Proton Magnetic Resonance Spectra of Metal Ammine Complexes. VI.* The *trans*-Effect in Cobalt(III) Amine Compounds as Studied by the Rate of Hydrogen-Deuterium Exchange

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The rate of the isotopic deuterium exchange has been measured for several cobalt(III) amine complexes in D_2O. The substituents CN^-, NO_2^-, and possibly SO_3^{2-} decelerate the exchange of the amine protons *trans* to these ligands, leading in some cases to a smaller rate for these protons than for the *cis* ones. On the other hand, the *trans*-proton labilizing ligands include F^-, Cl^-, Br^-, H_2O, CO_3^{2-}, $OCONH_2^-$, N_3^-, CH_3NH_2, CH_3COO^-, and the malonate, fumarate, and oxalate ions. The above observation clearly indicates that the HD exchange rate can be a measure of the *trans*-effect of these ligand molecules.

In previous papers,[1–4)] we have reported that the chemical shifts of amine protons of some cobalt(III) complexes are primarily determined by the magnetic anisotropy of the central metal ion. In pentaamine cobalt(III) compounds $[CoX(NH_3)_5]^{n+}$, the ammine proton chemical shifts could be quantitatively explained by using the theory based on the anisotropic magnetic field of the cobaltic ion along with the cobalt-59 chemical shifts. Small but significant discrepancies between the theory and the observations were noted for the *trans* hydrogens of the cyano- and nitro-pentaammine complexes. These hydrogens resonated at a field higher than that expected from the theory. The succeeding paper will deal with the assignment of the amine protons in the NMR spectra of bis(en) type complexes, where en is ethylenediamine. It will be shown that the chemical shifts of these protons can be explained in a manner similar to the pentaammines. The *trans* amine hydrogens of *cis*-$[Co(CN)_2en_2]^+$ appeared at a more shielded position than that the magnetic anisotropy of the metal ion would predict.

All the above phenomena seemed to point to an increase in the electron densities on these *trans* amine hydrogens. In other words, we attribute the discrepancies between the theory of chemical shift and the observed shift values to the inductive effects of the substituents. Thus, we expect that an increase or decrease in the electron density on a particular proton will be reflected in the rate of HD exchange of this proton. Here we report the results of measurements on the rate of hydrogen-deuterium exchange of ammine and amine protons of some cobalt(III) complexes. A part of the present paper has already been reported.[1)]

Experimental

Materials. All the complexes investigated in this work are known compounds and were prepared by well-established methods. The identity of the complex was confirmed spectrophotometrically. Deuterium oxide (99.8 atom % D minimum) and dimethyl sulfoxide-d_6 (99.5 atom % D minimum) were purchased from Stohler Isotope Chemicals (Cal., U.S.A.).

Measurements. All the measurements were made on a Varian T-60 NMR spectrometer operating at 60 MHz and at a temperature of 30 °C. All the complexes except $[Co(NO_2)(NH_3)_5](NO_3)_2$ were dissolved in deuterium oxide to almost saturation and the signal intensities corresponding to amine hydrogens were measured at suitable time intervals. *t*-Buthyl alcohol was added as an internal reference for intensity if necessary. Since the solubility of the nitropentaammine compound in D_2O was too small, it was decided to use the dimethyl sulfoxide-d_6/D_2O mixed solution (90 : 10 wt%) as the solvent. Amine hydrogen signals of ethylenediamine overlapped, in some instances heavily, with the HDO signal, which tended to hamper an accurate measurement of intensities.

