Proton Magnetic Resonance Spectra of Metal Ammine Complexes. VII.* Amine Proton Chemical Shifts in Bis(ethylenediamine)cobalt(III) Compounds

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Amine proton chemical shifts have been measured for some *cis*-bis(ethylenediamine)cobalt(III) complexes in trifluoroacetic acid. The shifts can be explained quantitatively by the magnetic anisotropy of the central metal ion and by assuming fast conformational inversion of chelate rings. Discrepancy between the observed and the computed shift values is apparent, however, for the *trans* hydrogens of the *cis*-dicyano compound, which may be due to the ground-state *trans*-effect of the cyanide ion. The chemical shifts of amine protons of *cis*-tetraammine and *cis*-bis(trimethylenediamine)compounds have been briefly discussed.

We have been interested in the proton chemical shifts of cobalt(III) ammine and amine compounds and have succeeded in explaining the ammine chemical shifts in pentaammine complexes $[CoX(NH_3)_5]^{n+}$.[1-5] In previous papers it was shown that the anisotropy of the paramagnetic term of the magnetic susceptibility of the central metal ion is responsible for the shift variation of coordinated ammonia molecules.

We here report the results of the chemical shift measurements on *cis*-bis(ethylenediamine)cobalt(III) compounds, *cis*-$[CoX_2en_2]$, in trifluoroacetic acid and the results are discussed in terms of the magnetic anisotropy of the cobalt ion. This paper makes the first step of our investigations on bis(en) complexes and an interpretation of the ethylenic part of the PMR spectra in relation to the conformation of en rings will be reported in subsequent publications. Although the PMR spectra of cobalt(III) ethylenediamine complexes have been studied by several workers,[6-21] no clear-cut explanation has been given, however, to chemical shifts and/or band shapes. Clifton and Pratt[12] enumerated several effects as probable causes of the different NH absorptions. These include the intramolecular hydrogen bonding between the *cis* amine groups and the ligand, the effects of magnetic anisotropy of the ligand, and a reduced polarity of the *trans* amine group due to polarization of the metal ion by the negative ligand. While it is clear that the substituent X must affect NH chemical shifts the reasons were not immediately apparent. Lantzke and Watts[11] considered similarly. Since they also had no quantitative measure of the extent of shielding or deshielding by each ligand, it was not possible to decide which hydrogens give rise to which resonance. Hendrickson and Jolly[15] may be the first to note the importance of the magnetic anisotropy of the central metal ion. Thus, they could predict that the *trans* protons resonate at higher field than the *cis* ones for weak-field ligand X and the opposite trend is possible for strong-field ligands.

Experimental

All the complexes used in this work are known compounds and were prepared by well-established methods. The complex prepared were identified spectrophotometrically. Trifluoroacetic acid of extra pure grade, purchased from Katayama Chemical Industries Co., Ltd., was used as the solvent. The measurement was made on a Varian A-60 or T-60 spectrometer at ambient probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal standard for the chemical shift.

Method of Calculation

Theoretical. In this paper the chemical shift difference between the *cis* and *trans* ammine protons will be considered. If we attribute this difference to the anisotropy of the temperature-independent paramagnetism or the second-order paramagnetism of the cobalt(III) ion, and if the point-dipole approximation is appropriate to the problem, we can derive an equation for the chemical shift of ligand protons under the influence of the magnetic anisotropy of the cobalt(III) ion. Under these conditions Ramsey's expression for chemical shielding is reduced to[1-4]

$$\sigma = \left(\frac{1}{R^3} - \frac{3RR}{R^5}\right)\chi^p \tag{1}$$

All the notations have their usual significances.[1-3] The paramagnetic term of the magnetic susceptibility of a cobalt(III) ion, χ^p, can generally be related[2,3] to the shielding constant of the cobalt-59 nucleus, $\sigma^p(^{59}Co)$, as

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

Here $\langle r^{-3}\rangle$ is an average of r^{-3} over a metal 3d orbital. Fujiwara *et al.*[22] discovered that the cobalt-59 chemical shift of the [Co(ABCDEF)] complex is given, to a good approximation, by the sum of contributions from each ligand A to F, see Fig. 1 and Ref. 3.

