Proton Magnetic Resonance Spectra of Metal Ammine Complexes. III.* Interpretation of the Chemical Shifts in Cobalt(III) Pentaammines

Yoshiaki Nakashima

Department of Physics, Faculty of Education, Wakayama University, Wakayama 640

(Received November 25, 1974)

The ammine proton chemical shifts of a series of compounds $[\mathrm{CoX(NH_3)_5}]^{n+}$ have been explained quantitatively. The shifts are ascribed to the paramagnetic anisotropy of central cobalt(III) ions. The discrepancies between the calculated and the observed shift values, though small, noted for the *trans* ammine protons of complexes with X=$\mathrm{CN^-}$ and $\mathrm{NO_2}^-$ may be caused by large inductive effects of these ligands.

In the preceding paper,[1] a theory of proton chemical shifts induced by the paramagnetic anisotropy of a central cobalt(III) ion was expounded. This paper is to show how well the above theory can explain the observed shift values of pentaammine cobalt(III) complexes. A qualitative explanation has already been reported.[2]

A pentaammine cobalt(III) ion contains two types of ammonia molecules, *cis* and *trans*. To take the $\mathrm{NH_3}$-rotation into account, we shall slightly modify Eqs. (28)—(30) of Ref. (1). If we take the z-axis as the symmetry axis of $[\mathrm{CoX(NH_3)_5}]$, we obtain

$$\sigma^{\mathrm{p}}_{\mathrm{xx}}(^1\mathrm{H}) = -(1-3\sin^2\theta\cos^2\phi) \times (3\sigma(\mathrm{NH_3})+\sigma(\mathrm{X}))/2R^3\langle r^{-3}\rangle \tag{1}$$

$$\sigma^{\mathrm{p}}_{\mathrm{yy}}(^1\mathrm{H}) = -(1-3\sin^2\theta\sin^2\phi) \times (3\sigma(\mathrm{NH_3})+\sigma(\mathrm{X}))/2R^3\langle r^{-3}\rangle \tag{2}$$

$$\sigma^{\mathrm{p}}_{\mathrm{zz}}(^1\mathrm{H}) = -(1-3\cos^2\theta)(4\sigma(\mathrm{NH_3}))/2R^3\langle r^{-3}\rangle \tag{3}$$

For *cis* ammine protons, we take the x-axis as the new z-axis and y- and z-axes as the new x- and y-axes. Thus, the following expressions apply to *cis* protons.

$$\sigma^{\mathrm{p}}_{\mathrm{xx}}(^1\mathrm{H}) = -(1-3\sin^2\theta'\cos^2\phi') \times (3\sigma(\mathrm{NH_3})+\sigma(\mathrm{X}))/2R^3\langle r^{-3}\rangle \tag{4}$$

$$\sigma^{\mathrm{p}}_{\mathrm{yy}}(^1\mathrm{H}) = -(1-3\sin^2\theta'\sin^2\phi') \times (4\sigma(\mathrm{NH_3}))/2R^3\langle r^{-3}\rangle \tag{5}$$

$$\sigma^{\mathrm{p}}_{\mathrm{zz}}(^1\mathrm{H}) = -(1-3\cos^2\theta') \times (3\sigma(\mathrm{NH_3})+\sigma(\mathrm{X}))/2R^3\langle r^{-3}\rangle \tag{6}$$

The definitions of θ, ϕ, θ', and ϕ' are in Fig. 1. After averaging over ϕ and ϕ' for *trans* and *cis* ammonias, respectively, the proton chemical shift in solution may be shown to be

$$\sigma^{\mathrm{p}}_{\mathrm{t}} = (3\cos^2\theta-1)(\sigma(\mathrm{NH_3})-\sigma(\mathrm{X}))/6R^3\langle r^{-3}\rangle \tag{7}$$

$$\sigma^{\mathrm{p}}_{\mathrm{c}} = -(3\cos^2\theta'-1)(\sigma(\mathrm{NH_3})-\sigma(\mathrm{X}))/12R^3\langle r^{-3}\rangle \tag{8}$$

where the subscripts t and c refer to *trans* and *cis* protons. Note that these equations give shift values relative to the shift of $[\mathrm{Co(NH_3)_6}]^{3+}$. It is seen that the shift of *trans* protons with respect to $[\mathrm{Co(NH_3)_6}]^{3+}$ is in the opposite direction to and twice that of *cis* protons.

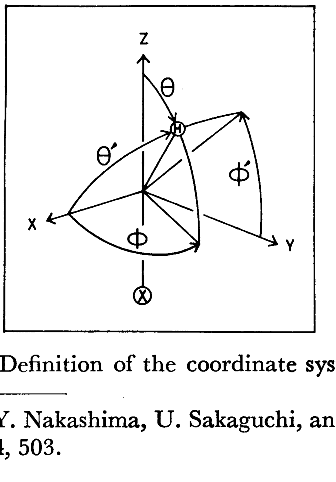

Fig. 1. Definition of the coordinate system.