Results and Discussion

The rate of hydrogen exchange in cobalt(III) amine complexes was first reported by Anderson *et al.*[5)] and the subsequent works of Block and Gold[6)] and Basolo and his coworkers[7–9)] established the following points: (i) the rate of HD exchange is specific hydroxide ion catalysed and is proportional to the concentration of OH^- ions, (ii) the observed pseudo-first-order rate constant is independent of the concentration of the metal ion, and (iii) the rate is unaffected by the added salt if the proper correction for the solution pH has been made according to (i). The results of Yamatera and Fujita[10)] appeared to put forward an important objection to (iii). All these workers and others[11–16)] reported that in a particular compound the amine protons *trans* to a substituent exchange faster than those *cis* to the substituent. However, this statement was necessarily non-definitive since these authors

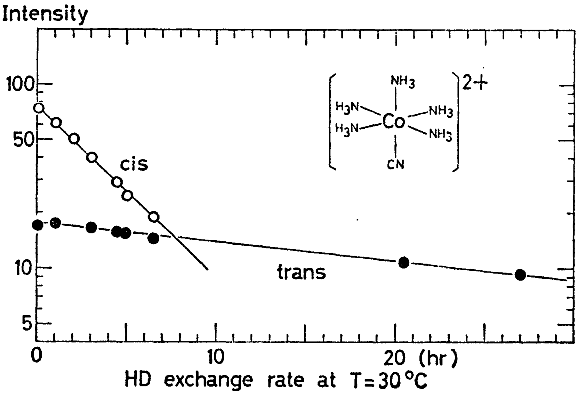

Fig. 1. The changes in ammine proton signal intensities of $[CoCN(NH_3)_5]^{2+}$ in D_2O.

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* Part V: H. Yoneda, K. Maeda, and U. Sakaguchi, *Chem. Lett.*, **1975**, 107.

measured the overall rates. Separate rates for *cis* and *trans* hydrogens were first obtained by Clifton and Pratt[11] for fumaratopentaammine cobalt(III) ion, followed by the measurements of Buckingham *et al.*[14] on $[CoCl(NH_3)_5]^{2+}$ and $[CoCl(CH_3NH_2)_5]^{2+}$. Basolo *et al.*[7–9] obtained two rate constants for *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ and *cis*-$[Co(NO_2)_2en_2]^+$ and Basolo and Pearson[17] stated, in their recent review, that it is not known whether the hydrogens exchanging faster are those *trans* to NO_2^- or to NH_3 and en. We solved this problem by obtaining a method for assigning NMR signals of coordinated NH_3 or en.[1–3] Thus, all the data described in the literature can now be considered to have reported that *trans* ammine protons are more labile against deuterium substitution than *cis* ones. Our present data offer another type of example, where the *trans* hydrogens are *less* labile. This is especially noted for compounds containing the cyanide, nitrite, and possibly sulfite ions.

Pentaamines. We have measured the exchange rate for cyano-, nitro-, and fluoro-pentaamine complexes. In this type of compounds, the assignment of the NMR signals follows immediately from their intensities. The result for the cyano compound is illustrated in Fig. 1. The data are summarized in Table 1 in terms of the pseudo-first-order rate constants. As is evident from Fig. 1, the *trans* hydrogens exchange an order of magnitude more slowly than the remaining four *cis* protons: $k_t=6.2\times10^{-6}$ s^{-1} and $k_c=6.0\times10^{-5}$ s^{-1}. k_t and k_c stand for the pseudo-first-order rate constants for *trans* and *cis* hydrogens. The nitropentaammine compound gives only a single absorption when it is dissolved in dimethyl sulfoxide or trifluoroacetic acid. This was shown[4] to be a mere coincidence of the *trans* and *cis* absorptions. For reasons mentioned previously, the rate for this compound was obtained in the dimethyl sulfoxide-d_6/D_2O mixed solvent. Separate rates for the *cis* and *trans* ammonia hydrogens can, however, be obtained by fitting the intensity-time data to an expression $[4\exp(-k_ct)+\exp(-k_tt)]$; see Fig. 2. It can readily be seen that the *trans* hydrogens are less labile than the *cis* ones. Since the rates of this compound were measured in mixed solvent, it may not pertinent to compare this data with those of the other complexes for which deuterium oxide was used as the solvent.