$$\sigma^p_{iso}(^{59}Co) = \sum_X (2/3)\sigma(X) \tag{3}$$

In this equation $\sigma^p_{iso}(^{59}Co)$ is the observed shift of the cobalt-59 resonance and $\sigma(X)$ is the contribution from the ligand X. $\sigma(X)$ values for typical ligands are given in Ref. 3. This additivity originates from the relations[3]

$$\sigma^p_{xx}(^{59}Co) = \sigma(C) + \sigma(D) + \sigma(E) + \sigma(F) \tag{4}$$

$$\sigma^p_{yy}(^{59}Co) = \sigma(A) + \sigma(B) + \sigma(E) + \sigma(F) \tag{5}$$

$$\sigma^p_{zz}(^{59}Co) = \sigma(A) + \sigma(B) + \sigma(C) + \sigma(D) \tag{6}$$

Although these equations can predict cobalt-59 chemical shifts with few exceptions and with a good accuracy,[22] it is somewhat open to question, whether they can

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* Part VI; U. Sakaguchi, K. Maeda, and H. Yoneda, This Bulletin, **49**, 397 (1976).

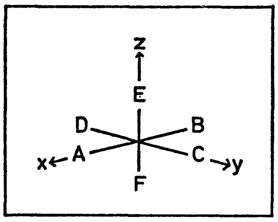

Fig. 1. The definition of the coordinate system for the complex [Co(ABCDEF)].

predict with any accuracy the anisotropy of cobalt-59 chemical shifts, which is relevant to the present investigation. In pentaammine cobalt(III) compounds, evidence has been given to their accuracy with which they predict the anisotropy.[4] If we assume the validity of the above additivity for *cis*-bis(en) complexes also, the proton chemical shift is given by an average of the following principal values of the shielding tensor.

$$\sigma_{xx} = -(1-3\sin^2\theta\cos^2\phi)(\sigma(\mathrm{C})+\sigma(\mathrm{D})+\sigma(\mathrm{E})+\sigma(\mathrm{F}))/2R^3\langle r^{-3}\rangle \tag{7}$$

$$\sigma_{yy} = -(1-3\sin^2\theta\sin^2\phi)(\sigma(\mathrm{A})+\sigma(\mathrm{B})+\sigma(\mathrm{E})+\sigma(\mathrm{F}))/2R^3\langle r^{-3}\rangle \tag{8}$$

$$\sigma_{zz} = -(1-3\cos^2\theta)(\sigma(\mathrm{A})+\sigma(\mathrm{B})+\sigma(\mathrm{C})+\sigma(\mathrm{D}))/2R^3\langle r^{-3}\rangle \tag{9}$$

We will show that these expressions, along with the data of cobalt-59 chemical shifts, can give a good description of the chemical shift variation of amine hydrogens of *cis*-$[\mathrm{CoX_2en_2}]$ ions.

Geometry of Complexes and Conformational Inversion of Chelate Rings. We approximate the arrangement of six nitrogen ligands around the cobalt ion to a regular octahedron and assume that all amine protons lie on the coordinate axes defined on this octahedron. The reason for this choice is as follows. First, we started with a more accurate model by using the crystallographically determined positions of amine protons in $(+)_{495}$-$[\mathrm{Coen_2(L\text{-}glu)}](\mathrm{ClO_4})$,[23] where L-glu represents the L-glutamate ion. In this molecule en rings assume the *gauche* conformation and the distance *R* between the amine proton(s) and the metal ion was calculated at around $R=2.53$ Å (4.77 a.u.). These geometrical factors coupled with Eqs. (7) to (9) render the chemical shift of eight amine protons of bis(en) compounds. For *cis*-$[\mathrm{CoCl(NO_2)en_2}]^+$, the shift values ranging from -0.48 ppm to $+0.75$ ppm (relative to the shift of $[\mathrm{Coen_3}]^{3+}$) were obtained. Thus, we should expect eight absorption lines, which is not in accord with the observation.[11] The discrepancies between the observed shift values and the computed ones are readily apparent for other *cis*-bis(en) complexes also. Therefore, we adopted a more realistic model, in which the fast conformational interconversion of the chelate rings are allowed. The shift values were calculated for amine protons situated at their averaged positions. In this model, four amine hydrogens *cis* to X are to appear as a single absorption, which should be the case with the *trans* protons. After taking the effect of fast conformational inversion into account, we obtain the chemical shift of *cis* $\mathrm{NH_2}$ as

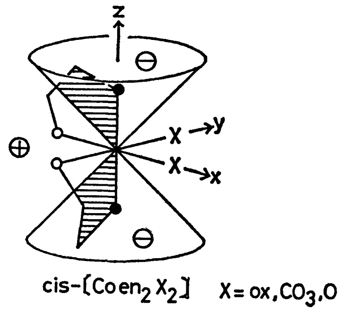

Fig. 2. A schematic presentation of the shift behavior expected for *cis*-$[\mathrm{CoX_2en_2}]$, where X is assumed to be a weak-field ligand. Plus and minus refer to up- and down-field shifts, respectively.

