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# NITROGEN-15 CHEMICAL SHIFTS IN METAL-AMMINE COMPLEXES. I.
# PENTAAMMINECOBALT(III) COMPLEXES

Yoshiaki NAKASHIMA, Masayuki MUTO, Ichiro TAKAGI, and Keiichi KAWANO*
Faculty of Education, Wakayama University, Wakayama 640
Institute for Protein Research, Osaka University, Suita, Osaka 565*

Nitrogen-15 chemical shifts have been measured directly for $[CoX(NH_3)_5]^{n+}$ ($X=NH_3, H_2O, Br^-$ and $NO_2^-$). The chemical shifts induced by paramagnetic anisotropy of Co(III) ion are of minor importance to the $^{15}N$ chemical shifts, in contrast with the previous result that they are of dominant importance to the $^1H$ chemical shifts in the same substances. According to the change of X, the $^{15}N$ chemical shifts of $NH_3$ trans and cis to X show different values.

There have been several pmr studies of ammine protons in $[CoX(NH_3)_5]^{n+}$.[1,2,3] One of the authors has been able to explain the behaviors of $^1H$ chemical shifts in these substances quantitatively, where an assumption that they are mainly attributed to the magnetic anisotropy of Co(III) ion was used.[4,5,6] But the chemical shifts of ammine protons show some change by the solvent, and some ambiguities remained. In contrast, there is a report that the chemical shifts of $^{15}N$ directly bound to cobalt are hardly affected by the solvent.[7]

The variations of the $^{15}N$ chemical shifts caused by changing X in $[CoX(NH_3)_5]^{n+}$ are very large compared with the chemical shifts induced by the paramagnetic anisotropy of Co(III) ion, as it will be explained later. From these facts, it is supposed that the $^{15}N$ chemical shift is related to the Co-N bond strength.

Lehman and Fung have observed $^{15}N$ chemical shifts for the same substances by INDOR.[3] In the present experiment we have observed the $^{15}N$ chemical shifts directly and compared the values with values estimated from the theory presented previously.

The materials used in the present experiment ($[CoX(NH_3)_5]^{n+}(NO_3^-)_n$) were synthesized after the well-established method.[8] The content of $^{15}N$ is about 30%. About 200 mg of the materials was dissolved in 1.5ml DMSO-$d_6$ in 10 mmϕ tube and spectra were accumulated 1000-10000 times.

The measurement of the $^{15}N$ resonance spectra was performed by a JEOL-PFT-100 pulse and Fourier transform NMR spectrometer operated at 10.14 MHz. Chemical shifts were relative to that of hexaamminecobalt(III)(recalculated from the shifts relative to external $^{15}NO_3^-$ 9)).

The spectra of $^{15}N$ NMR for $[CoBr(NH_3)_5]^{2+}$ and $[CoH_2O(NH_3)_5]^{3+}$ are shown in Fig.1. The line widths of $^{59}Co$ NMR have been presented for many Co(III) complexes,10) and the broader the line width of $^{59}Co$ NMR, the sharper the line width of directly bound $^{15}N$ NMR. The observed shifts are given in Table I.

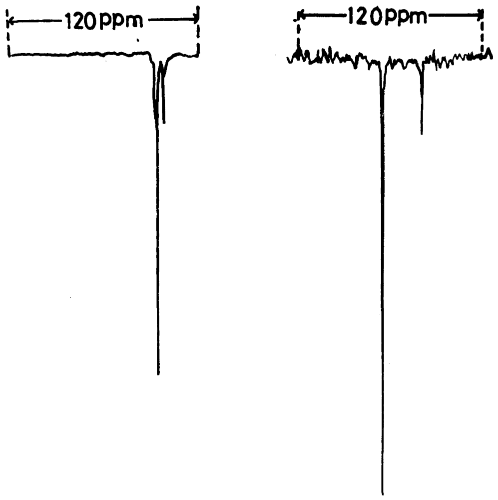

Fig.1

$^{15}N$ signals of $[CoBr(NH_3)_5]^{2+}$ and of $[CoH_2O(NH_3)_5]^{3+}$(right). Two signals are recognized. From their intensities, it is thought that the stronger one and the weaker one correspond to the $^{15}N$ resonance signals of cis and trans $NH_3$, respectively.

