above observations. The details are given in the Appendix. The results may be summarized as follows: this rule comes from the additivity valid for each (xx, yy, and zz) component of the shielding tensor.

$$\sigma^{\mathrm{p}}_{\mathrm{xx}}(^{59}\mathrm{Co}) = \sigma(\mathrm{C}) + \sigma(\mathrm{D}) + \sigma(\mathrm{E}) + \sigma(\mathrm{F}) \tag{23}$$

$$\sigma^{\mathrm{p}}_{\mathrm{yy}}(^{59}\mathrm{Co}) = \sigma(\mathrm{A}) + \sigma(\mathrm{B}) + \sigma(\mathrm{E}) + \sigma(\mathrm{F}) \tag{24}$$

$$\sigma^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co}) = \sigma(\mathrm{A}) + \sigma(\mathrm{B}) + \sigma(\mathrm{C}) + \sigma(\mathrm{D}) \tag{25}$$

where σ(X) is the contribution from a ligand X to the paramagnetic term of the cobalt-59 shielding. The σ(X) values of typical ligands are given in Table 1.

TABLE 1. σ(X) VALUES FOR SOME LIGANDS. DATA ARE TAKEN FROM REFS. (10) TO (12) AND (17).
ox = $C_2O_4^{2-}$, en = ethylenediamine, phen = phenanthroline.

X	σ (X)	Calcd from	
NH_3	−4860 ppm	−19440 ppm of	$[Co(NH_3)_6]$
en	−9205	−18410	$[Co(en)_3]$
Cl	−5910	−20140	$[Co(NH_3)_5Cl]$
Br	−5865	−20110	$[Co(NH_3)_5Br]$
NO_2	−4073	−18915	$[Co(NH_3)_5NO_2]$
CN	−2760	−18040	$[Co(NH_3)_5CN]$
N_3	−5655	−19970	$[Co(NH_3)_5N_3]$
OH	−6345	−20430	$[Co(NH_3)_5OH]$
H_2O	−6255	−20370	$[Co(NH_3)_5H_2O]$
CO_3	−12090	−21020	$[Co(NH_3)_4CO_3]$
ox	−11440	−19900	$[Co(en)_2ox]$
phen	−9135	−18270	$[Co(phen)_3]$

The method for obtaining these values is expounded in the Appendix. Thus, the cobalt-59 chemical shift for a complex [CoABCDEF] in solution is given by

$$\sigma^{\mathrm{p}}_{\mathrm{iso}}(^{59}\mathrm{Co}) = \sum_i \sigma^{\mathrm{p}}_{ii}(^{59}\mathrm{Co})/3 \tag{26}$$

$$= (2/3)\sum_X \sigma(X) \tag{27}$$

Substituting Eqs. (23) to (25) into Eq. (22), we obtain

$$\sigma^{\mathrm{p}}_{\mathrm{xx}}(^1\mathrm{H}) = -(1-3\sin^2\theta\cos^2\phi) \times (\sigma(\mathrm{C})+\sigma(\mathrm{D})+\sigma(\mathrm{E})+\sigma(\mathrm{F}))/2R^3\langle r^{-3}\rangle \tag{28}$$

$$\sigma^{\mathrm{p}}_{\mathrm{yy}}(^1\mathrm{H}) = -(1-3\sin^2\theta\sin^2\phi) \times (\sigma(\mathrm{A})+\sigma(\mathrm{B})+\sigma(\mathrm{E})+\sigma(\mathrm{F}))/2R^3\langle r^{-3}\rangle \tag{29}$$

$$\sigma^{\mathrm{p}}_{\mathrm{zz}}(^1\mathrm{H}) = -(1-3\cos^2\theta) \times (\sigma(\mathrm{A})+\sigma(\mathrm{B})+\sigma(\mathrm{C})+\sigma(\mathrm{D}))/2R^3\langle r^{-3}\rangle \tag{30}$$

The proton chemical shift in solution is given by

$$\sigma^{\mathrm{p}}_{\mathrm{iso}}({}^{1}\mathrm{H}) = \sum_{i}\sigma^{\mathrm{p}}_{ii}({}^{1}\mathrm{H})/3 \tag{31}$$

Discussion

Hendrickson and Jolly[18] have pointed out, in their interpretation of the PMR spectra of cobalt(III) pentaammines, the importance of the second-order paramagnetism of the central metal ion. However, their explanation for the shifts is only qualitative. They qualitatively explained a gradual change in chemical shifts when the sixth ligand is varied along the spectrochemical series. Buckingham and Stephens[19] were the first to try to treat quantitatively the chemical shift of a proton under the influence of the magnetic anisotropy of metal ions. They considered transition metal hydrides and made an almost *ab initio* calculation. Their calculation was, however, hampered by the paucity of experimental data necessary for the estimation of several parameters, resulting in a qualitative explanation.