$$\sigma_{\mathrm{iso}} \simeq -1.625(\sigma(\mathrm{en})/2-\sigma(\mathrm{X}))/6R^3\langle r^{-3}\rangle \tag{10}$$

For *trans* $\mathrm{NH_2}$ we have

$$\sigma_{\mathrm{iso}} \simeq 0.8125(\sigma(\mathrm{en})/2-\sigma(\mathrm{X}))/6R^3\langle r^{-3}\rangle \tag{11}$$

Likewise a singlet is expected for *trans*-$[\mathrm{CoXYen_2}]$ at a position specified by

$$\sigma_{\mathrm{iso}} \simeq 0.8125(\sigma(\mathrm{X})+\sigma(\mathrm{Y})-\sigma(\mathrm{en}))/6R^3\langle r^{-3}\rangle \tag{12}$$

This model leads to four absorption lines for *cis*-$[\mathrm{CoXYen_2}]$ corresponding to *trans* (to X) $\mathrm{NH_2}$, *trans* (to Y) $\mathrm{NH_2}$, and the two types of $\mathrm{NH_2}$ groups both *cis* to X and Y. This expectation is not in line with the observation.[11] Further, these equations give shift values which are in poorer agreement with the measurement than does the next model. Thus, we are led to the simplest model where all amine hydrogens are on the coordinate axes of a regular octahedron. In this model the *cis* hydrogens of *cis*-bis(en) compounds appear at

$$\sigma_{\mathrm{iso}} \simeq -2(\sigma(\mathrm{en})/2-\sigma(\mathrm{X}))/6R^3\langle r^{-3}\rangle \tag{13}$$

and the *trans* protons appear at

$$\sigma_{\mathrm{iso}} \simeq (\sigma(\mathrm{en})/2-\sigma(\mathrm{X}))/6R^3\langle r^{-3}\rangle \tag{14}$$

The expected shift pattern may roughly be summarized as follows; (i) the *cis* hydrogens resonate at lower magnetic field than the *trans* ones if the ligand X is lower than en in the spectrochemical series, and (ii) if X is a strong-field ligand, then the opposite behavior is expected, see Fig. 2. In Fig. 2, the angle between the cone and the z-axis is 54°44′ corresponding to $(3\cos^2\theta-1)=0$. It should be noted that Eqs. (7) to (14) give shift values as measured from the chemical shift of $[\mathrm{Coen_3}]^{3+}$. The value of $\langle r^{-3}\rangle$ was chosen to be 5.77 a.u.[2] of $[\mathrm{Co(NH_3)_6}]^{3+}$ for all the complexes investigated here.

Results

Typical examples of PMR spectra of *cis*-$[\mathrm{CoX_2en_2}]$ complexes in trifluoroacetic acid are given in Fig. 3. In Fig. 3, the absorptions around $\tau=3$ ppm are due to methylene protons and those ranging from $\tau=4$ to 6 ppm due to amine hydrogens. The results of our measurements on *cis*-bis(en) compounds with substituents $\mathrm{X=CN^-}$, $\mathrm{NO_2^-}$, $\mathrm{NCS^-}$, $\mathrm{N_3^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{CH_2ClCOO^-}$, and $\mathrm{X_2}$=oxalate ion are illustrated in Fig. 4,