Method of Calculation

The geometrical factors necessary for the calculation of Eqs. (7) and (8) can be estimated as follows. By taking the Co–N distance as 2.0 Å (3.78 a.u.) and the N–H distance as 1.0 Å (1.89 a.u.),[4] we obtain R=4.77 a.u. (2.52 Å). If we further assume a tetrahedral configuration for coordinated ammonia molecules, we obtain θ=22.0° and θ'=22.0°. The value of $<r^{-3}>$ is estimated from Eq. (14) of Ref. (1) using the data for $[\mathrm{Co(NH_3)_6}]^{3+}$. It is reported that $(E_{\mathrm{E}}-E_0)=(E_{\mathrm{T_{1g}}}-E_{\mathrm{A_{1g}}})=2.10\times10^4\ \mathrm{cm^{-1}}$,[5] $\sigma^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co})=-1.91\times10^{-2}$,[3] and $c_{\mathrm{M1}}=0.924$, $c_{\mathrm{L1}}=-0.61$, $S_\sigma=0.2$, $c_{\mathrm{M2}}=1.0$, $S_\pi=0$.[5] Substitution of these values into Eq. (14) of Ref. 1 gives 5.77 a.u. for $<r^{-3}>$. I asumed the same values of R, θ, θ', and $<r^{-3}>$ for all the complexes examined here. As seen from Eq. (14) of Ref. 1, $\sigma^{\mathrm{p}}_{\mathrm{zz}}(^{59}\mathrm{Co})$ can be considered to be constant over a series of pentaammines.[3] The contribution $\sigma(\mathrm{X})$ from a ligand X to cobalt-59 chemical shifts is summarized in Table 1 of Ref. 1. The relevant quantities in the present study are $\sigma(\mathrm{NH_3})=-4860$, $\sigma(\mathrm{CN})=-2760$, $\sigma(\mathrm{NO_2})=-4073$, $\sigma(\mathrm{H_2O})=-6255$, $\sigma(\mathrm{OH})=-6345$, $\sigma(\mathrm{Cl})=-5910$, and $\sigma(\mathrm{Br})=-5865$ ppm.

Results and Discussion

Clifton and Pratt[6] were probably the first to observe proton resonance spectra of cobalt(III) pentaammines. They found two $\mathrm{NH_3}$ resonances with an intensity ratio of 4 to 1, the intense absorption being at lower field. They suggested that the *cis* protons may be shifted to lower field than the *trans* by (i) intramolecular hydrogen bonding between the *cis* ammine groups and the sixth ligand X, (ii) the effects of magnetic anisotropy of X, and (iii) the reduced polarity of the *trans* ammine group due to polarization of the metal ion by the sixth ligand. As discussed by Lehman and Fung[7] and Hawkins,[8] the magnetic anisotropy effects cannot explain even the

---

* Part II: Y. Nakashima, U. Sakaguchi, and H. Yoneda, *Chem. Lett.*, **1974**, 503.

sign of chemical shifts. Thus, Lehman and Fung concluded that the point dipole approximation for the magnetic anisotropy of the sixth ligand is too great a simplification to account for the proton shifts. Hawkins argued that since the chemical shift differences were observed for a variety of substituents with widely differing hydrogen bonding capabilities, the intramolecular hydrogen bonding is of minor importance. The polarization effects were suggested as the dominant contributor. Hendrickson and Jolly[9] compared the proton resonance spectra of some pentaammine complexes of cobalt(III) with those of rhodium(III) and iridium(III). Since the latter compounds showed only a single peak, the low-lying paramagnetic states of Co(III) ion were suggested as responsible for the two peaks in cobalt complexes. They qualitatively explained the gradual change in chemical shifts when the sixth ligand was varied along the spectrochemical series.

I consider that the anisotropy in the second-order paramagnetism of the central cobalt ion has the dominant contribution. The calculated proton chemical shifts are illustrated in Fig. 2, together with the observed shift values.[2] 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 except for *trans* ammine protons. In view of the extreme approximations used, this agreement may be fortuitous but it is satisfying that correct orders of magnitude could be obtained for the chemical shifts. Therefore, it can be concluded that the proton chemical shifts in pentaammine cobalt(III) complexes can be attributed to the anisotropy in the second-order paramagnetism of the central cobaltic ion. Note that for a weak field ligand X ammine protons *trans* to X appear at higher field than *cis* ammines. If X lies higher in the spectrochemical series than NH_3, the shift pattern is reversed. This behavior is similar to the observation by Watabe *et al.*[10] that in α-aminocarboxylato cobalt(III) complexes the α (to NH_2) C–H proton appear at higher field when it is *trans* to an oxygen atom while it moves to lower field when *trans* to a nitrogen atom.