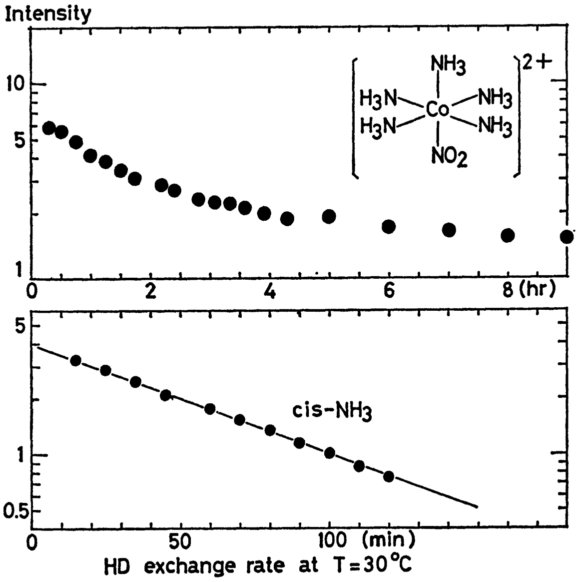


Fig. 2. HD exchange in $[Co(NO_2)(NH_3)_5]^{2+}$; (upper) experimental data, (lower) data analysed for *cis* ammine hydrogens.

TABLE 1.

Complex	k_c[a]	k_t[a]	Other rates[a]
$[CoCN(NH_3)_5](ClO_4)_2$	60	6.2	
$[CoNO_2(NH_3)_5](NO_3)_2$	180	17	
$[CoF(NH_3)_5](NO_3)_2$	58	(fast)	
cis-$[Co(CN)_2(NH_3)_4]Cl$	390	62	
$[Co\text{-}(CO_3)(NH_3)_4]_2SO_4$	1300	2200	
cis-$[Co(CH_3COO)_2$-$(NH_3)_4]ClO_4$	140	680	
cis-$NH_4[Co(SO_3)_2(NH_3)_4]$	(fast)	490[b]	
$[Co(NH_3)_4en](NO_3)_3$	1500	6500	3200[c]
cis-$[Co(CN)_2en_2]Cl$	680	310	

a) In units of 10^{-6} s^{-1}. b) For the assignment, see text. c) NH_2 protons.

Previously, Palmer and Basolo[8] obtained only a single rate constant for HD exchange in fluoro-, chloro-, bromo-, and nitro-pentaammine compounds. Basolo *et al.*[9] reported that all of the hydrogens of $[CoCl(NH_3)_5]^{2+}$ exchange at the same rate. Clifton and Pratt[11] showed that the rate of exchange of the *trans* ammonia protons is two orders of magnitude greater than that of the *cis* protons. Buckingham *et al.*[14] found that the *trans* hydrogens of $[CoCl(NH_3)_5]^{2+}$ and $[CoCl(CH_3NH_2)_5]^{2+}$ exchange with deuterium sixty times faster than the *cis* ones, thus invalidating the statement of Basolo *et al.* on the chloropentaammine complex. Further, for $[CoX(NH_3)_5]$ ($X=H_2O$, N_3^-, $OCONH_2^-$, Cl^-, and Br^-) they obtained spectra where the *trans* NH_3 was completely deuterated, leaving the four *cis* NH_3 groups substantially unaffected. Therefore, the *trans* ammine protons have been believed to be the more labile in pentaammine complexes containing H_2O, F^-, Cl^-, Br^-, N_3^-, $OCONH_2^-$, NO_2^-, and the fumarate ion.