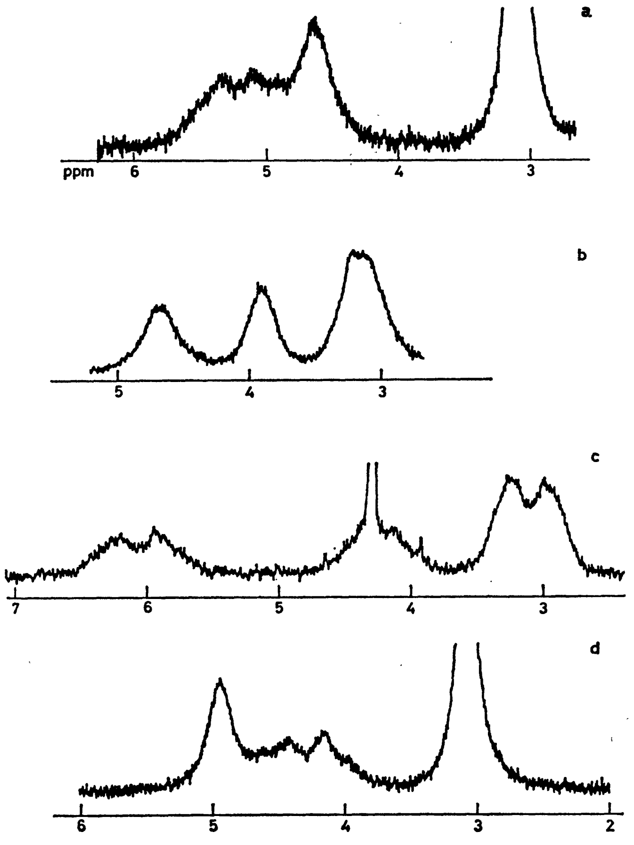

Fig. 3. Typical examples of the PMR spectra of *cis*-bis(en) complexes measured in trifluoroacetic acid. (a) *cis*-[Co(ox)en_2]$^+$, (b) *cis*-[$Co(CN)_2en_2$]$^+$, (c) *cis*-[$Co(CH_2ClCOO)_2en_2$]$^+$, and d) *cis*-[$Co(NO_2)_2en_2$]$^+$.

together with the computed shift values.

Discussion

cis-[CoX_2en_2]. We can see at once from Fig. 4 that the theory based on the magnetic anisotropy of the central cobalt(III) ion can explain not only the orders of magnitude of the chemical shifts of amine protons but also their exact values. From this we draw some important conclusions. First, it can be concluded that the chemical shift of these amine hydrogens are primarily determined by the anisotropy of the magnetic susceptibility of the metal ion. We employed several drastic approximations in computing the shielding constants. We approximated the symmetry around the cobalt ion to a regular octahedron and placed all amine protons on the coordinate axes. The same Co–H distances were assumed for all the complexes examined. Further, our model is based on the point-dipole approximation and the additivity of cobalt-59 chemical shifts. Fast conformational inversion was postulated to obtain a better agreement with the observation. The fact that we could obtain an excellent agreement with the observation notwithstanding all these approximations suggests that the magnetic anisotropy of the metal ion has the prime importance in determining the shift values of these compounds.

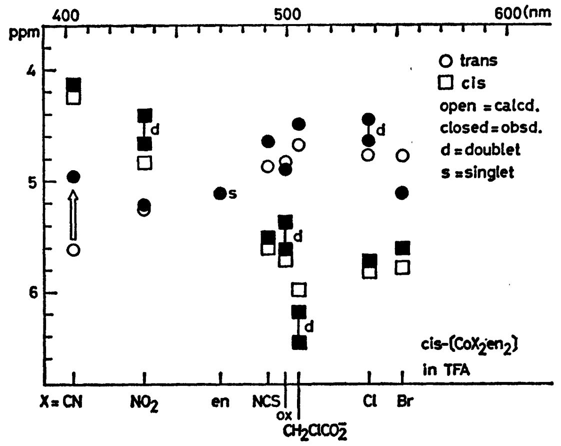

Fig. 4. A plot of the computed shift values of amine hydrogens against the observed shifts. TFA stands for trifluoroacetic acid.

In our model the effect of covalency between the cobalt and nitrogen or X atoms are taken into consideration implicitly *via* the shielding constants of cobalt-59 nuclei. The abscissa in Fig. 4 is the wavelengths of the first absorption maxima of the corresponding compounds. No simple linear relation exists between the shift values and the wavelengths of the first absorption maxima. This may be a clear indication that we should take the covalency into account. Hendrickson and Jolly[15] argued that the trend of the chemical shifts of [$CoX(NH_3)_5$] does not exactly match the spectrochemical series since in the shielding expression the exponential factor of the metal radial functions might be expected to vary.[24] With this reservation in mind we can expect the qualitative shift pattern as shown in Fig. 2.

While the agreement between the computed and the measured shifts is surprisingly good for complexes with NO_2^-, NCS,$^-$ Cl,$^-$ Br,$^-$ CH_2ClCOO,$^-$ and oxalate ion, the *trans* hydrogens of the dicyano compound appear at a position much higher than that expected from the theory. The shift of the *cis* hydrogens is fully explained. The discrepancy for the *trans* protons seems to be ascribed to the large inductive effect of the cyanide ion.[25] Fujiwara *et al.*[26] showed from the analysis of cobalt-59 chemical shifts that the Co–CN bond is the most covalent among the Co–O, Co–halogen, or Co–N bonds. Let us consider the CN–Co–NH_2 fragment with NH_2 *trans* to CN^-. The electron density on the NH_2 nitrogen atom will, thus, be restored to a great extent, with a concomitant weakening of the *trans* Co–NH_2 bonding. This will result in an enhanced shielding of the amine hydrogens under consideration, which is just in accord with the observation, see Fig. 4. These inductive effects were not properly taken into account in our model. An increase or decrease in electron density on an amine hydrogen atom will be detected as the rate of hydrogen deuterium exchange or as the pK_a value of the complex. Evidence supporting this deduction has really been obtained for pentaammine and *cis*-bis(en) complexes.[25,27] This result and its implication were discussed in Part VI of this series.