Table I

$^{15}N$ chemical shifts of some pentaamminecobalt(III) complexes relative to the signal of $[Co(NH_3)_6]^{3+}$ in DMSO-$d_6$(dimethyl sulfoxide).

|  | (ppm) |  |
|---|---|---|
|  | cis | trans |
| $[CoH_2O(NH_3)_5]^{3+}$ | -0.134 | 26.038 |
| $[CoCl(NH_3)_5]^{2+}$ a) | -0.334 | 13.476 |
| $[CoBr(NH_3)_5]^{2+}$ | 2.274 | 8.184 |
| $[CoNO_2(NH_3)_5]^{2+}$ | -9.598 | -8.427 |

a) : rom Ref.3.

Lehman and Fung have mistaken the sign of $^{1}H$ chemical shifts and so their sign of the $^{15}N$ chemical shifts(to higher magnetic field) from hexaamminecobalt(III) is doubtful. The $^{14}N$ chemical shifts in the same samples have been measured by Herbison-Evans and Richards, and they were to lower magnetic field for X=$H_2O$ and $Cl^-$ from $[Co(NH_3)_6]^{3+}$.[11] The results of Ref.3 are thus inconsistent with that of Ref.11. It was an aim of this experiment to know the correct direction of $^{15}N$ shifts in $[CoX(NH_3)_5]^{n+}$, relative to that in $[Co(NH_3)_6]^{3+}$. Our results are consistent with that of Ref.3 in the sign of the chemical shifts, and then we can proceed our discussion with these data.

Generally magnetic shielding constant $\sigma$ consists of the following three terms.[12]

$\sigma_D$ : Diamagnetic term by the electrons of the observed atom.

$\sigma_P$ : Paramagnetic term by the electrons of the observed atom.

$\sigma_\Lambda$ : Long-range magnetic terms by other atoms in the molecule.

$$\sigma = \sigma_D + \sigma_P + \sigma_\Lambda \qquad (1).$$

In the present case, the chemical shifts induced by the magnetic anisotropy of Co(III) ion may be the dominant part in $\sigma_\Lambda$. Provided the bond length of Co-N is 2Å,[13] the dipole approximation for the magnetic anisotropy of Co(III) ion is adequate. (The details about this terms will be discussed in subsequent papers.) One of the authors has presented a theory for the chemical shift induced by Co(III) ion under the dipole approximation.[6] As seen from eqs.(7) and (8) of Ref.6 the $^{15}N$ chemical shifts of the ammonias trans and cis to X in solution are expressed, respectively, as

$$\sigma_\Lambda = \langle r^{-3}\rangle_{3d}^{-1}[\sigma(NH_3) - \sigma(X)]/3R^3 \qquad (2) \quad \text{(for trans)},$$

$$\sigma_\Lambda = -\langle r^{-3}\rangle_{3d}^{-1}[\sigma(NH_3) - \sigma(X)]/6R^3 \qquad (3) \quad \text{(for cis)},$$

(where we take Θ=0 and Θ'=0 in Fig.2.) The relevant quantities in the present study have been presented in Ref.6 except R=2Å(3.79 a.u.). The frame-work of pentaammine-cobalt(III) is shown in Fig.2. The calculated shift values for cis and trans $^{15}N$(from eqs.(2) and (3)) are given in Table II.

The calculated shift values in Table II are $\sigma_\Lambda$ in eq.(1), and chemical shifts in

Table I correspond to $\sigma$ in eq.(1). Subtracting the $\sigma_\Lambda$ from the $\sigma$, $\sigma_D + \sigma_P$ is obtained. The $\sigma_D + \sigma_P$ is plotted against the reciprocals of the energy difference between $^1A_1$ and $^1E$, and are shown in Fig.3. All shift values are from $[Co(NH_3)_6]^{3+}$. The sign and magnitude of $\sigma_D + \sigma_P$ may be directly related to the Co-N bond strength.

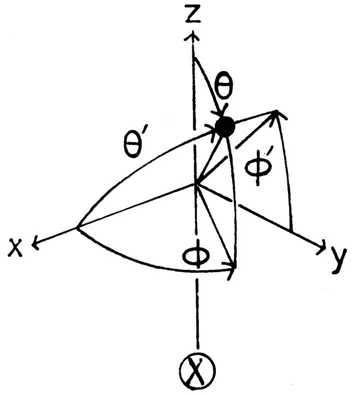

Fig.2

Trans and cis $NH_3$ are assumed to be on the Z-axis and on the X-axis respectively.

Table II

$^{15}N$ chemical shifts of some pentaammine-cobalt(III) complexes calculated from eqs.(2) and (3).

