August, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***62,*** *2455—2460 (1989)* 2455

Nitrogen-15 NMR Chemical Shifts in Metal–Ammine Complexes. II.[1] Cobalt(III) Ammine and Amine Complexes

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(Received December 5, 1988)

^{15}N nuclear magnetic resonance spectra were measured for $[CoX(^{15}NH_3)]^{n+}$ (X=CN$^-$, $^{15}NH_3$, H_2O, and Br$^-$) and *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ (X_2=$(CN^-)_2$, $(NO_2^-)_2$, en-^{15}N,^{15}N, ox^{2-}, and $(H_2O)_2$; en-^{15}N,^{15}N and ox^{2-} represent the ^{15}N-enriched ethylenediamine and oxalate ion, respectively). Two sharp signals of ^{15}N NMR were observed for $[CoX(^{15}NH_3)_5]^{n+}$ except for the cases of X=$^{15}NH_3$ and NO_2^-. The signals of ^{15}N NMR in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$, were assigned on the basis of the selectively proton irradiated spectra at frequencies which had been already assigned to each amino proton. The chemical shifts of ^{15}N NMR are correlated to the Co–N bond strength; it is expected that the stronger is the Co–N bond, the greater is the shift of the ^{15}N NMR signal to a higher field. When we express $[CoX(^{15}NH_3)_5]^{n+}$ and *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ as $[CoXN_5]^{n+}$ and *cis*-$[CoX_2N_4]^{n+}$, the effect on the ^{15}N NMR chemical shifts by the substituent X is roughly additive.

One of the authors (Y.N.) has been able to semiquantitatively explain the behaviors of the ^{1}H NMR chemical shifts in $[CoX(NH_3)_5]^{n+}$ by assuming that the induced ^{1}H NMR chemical shifts by changing X are mainly due to a change in the magnetic anisotropy of the Co(III) ion.[2–4] However, there were some descrepancies between the calculated and observed values. They were significantly large for the protons of NH_3 trans to X in complexes with X=CN$^-$ and NO_2^-. The chemical shift of the observed signals to higher fields than the calculated ones might be caused by increased electron densities on the trans ammine protons induced by the large inductive effects of X. The H–D exchange rates of the ammine protons were related to their acidity.[5] The trans ammine protons exchange more slowly than the cis ones with X=CN$^-$ and NO_2^-.[5] On the other hand, though the trans ammine protons exchange faster than the cis ones with X=H_2O, Cl$^-$, and Br$^-$, there has been no evidence of decreased electron densities of the trans ammine protons in the ^{1}H NMR chemical shifts.[4] ^{1}H NMR chemical shifts of ammine protons are easily affected by the solvent; in contrast, though, it has been reported that the chemical shifts of the NMR signals of ^{15}N directly bound to cobalt(III) are hardly affected by the solvent.[6] It is, therefore, expected that information concerning the Co–N bond strength and the acidity of ammine protons can be obtained from ^{15}N NMR chemical shifts with no solvent effect.

Lehman and Fung measured the ^{15}N NMR for $[CoX(^{15}NH_3)_5]^{n+}$ by the use of the INDOR technique, and then erroneously assigned the ^{1}H NMR chemical shift signals.[7] Thus, we doubted the shift directions of the ^{15}N NMR signals since their assignments of the ^{15}N NMR signals depended upon those of the proton signals.[7] The ^{14}N NMR signals of the same samples were also measured by Herbison-Evans and Richards.[8] The signals of $[Co(H_2O)(NH_3)_5]^{3+}$ and $[CoCl(NH_3)_5]^{2+}$ were single and the shift values were lower than that of $[Co(NH_3)_6]^{3+}$. It was one aim of the present work to determine the correct ^{15}N shift values of $[CoX(^{15}NH_3)_5]^{n+}$ relative to that of $[Co(^{15}NH_3)_6]^{3+}$ by directly observing the ^{15}N NMR signals. Furthermore, it would be interesting to find out whether the effect of substituent X_2 on the chemical shifts of ^{15}N NMR signals in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ is additive or not.