We formulated the theory of proton chemical shifts in such a way as to use cobalt-59 chemical shifts. This is because a vast amount of data has been accumulated for many cobaltic compounds. The results obtained here afford a quantitative explanation of proton chemical shifts in cobalt(III) ammines. This we will show in subsequent publications.

Appendix

It seems worthwhile to determine the origin and the implication of the empirical additivity rule for cobalt-59 chemical shifts. As in previous discussions, we use the O_h approximation. The energy levels pertinent to the present discussion are the ground level ${}^{1}\mathrm{A}_{1g}$ and the excited level ${}^{1}\mathrm{T}_{1g}$.

Now, the excited state ${}^{1}\mathrm{T}_{1g}$ is obtained by a one-electron excitation from the t_{2g} to the e_g state. The energy of the ${}^{1}\mathrm{T}_{1g}$ state may be considered to contain the following terms;[7] $5\times\varepsilon(t_{2g})$, $\varepsilon(e_g)$, the electron repulsion energies, and the configuration interaction energies, where $\varepsilon(t_{2g})$ is the one-electron energy of the t_{2g} state and $\varepsilon(e_g)$ the corresponding energy of the e_g state.

$$E_{\mathrm{E}} = 5\varepsilon(t_{2g}) + \varepsilon(e_g) + \cdots \tag{A1}$$

Similarly, the energy of the ground state ${}^{1}\mathrm{A}_{1g}$ is given by

$$E_0 = 6\varepsilon(t_{2g}) + \cdots \tag{A2}$$

Contributions from kinetic and potential energies of valence electrons in the field of metal core have been included in $\varepsilon(t_{2g})$ and $\varepsilon(e_g)$. We assume that of these terms only $\varepsilon(t_{2g})$ and $\varepsilon(e_g)$ vary from ligand to ligand and the others remain almost unaltered. This assumption is equivalent to that of Yamatera,[7] who has been successful in explaining the shifts and splittings of the absorption spectra of diamagnetic cobalt complexes. The justification for this assumption can be found in his paper. The change in the denominator of Eq. (14), $(E_{\mathrm{E}}-E_0)$, on going from one complex to another is therefore set equal to the change in $(\varepsilon(t_{2g})-\varepsilon(e_g))$.

In a simple molecular orbital scheme,[20] the energies $\varepsilon(t_{2g})$ and $\varepsilon(e_g)$ are given by

$$\varepsilon(t_{2g}) = H_{\mathrm{MM}}(t_{2g}) + S_{\pi}^{2}H_{\mathrm{MM}}(t_{2g})H_{\pi}(H_{\mathrm{MM}}(t_{2g})-H_{\pi})^{-1} \tag{A3}$$

$$\varepsilon(e_g) = H_{\mathrm{MM}}(e_g) + S_{\sigma}^{2}H_{\mathrm{MM}}(e_g)H_{\sigma}(H_{\mathrm{MM}}(e_g)-H_{\sigma})^{-1} \tag{A4}$$

where we define

$$H_{\mathrm{MM}}(t_{2g}) = \langle 3d_{xy}|H|3d_{xy}\rangle \tag{A5}$$

$$H_{\mathrm{MM}}(e_g) = \langle 3d_{x^2-y^2}|H|3d_{x^2-y^2}\rangle \tag{A6}$$

$$H_{\sigma} = \langle \Phi_{\mathrm{L1}}|H|\Phi_{\mathrm{L1}}\rangle \tag{A7}$$

$$H_{\pi} = \langle \Phi_{\mathrm{L2}}|H|\Phi_{\mathrm{L2}}\rangle \tag{A8}$$

and

$$H = H_{\mathrm{core}} + U \tag{A9}$$

H_{core} is the energy of an electron in the field of the metal core and U the potential energy of an electron in the field of the ligands. In Eqs. (A3) and (A4), the following relations have been used.[20]

$$\langle 3d_{x^2-y^2}|H|\Phi_{\mathrm{L1}}\rangle \simeq S_{\sigma}(H_{\mathrm{MM}}(e_g)H_{\sigma})^{1/2} \tag{A10}$$

$$\langle 3d_{xy}|H|\Phi_{\mathrm{L2}}\rangle \simeq S_{\pi}(H_{\mathrm{MM}}(t_{2g})H_{\pi})^{1/2} \tag{A11}$$