Tetraammines. We here discuss the empirical rule of Jolly *et al.*[14] for tetraammine cobalt(III) complexes. They found that if we assume that the chemical shift of a coordinated ammonia molecule is the sum of five terms characteristic of the other five ligands and their positions, then it is possible, using the data of a series of compounds $[CoX(NH_3)_5]$, to estimate the chemical shift values of ammonia molecules in tetraammine complexes. It seems worthwhile to show that this empirical rule can be accomodated properly in our theory which is based on the magnetic anisotorpy of the cobalt(III) ion. For the pentaammine compound, we take the z-axis as the symmetry axis of the molecule. The chemical shift of the *trans* ammonia protons of this molecule is given by[3]

$$\sigma_{\text{iso}} \simeq (3\cos^2\theta-1)(\sigma(\text{NH}_3) - \sigma(\text{X}))/6R^3\langle r^{-3}\rangle \tag{15}$$

Similarly the shielding constant of the *cis* protons is given, after allowing for the rapid rotation of ammonia molecules around their C_3 axes, by the expression

$$\sigma_{\text{iso}} \simeq -(3\cos^2\theta-1)(\sigma(\text{NH}_3) - \sigma(\text{X}))/12R^3\langle r^{-3}\rangle \tag{16}$$

Here θ is the angle between the Co–N and Co–H axes and is unaffected by the NH_3 rotation. The above equations may be reinterpreted in the following way. If we define the quantity Δ_X, which is characteristic of the ligand X, by

$$\Delta_{\text{X}} \equiv (3\cos^2\theta-1)(\sigma(\text{NH}_3) - \sigma(\text{X}))/12R^3\langle r^{-3}\rangle \tag{17}$$

Eqs. (15) and (16) indicate that the contribution of the ligand X to the chemical shift of the *trans* protons is $2\Delta_X$ and that to the *cis* protons is $-\Delta_X$. On the other hand, in *cis*-$[CoXY(NH_3)_4]$ the chemical shift of the ammonia protons *cis* to both X and Y is shown, after taking the NH_3 rotation into account, to be given by

$$\begin{aligned}\sigma_{\text{iso}} &\simeq (3\cos^2\theta-1)(\sigma(\text{X}) + \sigma(\text{Y}) - 2\sigma(\text{NH}_3))/\\ &\quad 12R^3\langle r^{-3}\rangle && (18)\\ &\equiv (-\Delta_{\text{X}}) + (-\Delta_{\text{Y}}) && (19)\end{aligned}$$

Likewise, for the ammonia molecule *trans* to X and *cis* to Y the following expression holds.

$$\sigma_{\text{iso}} \simeq (2\Delta_{\text{X}}) + (-\Delta_{\text{Y}}) \tag{20}$$

In view of the fact that Jolly *et al.* chose the chemical shift of $[Co(NH_3)_6]^{3+}$ as the reference and set it equal to zero, the above equations are just the analytical expressions of their empirical rule. More importantly the above results imply that the chemical shifts of coordinated ammonia molecules are dominated by the magnetic anisotropy of the central metal ion.

cis-Bis(trimethylenediamine) Complexes; Here we will briefly examine the chemical shift of amine protons of *cis*-$[CoX_2tn_2]$, where tn is trimethylenediamine. Kawaguchi and Kawaguchi[28] obtained the PMR spectra of *cis*-bis(tn) compounds containing the cyanide, azide, and thiocyanate ions as the ligand X. While the *trans* isomers exhibit a single absorption in the amine proton region, the *cis* compounds show a well-resolved doublet. Since it is highly probable that the chemical shifts of these amine protons are governed by the magnetic anisotropy of the metal ion, we would like to assign the amine signals according to Eqs. (13) and (14). The *trans* NH_2 may be more deshielded than the *cis* one when the substituent X is the cyanide ion. Thus, it follows that in *cis*-$[Co(CN)_2tn_2]^+$ the absorption centered at about 5.7 ppm from DSS is due to the *trans* hydrogens and that at 6.87 ppm is due to the *cis* ones. Similarly in the azido-containing complex the peak resonating at 6.1 ppm can be attributed to the *trans* amine protons.

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