Experimental

Materials. The $[CoX(^{15}NH_3)_5](NO_3^-)_n$ (X=NO_2^-, $^{15}NH_3$, H_2O, and Br$^-$) and the *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ (X_2=$(CN^-)_2$, $(NO_2^-)_2$, en-^{15}N,^{15}N, ox^{2-}, and $(H_2O)_2$) were synthesized according to the well-established methods.[9] The $[Co(CN)(NH_3)_5](ClO_4)_2$ containing $^{15}NH_3$ was synthesized by the method of Sibert.[10] The en-^{15}N,^{15}N·2HCl and $^{15}NH_3$ were obtained from British Oxygen Co., Ltd., and their ^{15}N contents were 98 and 99.5%, respectively. Ligands diluted 30 to 40% of ^{15}N were used in all preparations of the complexes.

Equipments and Measurements. About 200 mg of each complex was dissolved in 1.5 ml of DMSO-d_6 in a 10-mmϕ tube and 1000—10000 transients were accumulated for $[CoX(^{15}NH_3)_5]^{n+}$. About 100 mg was dissolved in 1.5 ml of a DCl-D_2O solution (pD=2) in a 10-mmϕ tube and 1000—10000 transients were accumulated for *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$. *cis*-$[Co(H_2O)_2(en\text{-}^{15}N,^{15}N)_2]^{3+}$ was dissolved in CF_3COOD. ^{15}N NMR spectra were recorded on a JEOL PFT-100 pulsed Fourier transform NMR spectrometer operated at 10.1 MHz. Only that of $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$ (Fig. 2) was measured for a 0.1 M aqueous solution (1M=1 mol dm^{-3}) on a JEOL JNM-FX60 spectrometer at 6.06 MHz (204000 repetitions). $Na^{15}NO_2$ or $Na^{15}NO_3$ was used as an external reference of ^{15}N NMR signals.

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Results

Hexaammine- and Pentaamminecobalt(III) Complexes. The ^{15}N resonance spectra of $[CoX(^{15}NH_3)_5]^{n+}$ ($X=CN^-$, NO_2^-, $^{15}NH_3$, H_2O, and Br^-) are shown in Fig. 1. The ^{59}Co resonance spectra have already been measured for several Co(III) complexes.[11] By comparing ^{15}N and ^{59}Co NMR spectra, it was found that the broader is the line of the ^{59}Co NMR signal, the sharper is the line of ^{15}N NMR signal of $^{15}NH_3$ group directly bound to Co(III) ion. The ^{15}N NMR signal of $[Co(^{15}NH_3)_6]^{3+}$ is broad and complicated. This is due to coupling between the ^{15}N and ^{59}Co nuclei, resulting in the slow quadrupolar relaxation rate of the nuclear magnetic moment of ^{59}Co under high symmetry around the ^{59}Co nucleous.[12] In $[CoX(^{15}NH_3)_5]^{n+}$ the resonance signal of ^{15}N trans to X was distinguished from that of the cis on the basis of their intensities. The chemical shift values are given in Table 1. We erroneously reported the shift value of $[Co(^{15}NH_3)_6]^{3+}$ in a previous report,[1] taking the signal position of the impurity. In the present study, the central position of the broad signal was adopted as the correct shift value.[12] It can be seen from Table 1 that the ^{15}N NMR signal of the trans $^{15}NH_3$ of $[CoX(^{15}NH_3)_5]^{n+}$ appears at a higher field from that of $[Co(^{15}NH_3)_6]^{3+}$ and the cis one at a lower field with $X=H_2O$, Cl^-, and Br^-. In contrast, the trans $^{15}NH_3$ with $X=CN^-$ gives an ^{15}N signal at a lower field and a cis one at a higher field. The ^{15}N NMR signals of $[Co(NO_2)(^{15}NH_3)_5]^{2+}$ were broad and not clearly separated.

Table 1. ^{15}N NMR Shift Values in $[CoX(^{15}NH_3)_5]^{n+}$ Relative to That of $[Co(^{15}NH_3)_6]^{3+}$

X	Trans	Cis
CN^-	−23.9	1.7
NO_2^- [b]	−11	−16
NH_3	0.0[a]	0.0[a]
H_2O	20.7	−5.5
Cl^- [c]	8.6	−6.2
Br^-	2.8	−3.0

a) The shift value (418.2 ppm) of $[Co(^{15}NH_3)_6]^{3+}$ as a standard of $^{15}NO_3^-$ was calculated from that as a standard of $^{15}NO_2^-$. b) The ^{15}N resonance signals of $[Co(NO_2)(^{15}NH_3)_5]^{2+}$ were not as sharp as that of the other $[CoX(^{15}NH_3)_5]^{n+}$ complexes as shown in Fig. 1. Therefore, the appropriate shift positions were given, which differ to some extent from those in Part I.[1] c) The values are from Ref. 7. The chemical shift values were recalculated considering the difference of 6.5 ppm between the present and the literature values of $[Co(^{15}NH_3)_6]^{3+}$.