In summary, the substituents $X=CN^-$ and NO_2^- decelerate the *trans* hydrogens, while F^-, Cl^-, Br^-, H_2O, N_3^-, $OCONH_2^-$, CH_3NH_2, and the fumarate ion labilize the *trans* protons.

cis-*Tetraammine and* cis-*Bis(ethylenediamine) Complexes.* Block and Gold[6] and Basolo *et al.*[9] reported only one rate constant for $[Co(ox)(NH_3)_4]^+$ and *cis*-$[Co(NH_3)_2en_2]^{3+}$, where ox is the oxalate ion. Clifton and Pratt[11] observed that in *cis*-$[CoCl_2en_2]^+$ the *trans* protons are the faster, but their measurements of the rates were complicated by aquation and a subsequent isomerization of the complex. The only examples where separate rates for *trans* and *cis* hydrogens were obtained were *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ and *cis*-$[Co(NO_2)_2en_2]^+$.[8]

The complexes of the types *cis*-$[CoX_2(NH_3)_4]$ and *cis*-$[CoX_2en_2]$ exhibit two singlets with an intensity ratio 1 : 1 if these compounds are dissolved in D_2O. Thus, the signal assignment to the *trans* and *cis* hydrogens is not so straightforward as in pentaammine complexes. In the previous papers, we outlined the method for the assignment. Qualitatively, the *trans* hydrogens are more deshielded than the *cis* ones if the ligand X is a strong-field ligand, *e.g.*, CN^- or NO_2^-. For a weak ligand X, the *trans* hydrogens resonate at higher magnetic field. In this way we could assign almost all resonances examined in this work.

Figure 3 gives the result for *cis*-$[Co(CN)_2en_2]^+$. As in the case of the cyanopentaammine complex, the cyanide ion can be seen to decelerate the *trans* protons. The result for *cis*-$[Co(CN)_2(NH_3)_4]^+$ is illustrated in Fig. 4, which also shows that the *trans* hydrogens appearing at lower field than the *cis* ones are the less labile against deuterium substitution. The rate of the *trans* protons is about one-sixth of that of the *cis* protons. For *cis*-$[CoX_2(NH_3)_4]$ containing CH_3COO^-, en, and CO_3^{2-}, it was found that the *trans* protons are the more labile: see Fig. 5 and Table 1.

The complex *cis*-$[Co(SO_3)_2(NH_3)_4]^-$ shows two absorptions in water, while in D_2O only one signal can be observed, at a position coincident with that of the high field signal observed in water. This indicates that the low field signal disappears rapidly on dissolving in D_2O. Since no cobalt-59 chemical shift value is available for sulfito-containing compounds, we can make no assignment for these signals. However, it is highly probable that the high field signal which exchanges slowly is due to the *trans* ammonia. Numerous examples suggestive of a large *trans*-ligand labilizing effect of the sulfite ion are well documented.[17-20] Thus, it will be reasonable to assume that the *trans* hydrogens are upfield shifted owing to this *trans*-labilizing effect (see below). This deduction is not inconsistent with the slower rate for these *trans* hydrogens.

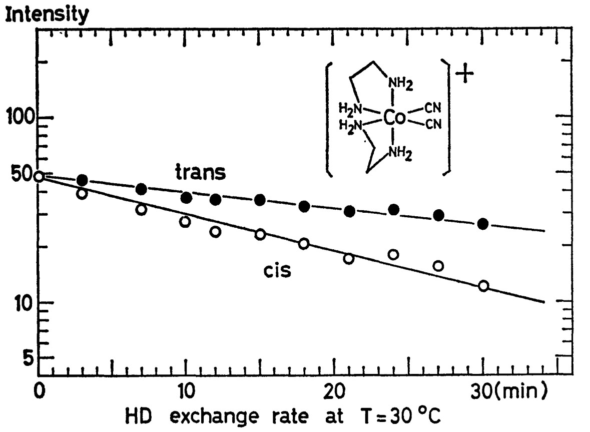


Fig. 3. The rate of hydrogen exchange in *cis*-$[Co(CN)_2en_2]^+$.