Further, the coefficients c_{M1} and c_{L1} should obey the normalization condition,

$$c_{\mathrm{M1}}^{2} + 2c_{\mathrm{M1}}c_{\mathrm{L1}}S_{\sigma} + c_{\mathrm{L1}}^{2} = 1 \tag{A12}$$

$$c_{\mathrm{M2}}^{2} + 2c_{\mathrm{M2}}c_{\mathrm{L2}}S_{\pi} + c_{\mathrm{L2}}^{2} = 1 \tag{A13}$$

If we assume that the value of $H_{\mathrm{MM}}(e_g)$ is little influenced by ligand substitution,[7] Eqs. (A3) and (A12) indicate that $\varepsilon(e_g)$, c_{M1}, and c_{L1} are functions of two independent variables, S_{σ} and H_{σ}. Likewise, $\varepsilon(t_{2g})$, c_{M2}, and c_{L2} can be considered to be functions of S_{π} and H_{π}. Thus, under these conditions $\sigma^{\mathrm{p}}_{zz}({}^{59}\mathrm{Co})$ is a function of four variables: S_{σ}, S_{π}, H_{σ}, and H_{π}, the values of which vary of course from ligand to ligand. However, the changes in these values upon going from one complex to another may be assumed to be much smaller than the corresponding values in the parent complex.[7] Therefore, we might as well develop $\sigma^{\mathrm{p}}_{zz}({}^{59}\mathrm{Co})$ into a power series in these increments. For convenience, we denote the zz component of the shielding tensor for a complex [Co-ABCDEF] as $\sigma^{\mathrm{p}}_{zz}(\mathrm{ABCDEF})$ (see Fig. 1).

$$\begin{aligned}\sigma^{\mathrm{p}}_{zz}(\mathrm{ABCDEF}) = {}& \sigma^{\mathrm{p}}_{zz}(000000)\\ &+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial S_{\sigma}}\sum_{\mathrm{X}}(s^{\sigma}_{\mathrm{X}}-s^{\sigma}_{0})+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial H_{\sigma}}\sum_{\mathrm{X}}(\varepsilon^{\sigma}_{\mathrm{X}}-\varepsilon^{\sigma}_{0})\\ &+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial S_{\pi}}\sum_{\mathrm{X}}(s^{\pi}_{\mathrm{X}}-s^{\pi}_{0})+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial H_{\pi}}\sum_{\mathrm{X}}(\varepsilon^{\pi}_{\mathrm{X}}-\varepsilon^{\pi}_{0})\\ &+(\text{second-order terms})\end{aligned} \tag{A14}$$

Note that the summation runs from A to D. We have employed the relation

$$S_{\sigma} = \sum s^{\sigma}_{\mathrm{X}},\quad s^{\sigma}_{\mathrm{X}} = \langle 3d_{x^2-y^2}|\pm\sigma_{\mathrm{X}}\rangle/2 \tag{A15}$$

$$S_{\pi} = \sum s^{\pi}_{\mathrm{X}},\quad s^{\pi}_{\mathrm{X}} = \langle 3d_{xy}|\pm\pi_{\mathrm{X}}\rangle/2 \tag{A16}$$

$$H_{\sigma} = \sum \varepsilon^{\sigma}_{\mathrm{X}},\quad \varepsilon^{\sigma}_{\mathrm{X}} = \langle \sigma_{\mathrm{X}}|H|\sigma_{\mathrm{X}}\rangle/4 \tag{A17}$$

$$H_{\pi} = \sum \varepsilon^{\pi}_{\mathrm{X}},\quad \varepsilon^{\pi}_{\mathrm{X}} = \langle \pi_{\mathrm{X}}|H|\pi_{\mathrm{X}}\rangle/4 \tag{A18}$$

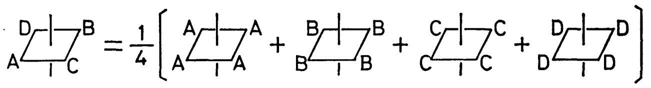
where X=A, B, C, and D and the subscript o represents some "reference" ligand, *e.g.* NH_3 or ethylenediamine. Equation (A14) can be recast into

$$\sigma^{\mathrm{p}}_{zz}(\mathrm{ABCDEF}) = \sigma(\mathrm{A}) + \sigma(\mathrm{B}) + \sigma(\mathrm{C}) + \sigma(\mathrm{D}) \tag{A19}$$