Table 2. ^{15}N NMR Shift Values in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ Relative to That of $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$

X_2	Trans	Cis
$(CN^-)_2$	−16.6	4.0
$(NO_2^-)_2$	−2.8	−2.8
en	0.0[a]	0.0[a]
ox^{2-}	8.1	−8.9
$(H_2O)_2$	9.4	−8.0

a) The shift value (392.0 ppm) of $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$ was calculated from that as a standard of $^{15}NO_2^-$.

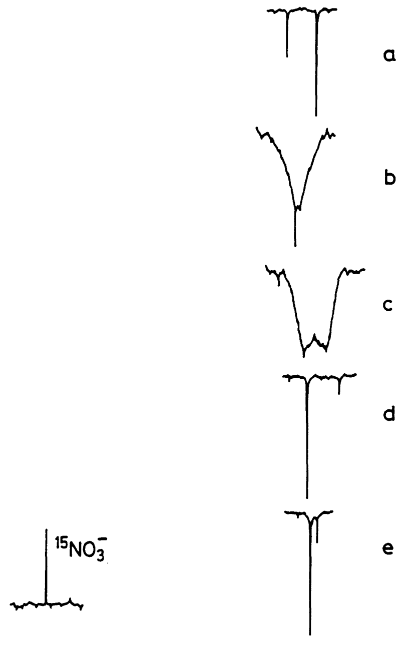

Fig. 1. ^{15}N NMR spectra of (a) $[Co(CN)(^{15}NH_3)_5]^{2+}$, (b) $[Co(NO_2)(^{15}NH_3)_5]^{2+}$, (c) $[Co(^{15}NH_3)_6]^{3+}$, (d) $[Co(H_2O)(^{15}NH_3)_5]^{3+}$, and (e) $[CoBr(^{15}NH_3)_5]^{2+}$.

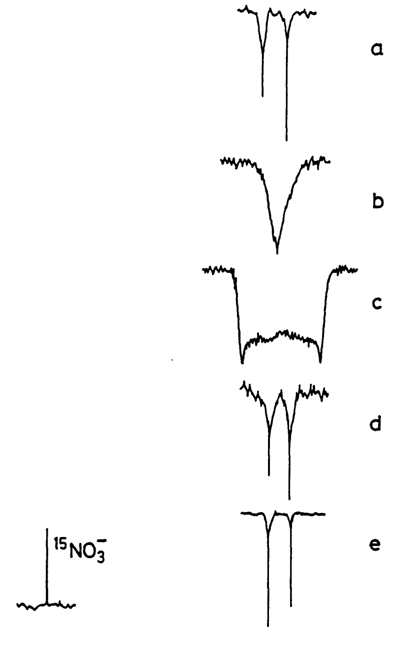

Fig. 2. ^{15}N NMR spectra of (a) *cis*-$[Co(CN)_2(en\text{-}^{15}N,^{15}N)_2]^+$, (b) *cis*-$[Co(NO_2)_2(en\text{-}^{15}N,^{15}N)_2]^+$, (c) $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$, (d) $[Co(ox)(en\text{-}^{15}N,^{15}N)_2]^+$, and (e) *cis*-$[Co(H_2O)_2(en\text{-}^{15}N,^{15}N)_2]^{3+}$.