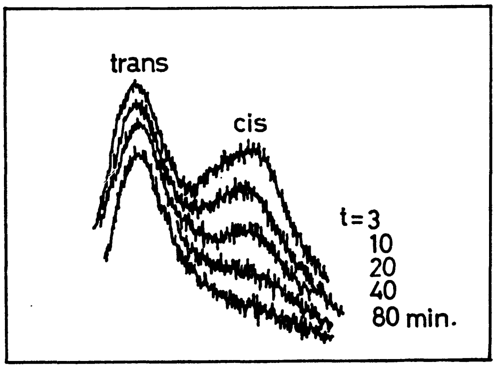
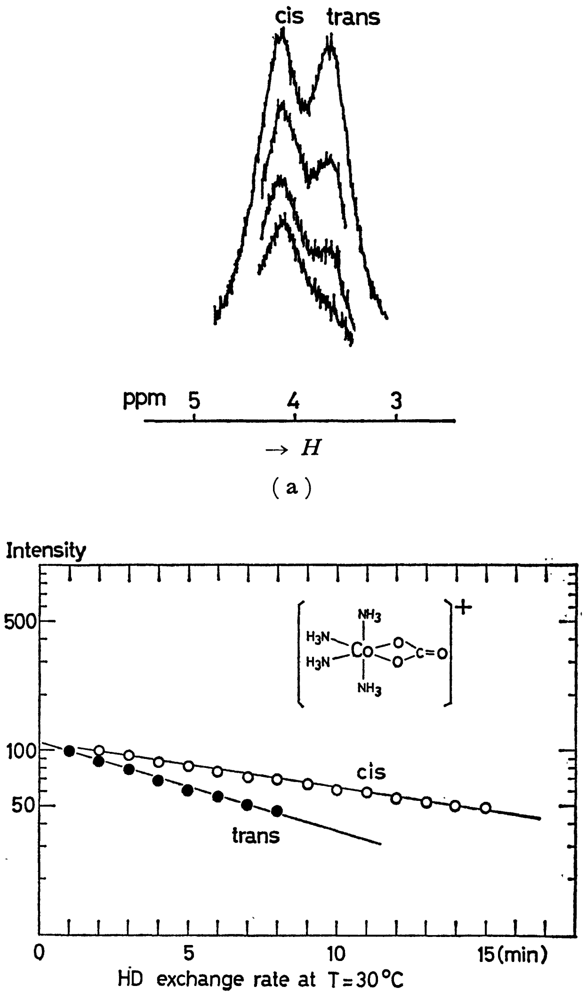


Fig. 4. The spectra of *cis*-$[Co(CN)_2(NH_3)_4]^+$ in D_2O observed at suitable time intervals after dissolution.

Separate rates for the *cis* and *trans* hydrogens of *cis*-$[Co(NO_2)_2en_2]^+$ and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ have been reported by Palmer and Basolo.[8] They noticed that the slower rates are about the same as the rates for the corresponding *trans* isomers and therefore they assigned the greater lability to the *trans* hydrogens. Their assignments, however, didn't seem to be sound enough and we re-examined both complexes. The complex *cis*-$[Co(NO_2)_2en_2]^+$ shows two NH_2 resonances. The signal situated at lower field exchanges with deuterium and disappears rapidly. The high field line exchanges much more slowly.



(a)

(b)

Fig. 5. (a) The spectra of $[CoCO_3(NH_3)_4]^+$ taken at every four minutes. (b) The plot of the signal intensities of ammine hydrogens in $[CoCO_3(NH_3)_4]^+$ against time.

In the preceding papers, we assigned the low field signal to the *trans* amines based on the magnetic anisotropy of the cobalt ion. If our assignment is correct, then it follows that the *trans* hydrogens are the more labile. This is in line with the deduction of Basolo and Palmer. *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ exhibits only a single absorption in D_2O and in acidified D_2O. Therefore, we cannot tell which hydrogens are exchanging faster. It is to be noted that in $[Co(NO_2)(NH_3)_5]^{2+}$ the *trans* hydrogens are the slower, while in *cis*-$[Co(NO_2)_2en_2]^+$ and probably in *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ they are the faster. We cannot at present give any explanation for this observation.