Here

$$\begin{aligned}\sigma(\mathrm{X}) = {}& \tfrac{1}{4}\Big[\sigma^{\mathrm{p}}_{zz}(000000)\\ &+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial S_{\sigma}}4(s^{\sigma}_{\mathrm{X}}-s^{\sigma}_{0})+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial H_{\sigma}}4(\varepsilon^{\sigma}_{\mathrm{X}}-\varepsilon^{\sigma}_{0})\\ &+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial S_{\pi}}4(s^{\pi}_{\mathrm{X}}-s^{\pi}_{0})+\frac{\partial\sigma^{\mathrm{p}}_{zz}}{\partial H_{\pi}}4(\varepsilon^{\pi}_{\mathrm{X}}-\varepsilon^{\pi}_{0})\Big]\\ = {}& \sigma^{\mathrm{p}}_{zz}(\mathrm{XXXX00})/4\end{aligned} \tag{A20}$$

is just one fourth of the zz component of the shielding tensor for a complex [Co(XXXX00)], which is in turn equal, in the O_h approximation, to that for [Co(XXXXXX)]. Thus, the situation may be visualized simply as



In the O_h approximation, the xx and yy components can be obtained by interchanging the symbols in parentheses.

$$\sigma^p_{xx}(\mathrm{ABCDEF}) = \sigma(\mathrm{C}) + \sigma(\mathrm{D}) + \sigma(\mathrm{E}) + \sigma(\mathrm{F}) \quad (\mathrm{A21})$$

$$\sigma^p_{yy}(\mathrm{ABCDEF}) = \sigma(\mathrm{A}) + \sigma(\mathrm{B}) + \sigma(\mathrm{E}) + \sigma(\mathrm{F}) \quad (\mathrm{A22})$$

The cobalt-59 chemical shift for a complex [Co(ABCDEF)] in solution is given by Eqs. (26) and (27) in the text.

Fujiwara *et al.*[6] reported $\sigma^p_{iso}(^{59}\mathrm{Co}) = -19440$ ppm for $[\mathrm{Co(NH_3)_6}]^{3+}$. This value can be used, along with

$$\sigma^p_{iso}(^{59}\mathrm{Co}) = (2/3)6\sigma(\mathrm{NH_3}) = 4\sigma(\mathrm{NH_3}) \quad (\mathrm{A23})$$

to obtain $\sigma(\mathrm{NH_3}) = -4860$ ppm, which is in turn used to evaluate σ(X) from data on $[\mathrm{CoX(NH_3)_5}]$ (X=$\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{CN^-}$, $\mathrm{OH^-}$, $\mathrm{NO_2^-}$, $\mathrm{N_3^-}$, and $\mathrm{H_2O}$). These values are summarized in Table 1.

The results obtained here permit us to estimate the chemical shift anisotropy of a cobalt-59 nucleus. It is clear from the procedure that the method used here can be applied to those physical quantities that are closely connected to the optical transitions of six-coordinated metal complexes. In fact, if the physical quantity under consideration is the energy of the electronic transition itself, we can obtain results which are in complete agreement with those reported by Yamatera.[7]

The authors thank Prof. S. Fujiwara and Dr. A. Yamasaki, Tokyo University, for informing them of the cobalt-59 chemical shift data prior to publication and for stimulating discussions.

References

1) H. Yoneda and Y. Nakashima, This Bulletin, **47**, 669 (1974).

2) Y. Nakashima, U. Sakaguchi, and H. Yoneda, *Chem. Lett.*, **1974**, 503.

3) H. Yoneda, U. Sakaguchi, and Y. Nakashima, This Bulletin, **48**, 209 (1975).

4) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950); *ibid.*, **86**, 243 (1952).

5) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

6) S. Fujiwara, F. Yajima, and A. Yamasaki, *J. Mag. Resonance*, **1**, 203 (1969).

7) H. Yamatera, This Bulletin, **31**, 95 (1958).

8) W. G. Proctor and F. C. Yu, *Phys. Rev.*, **81**, 20 (1951).

9) S. S. Dharmatti and C. R. Kanekar, *J. Chem. Phys.*, **31**, 1436 (1960).

10) C. R. Kanekar, M. M. Dhingra, V. R. Marathe, and R. Nagarajan, *J. Chem. Phys.*, **46**, 2009 (1967).

11) A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, **2**, 39 (1968).

12) N. S. Biradar and M. A. Pujar, *Z. Anorg. Allg. Chem.*, **391**, 54 (1972).

13) Y. Koike, F. Yajima, A. Yamasaki, and S. Fujiwara, *Chem. Lett.*, **1974**, 177.

14) R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc. Ser. A*, **242**, 455 (1957).

15) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1959).

16) G. P. Betteridge and R. M. Golding, *J. Chem. Phys.*, **51**, 2497 (1969).

17) F. Yajima, Y. Koike, A. Yamasaki, and S. Fujiwara, This Bulletin, **47**, 1442 (1974).

18) D. N. Hendrickson and W. L. Jolly, *Inorg. Chem.*, **9**, 1197 (1970).

19) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.* **1964**, 2747.

20) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," Benjamin Inc., N. Y. (1965).