Tris- and *cis*-Bis(ethylenediamine)cobalt(III) Complexes. The ^{15}N NMR spectra of the *cis*-[CoX$_2$(en-^{15}N,^{15}N)$_2$]$^{n+}$ (X$_2$=(CN$^-$)$_2$, (NO$_2$$^-$)$_2$, en-^{15}N,^{15}N, ox^{2-}, and (H$_2$O)$_2$) are shown in Fig. 2. The observed shift values are given in Table 2. The ^{15}N NMR signal of [Co(en-^{15}N,^{15}N)$_3$]$^{3+}$ was very broad for the same reason as that of [Co(^{15}NH$_3$)$_6$]$^{3+}$.[12] The central position of the signal was adopted as its chemical shift value. Each of the two ^{15}N NMR signals of [Co(ox)(en-^{15}N,^{15}N)$_2$]$^+$ could be assigned on the basis of the spectra selectively irradiated at the resonance frequency of amino protons,[5,13] as shown in Fig. 3. The intensity of the ^{15}N NMR signal in a lower field was more strongly enhanced when the amino proton signal at −5.1 ppm (-NH$_2$ cis to X) was irradiated, as shown in Fig. 3c. Thus, the ^{15}N NMR signal in the lower field corresponds to that of the amino group cis to O$^-$ in X$_2$=ox^{2-}. Accordingly, the ^{15}N NMR signal in the higher field should correspond to that of the amino group trans to O$^-$; this was ascertained from selective irradiation, as shown in Fig. 3d. In contrast, the selectively proton-decoupled ^{15}N NMR spectra of *cis*-[Co(CN)$_2$(en-^{15}N,^{15}N)$_2$]$^+$ revealed that the lower-field signal corresponds to that of the amino group trans to CN$^-$, and the higher-field signal to the cis one. These findings were also confirmed regarding the proton spectra selectively irradiated at ^{15}N NMR signal frequencies, based on the fact that the ^{1}H NMR signal in a higher field was that of the amino group cis to CN$^-$ in X$_2$=(CN$^-$)$_2$.[5,13–15] The ^{15}N NMR signal for *cis*-[Co(NO$_2$)$_2$(en-^{15}N,^{15}N)$_2$]$^+$ was not clearly separated, being broader than that in [Co(NO$_2$)(^{15}NH$_3$)$_5$]$^{2+}$, as shown in Fig. 2b.

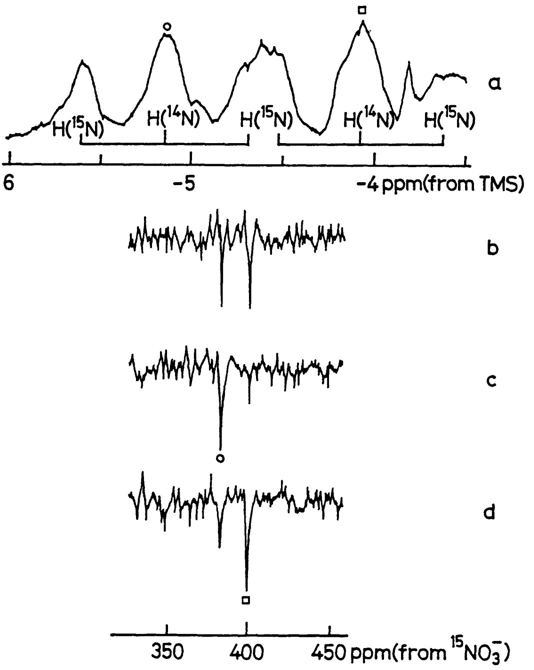

Fig. 3. (a) ^{1}H NMR spectrum of the amino group in [Co(ox)(en-^{15}N,^{15}N)$_2$]$^+$ at 99.5 MHz, (b) Proton noise decoupled ^{15}N NMR spectrum at 10.1 MHz, (c) ^{15}N NMR spectrum selectively irradiated at the frequency of the amino proton cis to O$^-$ (at −5.1 ppm), (d) ^{15}N NMR spectrum selectively irradiated at the frequency of the amino proton trans to O$^-$ (at −4.2 ppm).

Discussion

Generally, the magnetic shielding constant consists of three terms, as follows:

$$\sigma = \sigma_D + \sigma_P + \sigma_L, \qquad (1)$$

where σ_D and σ_P are diamagnetic and paramagnetic terms, respectively, due to the electron of the observed atom; σ_L is the long-range magnetic term due to the other atoms in the molecule.[16] Solvent effects are not considered in this equation.

Hexaammine- and Pentaamminecobalt(III) Complexes. In the present case, the chemical shift induced by the magnetic anisotropy of the Co(III) ion may be the dominant part in σ_L. As shown in Eqs. 7 and 8 of Ref. 4, the ^{15}N NMR chemical shift induced by the Co(III) ion of ^{15}NH$_3$ in [CoX(^{15}NH$_3$)$_5$]$^{n+}$ can be expressed relative to that of [Co(^{15}NH$_3$)$_6$]$^{3+}$, as follows:

$$\sigma_L = [\sigma(\mathrm{NH_3}) - \sigma(\mathrm{X})]/3R^3\langle r^{-3}\rangle \text{ for trans } (\theta=0)$$