The trans-*Effect.* As is evident from the previous discussions, the exchange rate of amine hydrogens is greatly affected by the substituent *trans* to the protons under consideration. In conjunction with all the literature data, it can be concluded that the effect of the ligand X is primarily the most prominent on the *trans* (to X) hydrogens.

In general, coordinated ligand molecules are under the electron-withdrawing effect of the positively charged metal ions. Therefore, if the Co–NH_3 bond become strengthened for some reason, the electron density on this nitrogen atom will be decreased, with a concomitant labilization of the hydrogen atoms attached to this nitrogen. Conversely, if the Co–N bond is weakened, the electron density on this nitrogen atom will be restored, with the result that the hydrogen atoms bound to this nitrogen atom become less labile. This reasoning explains almost all the foregoing observations. Fujiwara *et al.*[21] have shown from the analysis of their cobalt-59 chemical shift data that the cobalt-cyanide, cobalt-nitro, and cobalt-sulfur bondings are much more covalent than the other Co-oxygen, Co-halogen(pseudohalogen), and Co-nitrogen bondings. Thus, if we presume that the cobalt-nitrogen bonds *trans* to the cyanide, nitrite, and sulfite ions assume the more ionic character, the deceleration of the exchange rates of the hydrogens attached to these nitrogen atoms may be expected.

If we assume that the rate of HD exchange results at least partially from the ground-state weakening of the *trans* Co–N bonds, we can expect the structural *trans*-effect especially for complexes with *trans*-decelerating ligands. It is rather difficult, as pointed out by Pratt and Thorp,[18] to decide whether any bond-length variation is significant and therefore whether this can be ascribed to effects of the lattice and the counter ion(s). With this in mind, we first note that Snow[22] added the carbonato ion to a growing list of anions including NO_2^-, Cl^-, thiosulfate, and thiocyanate (both sulfur ligands are sulfur-bonded) which do not show the structural *trans*-effect in ammine cobalt(III) compounds. The crystal and molecular structures of $[CoCN(NH_3)_5]Cl_2$ and $[CoCN(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$ have been determined by Ozbirn and Jacobson.[23] Although they did not state so explicitly in their paper, the *trans* Co–N bonds in both complexes are definitely longer than the *cis* ones. The differences of the bond lengths are 0.031 and 0.027 Å for the former and the latter compounds, respectively, which are well beyond the experimental uncertainties of thier work. Elder and Trkula[24] reported that the large *trans*-effect of sulfite ion is evident in the molecular structure of $[Co(SO_3)(NH_3)_5]^+$, where the *trans* Co–N bond length is 2.055(2)Å and the corresponding *cis* ones are 1.962—1.972(average= 1.966(4))Å. In *trans*-$[Co(SO_3)(NCS)en_2]\cdot 2H_2O$, the sulfite ion is reported,[25] however, to cause no significant bond lengthening. As is apparent from the examples of the sulfito- and nitro-containing compounds, the results of the molecular structure determination do not completely parallel the hydrogen exchange rates. In some cases, however, the *trans*-bond lengthening effect has really been observed.

Conclusion

Thr rate of HD exchange can be considered to be a manifestation of the *trans*-effect; the cyanide, nitrite, and possibly sulfite ions decelerate the exchange of *trans* hydrogens while F^-, Cl^-, Br^-, H_2O, N_3^-, CH_3COO^-, CO_3^{2-}, $OCONH_2^-$, ox, CH_3NH_2, and malonate ion tend to labilize the *trans* NH hydrogens. It will be noted that these *trans*-accelerating ligands are all weak-field ligands and are situated at lower positions than NH_3 or en in the spectrochemical series. This correlation of the HD exchange rate with the spectrochemical series has been rationalized qualitatively in terms of the electron donating or withdrawing power of the substituents. Furthermore, the crystal structure data seem to indicate that the effect of substituents, especially that of the *trans*-decelerating ligands, results at least partially from the ground-state weakening of the *trans* Co–N bonds.

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