In a previous communication,[11] the proton shifts in $[CoX(NH_3)_5]$ were treated in the following way. After taking the NH_3-rotation into account, the proton shift in solution may be written

$$\sigma_t^p = [\sigma_{zz}^p(^{59}Co) - \sigma_{xx}^p(^{59}Co)](3\cos^2\theta - 1)/6R^3\langle r^{-3}\rangle \tag{9}$$

$$\sigma_c^p = -[\sigma_{zz}^p(^{59}Co) - \sigma_{xx}^p(^{59}Co)](3\cos^2\theta' - 1)/12R^3\langle r^{-3}\rangle \tag{10}$$

These results are easily obtained from Eq. (22) of Ref. (1). The following equation applies to complexes of C_{4v} symmetry.

$$\sigma_{iso}^p(^1H) = [2\sigma_{xx}^p(^{59}Co) + \sigma_{zz}^p(^{59}Co)]/3 \tag{11}$$

Thus, Eqs. (9) and (10) are reduced to

$$\sigma_t^p = [\sigma_{zz}^p(^{59}Co) - \sigma_{iso}^p(^{59}Co)](3\cos^2\theta - 1)/4R^3\langle r^{-3}\rangle \tag{12}$$

$$\sigma_c^p = -[\sigma_{zz}^p(^{59}Co) - \sigma_{iso}^p(^{59}Co)](3\cos^2\theta' - 1)/8R^3\langle r^{-3}\rangle \tag{13}$$

As stated earlier, $\sigma_{zz}^p(^{59}Co)$ can be considered to be constant for pentaammines. This result indicates that the proton chemical shifts should be directly proportional to the cobalt-59 chemical shifts. Since the details have been reported,[11] it suffices to say that Eqs. (12) and (13) can give almost the same results for pentaammines as those in Fig. 2. However, the above procedure does not allow us to treat complexes of low symmetries.

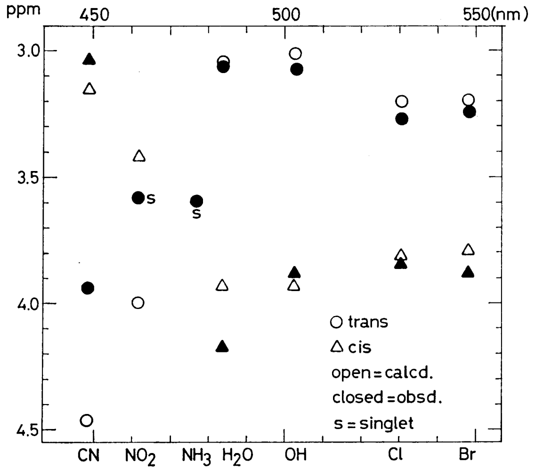

Fig. 2. Comparison of the calculated shift values with the observed values. Shifts are from DSS internal standard and the abscissa is the reciprocal of the excitation energy of the first absorption band ($E_E - E_{A1}$).

Discrepancies between the calculated and the observed shift values, though small, may be noted for *trans* ammines of compounds with X=CN^- and NO_2^-. The cause of these discrepancies may be in the approximations used: disregard of the possible variation of Co–N distances, neglect of several overlap integrals, neglect of the probable change in $\langle r^{-3}\rangle$, or the point dipole approximation itself. Solvent effects may have some contribution.[9] It is also probable that the additivity of cobalt-59 chemical shifts is not sufficiently exact to predict the anisotropy of the shifts. To eliminate several of these possibilities, we are measuring the rate of isotopic deuterium exchange in these complexes. The observed upfield shifts for *trans* ammines of X=CN^- and NO_2^- point to an increase of electron densities on these ammine protons. Thus, it is expected that the *trans* protons are exchanged much more slowly than the *cis* protons. Preliminary results of HD exchange confirmed this expectation. The details will be published in subsequent papers.

I wish to thank Prof. H. Yoneda and Dr. U. Sakaguchi, Hiroshima University, for helpful discussions.

References

1) Y. Nakashima, U. Sakaguchi, and H. Yoneda, This Bulletin, **48**, 762 (1975).

2) H. Yoneda and Y. Nakashima, *ibid.*, **47**, 669 (1974).

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

4) a) M. Iwata and Y. Saito, *Acta Crystallogr.*, **B29**, 822 (1973); b) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham (1968), p. 270.

5) See, for example, H. Yamatera, *J. Inst. Polytech. Osaka City Univ.*, **5C**, 163 (1956).

6) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, **1963**, 339.

7) J. W. Lehman and B. M. Fung, *Inorg. Chem.*, **11**, 214 (1972).

8) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, N.Y. (1971), Chapt. 6.

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

10) M. Watabe, K. Onuki, and S. Yoshikawa, to be published.

11) Y. Nakashima, U. Sakaguchi, and H. Yoneda, *Chem. Lett.*, **1974**, 503; Part II.