and

$$\sigma_L = -[\sigma(\mathrm{NH_3}) - \sigma(\mathrm{X})]/6R^3\langle r^{-3}\rangle \text{ for cis } (\theta'=0),$$

where parameters σ(NH$_3$) and σ(X) are the paramagnetic shielding constants of ^{59}Co contributed by ligands NH$_3$ and X, respectively.[3,4] The relevant quantities used in the present study, except for R (adopted 2 Å as Co-N bond length[17]), have already been presented in Refs. 3 and 4. Subtracting the calculated σ_L from the observed σ, σ_D+σ_P are obtained from Eq. 1. These values are given in Table 3. The contributions of σ_L are less than about 2 ppm and σ_D+σ_P plays a main role in the ^{15}N NMR chemical shifts for [CoX(^{15}NH$_3$)$_5$]$^{n+}$, whereas σ_L does the same in the ^{1}H NMR chemical shifts. The ^{14}N NMR spectra of free NH$_3$ and [Co(NH$_3$)$_6$]$^{3+}$ were measured in liquid by Herbison-Evans and Richards and later by Bramley et al.[8,18] The chemical shift due to complex formation was to a higher field (about 50 ppm in Ref. 8 and a bout 130 ppm in Ref. 18). In their reports, the ^{14}N NMR chemical shift was mainly caused by the

Table 3. ^{15}N NMR Shift Values, σ_L and (σ_D+σ_P) in [CoX(^{15}NH$_3$)$_5$]$^{n+}$ Relative to That of [Co(^{15}NH$_3$)$_6$]$^{3+}$

	σ_L		(σ_D+σ_P)	
X	Trans	Cis	Trans	Cis
CN$^-$	−2.3	1.1	−21.6	0.6
NH$_3$	0.0	0.0	0.0	0.0
H$_2$O	1.5	−0.8	19.2	−4.7
Cl$^-$	1.2	−0.6	7.4	−5.6
Br$^-$	1.0	−0.5	1.8	−2.5

magnetically-susceptible nonbonding paired electrons of NH_3 (σ_P). Regarding complex formation, these are constrained largely between the metal and nitrogen atoms as a bonding electron pair, and are considerably less susceptible to the magnetic field; thus, they contribute less to the nitrogen σ_P part in Ramsay's formula.[16] We calculated a higher shift value (70 ppm), based on the same ideas presented in Refs. 8 and 18.[19]

The contribution of NH_3 makes the hydrogens acidic; therefore, the protons can possibly be exchanged with those (deuterons) in the solution. For $[CoX(NH_3)_5]^{n+}$ complexes with $X=H_2O$, Cl^-, Br^-, or other weaker ligands than NH_3 in the spectrochemical series, it has been considered that the H-D exchange rates of the protons of NH_3 trans to X are faster than that of the cis ones.[5,21,25] With $X=CN^-$, the case is inverse.[5,21] With $X=NO_2^-$, the ^1H NMR signal did not split to each of the trans and cis signals of NH_3. Sakaguchi et al. have speculated from plots of the an H-D exchange rates that the protons of the trans NH_3 undergo an H-D exchange more slowly than that of the cis group (with $X=CN^-$ and NO_2^-).[5] It could be said that the protons of NH_3 (trans or cis to X), whose ^{15}N NMR signal shifts to a higher field than another, undergo an H-D exchange faster than those of another NH_3 in $[CoX(NH_3)_5]^{n+}$. With $X=Cl^-$, the higher-field shift of the ^{15}N NMR signal of NH_3 trans to Cl^- corresponds to a faster H-D exchange rate of the protons. It can be seen from Table 3 that if X is a weaker ligand than $^{15}NH_3$ in the spectrochemical series, the ^{15}N NMR signal of $^{15}NH_3$ trans to X shifts to a higher field from that in $X=NH_3$ and cis signal to a lower field. Provided that the higher the magnetic field of ^{15}N NMR signal, the faster the H-D exchange rate of ammine protons and the stronger the Co-N bond, the shift directions are consistent with the findings of the H-D exchange rate of NH_3.[5,21] The lower-field shift of the ^{15}N NMR signal of the trans $^{15}NH_3$ in $[Co(CN)(^{15}NH_3)]^{2+}$ corresponds to a decrease in the H-D exchange rate of ammine protons trans to CN^-.[5,21,25] In the process of the synthesis of $[Co(CN)(NH_3)_5]^{2+}$, ^{15}N was introduced in the last step, as shown below:

$$[Co(CN)(NH_3)_4(H_2O)]^{2+} + {}^{15}NH_3 + {}^{15}NH_4Cl \rightarrow [Co(CN)({}^{15}NH_3)_n(NH_3)_{5-n}]^{2+} + HCl.$$