(ppm)

| | cis | trans |
|---|---|---|
| $[CoH_2O(NH_3)_5]^{3+}$ | -0.74 | 1.48 |
| $[CoCl(NH_3)_5]^{2+}$ | -0.55 | 1.11 |
| $[CoBr(NH_3)_5]^{2+}$ | -0.54 | 1.07 |
| $[CoNO_2(NH_3)_5]^{2+}$ | 0.42 | -0.83 |

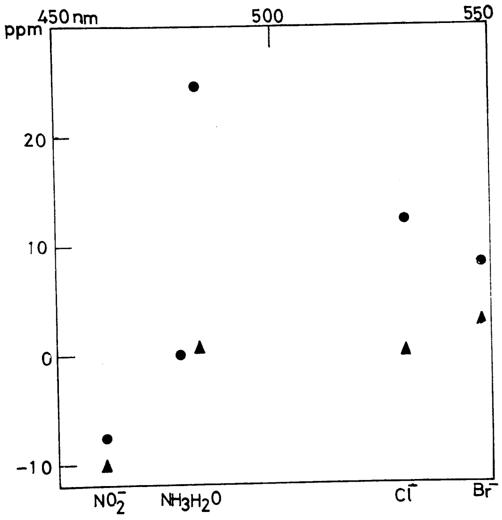

Fig.3

$\sigma_D + \sigma_P$ is plotted against the reciprocals of the difference between $E(^1E)$ and $E(^1A_1)$. Closed circles and triangles stand for the $^{15}N$ resonance shifts of trans $NH_3$ and cis $NH_3$ in $[CoX(NH_3)_5]^{n+}_,$ respectively. All shift values are relative to $[Co(NH_3)_6]^{3+}$.

When free $^{14}NH_3$ is bound to cobalt, the resonance position of $^{14}N$ shifts to higher field by about 50 ppm in $[Co(NH_3)_6]^{3+}$, and the reason is mainly attributed to $\sigma_P$ of $\sigma_D + \sigma_P$.11) Since nitrogen chemical shifts obtained from $^{14}N$ and $^{15}N$ NMR data may be used interchangeably, $n\rightarrow\pi^*$ transition of the lone pair of $^{15}NH_3$ may be of dominant importance.11,14)

As the Co-N bond is strengthened, the value of $\Delta E$ in $\sigma_P(\sigma_P=-(2/\Delta E)[<0|\sum_j m_j/r_j^3|n> \times<n|\sum_j m_j|0> + C.C.])$ increases and the absolute value of $\sigma_P$ decreases. Thus the $^{15}N$ resonance shifts to higher field. According to the above discussion, the Co-N bond trans to X is more tightly bound than that of $[Co(NH_3)_6]^{3+}$ when X=$H_2O$, $Cl^-$ and $Br^-$. The Co-N bond cis to X is also more tightly bound but not so as that of the trans. The stronger the Co-N bond is, the more the electron densities which flow into cobalt from $NH_3$ will increase and the electron densities on the proton will decrease. It is understandable from the above discussion, that the H-D exchange for $NH_3$ protons trans to X is more rapid than that of the cis(X=$H_2O$,$Cl^-$,$Br^-$).1)

The $^1H$ chemical shifts in $[CoX(NH_3)_5]^{n+}$ have not shown the above trans effect.6) In contrast to the $^{15}N$ chemical shifts, the $^1H$ chemical shifts of coordinated $NH_3$ are easily affected by the solvent.15) These two facts are related with each other and the details will be discussed in subsequent papers.

When X is $NO_2^-$, the $^{15}N$ chemical shifts show different behaviors from the above cases. The cis $^{15}N$ shows a greater shift than that of the trans, but their absolute shift values are not so different from each other. From the shift values of $^{15}N$, it is seen that the trans Co-N bond is stronger than the cis one and both are weaker than that of $[Co(NH_3)_6]^{3+}$. From the above discussion, the H-D exchange of the trans ammine protons should be more rapid than that of the cis in $[CoNO_2(NH_3)_5]^{2+}$. This is inconsistent with the experiment by Yoneda *et al.*.16) This contradiction may be interpreted in terms of the hydrogen bonds between the protons of $NH_3$ and the oxygens of $NO_2^-$. Further details of this study will be discussed elsewhere.

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9) The authors wish to thank Professor Y. Kyogoku, at Osaka University, for the helpful discussion and for giving the chance to use JEOL-PFT-100.

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