The ^1H NMR signal of the last product is shown in Fig. 4. It can be seen from Fig. 4 that the NH_3 trans to CN^- was much more substituted by $^{15}NH_3$ than the cis. It may be considered that the lower-field shift of the ^{15}N NMR signal, the decrease in the H-D exchange rate, and the weakened Co-N bond strength for the NH_3 trans to CN^- are caused by the same origin, i.e., an inductive trans effect of CN^-. Similar phenomena have been observed by Halpern et al. in the synthesis of *trans*-$[Co(^{15}NH_3)(SO_3)(NH_3)_4]^+$, where the NH_3 trans to SO_3^{2-} was mostly substituted by $^{15}NH_3$, though the cis NH_3 was not. It was caused by a marked trans-labilizing influence of the S bonded sulfito ligand.[22]

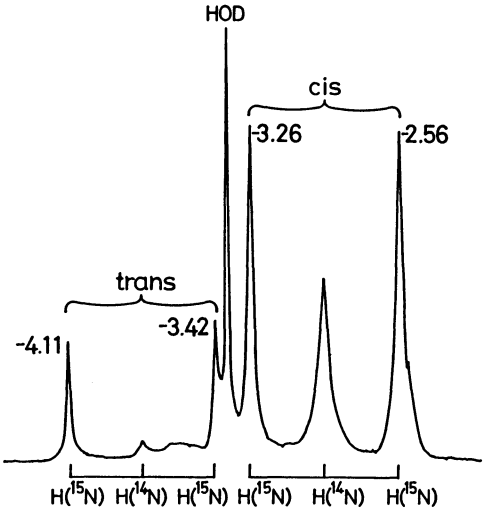

Fig. 4. ^1H NMR spectrum of $[Co(CN)(^{15}NH_3)_n(NH_3)_{5-n}]^{2+}$ in DMSO-d_6. Shift values are ppm from an external reference (TMS). Coupling constants, $^1J_{NH}$ are 68 and 70 Hz for trans and cis NH_3 respectively (measured at 99.5 MHz).

As mentioned above, the shift direction of ^{15}N NMR signals of trans and cis $^{15}NH_3$ in $[CoX(NH_3)_5]^{n+}$ are correlated to the H-D exchange rates and the Co-N bond strengths, though the relation can not be quantitatively interpreted at present.

The ^{14}N NMR signals are broad owing to a quadrupolar relaxation of ^{14}N nucleous; the ^{14}N NMR signals were inseparable from each of the trans and cis signals. The ^{15}N NMR signals were separated into two sharp signals without problems related to the quadrupolar relaxation of ^{15}N nucleous (Fig. 1), except for $X=NO_2^-$ and $^{15}NH_3$. These exceptions are due to coupling between the ^{15}N and ^{59}Co nuclei. The lower-field shifts of ^{14}N NMR signals for $X=H_2O$ and Cl^- from $[Co(^{14}NH_3)_6]^{3+}$ in Ref. 8. represent the weighted mean values of one trans and four cis shifts of the corresponding ^{15}N signals.

Tris- and *cis*-Bis(ethylenediamine)cobalt(III) Complexes. The ^{15}N NMR shift value of $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$ was obtained from the central position of the broad signal. In *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ with $X_2=ox^{2-}$, CO_3^{2-} (weaker ligands than en), the higher-field shifts of the ^1H NMR signals of the trans amino protons are consistent with the theory of anisotropy of Co(III) ion.[3,13] The assignment of the NMR signals and the H-D exchange in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ have been studied in more detail by Nakazawa et al.,[14] where one half of the trans aminoproton signals undergoes a large counterion-dependent shift in DMSO-d_6; it is therefore assigned to the trans hydrogens directed approximately parallel to the molecular two-fold axis of the complexes with $X_2=(CN^-)_2$,

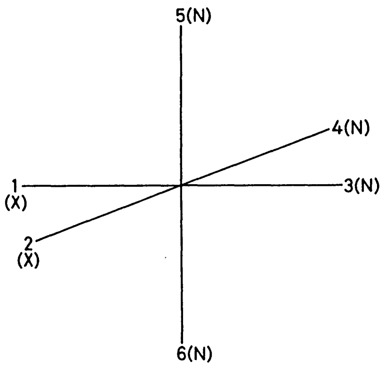

Fig. 5. Framework of *cis*-$[CoX_2N_4]^{n+}$ with numbering of ligating atoms.

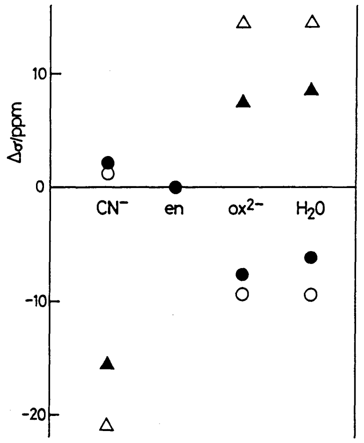

Fig. 6. Plots of ^{15}N NMR shift values $(\sigma_D+\sigma_P)$ of $-^{15}NH_2$ in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$. Circles and triangles are for cis and trans to X, respectively (open for calculated; solid for observed (Table 4)). The calculated values are $\{(\sigma_D+\sigma_P)(\text{trans})+(\sigma_D+\sigma_P)(\text{cis})\}$ and $\{(\sigma_D+\sigma_P)(\text{cis})\times 2\}$ (Table 3), for trans and cis ^{15}N to X, respectively (see text). The calculated value for the aqua complex was also used for the oxalato one.

Table 4. ^{15}N NMR Shift Values, σ_L and $(\sigma_D+\sigma_P)$ in *cis*-$[CoX_2(en\text{-}^{15}N,^{15}N)_2]^{n+}$ Relative to That of $[Co(en\text{-}^{15}N,^{15}N)_3]^{3+}$

	σ_L		$(\sigma_D+\sigma_P)$	
X_2	Trans	Cis	Trans	Cis
$(CN^-)_2$	−1.0	1.9	−15.6	2.1
en	0.0	0.0	0.0	0.0
ox^{2-}	0.6	−1.2	7.5	−7.7
$(H_2O)_2$	0.9	−1.8	8.5	−6.2

$(NO_2^-)_2$, $acac^-$, ox^{2-}, and mal^{2-}. On the other hand, we found that upon deuteration of amino protons, the noise-decoupled NMR signal of the ^{13}C adjacent to the deuterated amino nitrogen shifted by about 0.15 ppm per substituted deuteron to a higher field.[15] The lower-field signal of the $^{13}C\{^1H\}$NMR spectrum in *cis*-$[Co(CN)_2(en)_2]^+$ splits at first; this has already been assigned to that of the ^{13}C adjacent to the $-NH_2$ cis to CN^-.[23] Thus, the amino protons cis to CN^- were deuterated first, and the adjacent ^{13}C NMR signal shifted to a higher field in acidified D_2O. This result is different from that found by Nakazawa et al.

Assignments of ^{15}N NMR signals were confirmed by the selective irradiation of the ^{1}H NMR signals of $-^{15}NH_2$. Accordingly, the assignments of the ^{1}H NMR signals of $-NH_2$ are very important for the assignment of the ^{15}N NMR signals. The results for $X_2=(NO_2^-)_2$ and ox^{2-} were the same as those by Nakazawa et al. and might also be similar for $X_2=acac^-$ and mal^{2-}.

The additivity of the effect of the substituent X on the ^{15}N NMR chemical shifts was examined in the aforementioned $[CoXN_5]^{n+}$- and *cis*-$[CoX_2N_4]^{n+}$-type complexes, as shown below. The effect is separated into two parts: trans and cis. Each can be easily obtained from experimental data for $[CoXN_5]^{n+}$ complexes. On the basis of this data, the ^{15}N MMR shift values for *cis*-$[CoX_2N_4]^{n+}$ complexes can be estimated. The framework of *cis*-$[CoX_2N_4]^{n+}$ is shown with numbering of ligating atoms in Fig. 5. The trans nitrogen atoms located at positions 3 and 4 are subject to a trans effect from one X and a cis effect from another X. The cis nitrogen atoms at positions 5 and 6 are subject to only a cis effect from X at positions 1 and 2. The calculated values are shown along with the observed ones (Table 4) in Fig. 6. It seems to be roughly additive between the trans and the cis effects, thus postulated to be separately caused by ligand X on the ^{15}N NMR chemical shifts.

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