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PROTON MAGNETIC RESONANCE SPECTRA OF METAL AMMINE COMPLEXES. V.* THE TRANS-EFFECT IN COBALT(III) AMMINES AS EVIDENCED BY THE RATE OF ISOTOPIC DEUTERIUM EXCHANGE

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The rate of hydrogen exchange has been measured on cobalt(III) ammines and found to reflect the trans-effect. We confirmed that large inductive effects of CN^- and, in some cases, NO_2^- offset the effect of the magnetic anisotropy of cobalt, which accounts for ammine proton chemical shifts in most complexes.

In previous papers,[1-3] we have reported that proton chemical shifts of cobalt(III) ammines can be attributed to the paramagnetic anisotropy of the central cobaltic ion. We explained quantitatively the shifts in $[CoX(NH_3)_5]$. Small but significant discrepancies were noted, however, for trans ammine protons of cyano- and nitro-pentaammine cobalt(III) ions. Observed upfield shifts pointed to an increase of electron densities on these protons. To test this possibility, we have investigated the rate of HD isotopic exchange in D_2O on several cobalt(III) ammines by measuring at suitable time intervals the NMR intensities.

The result for $[CoCN(NH_3)_5]^{2+}$ is illustrated in Fig. 1. The rate for trans ammine protons is an order smaller than that for cis protons; $k_c = 2.6\times10^{-5}\,sec^{-1}$ and $k_t = 2.7\times10^{-6}\,sec^{-1}$, where the subscripts c and t refer to cis and trans protons. It was found by many workers[4-11] that the rate of hydrogen exchange in metal ammines is specific hydroxide ion catalyzed. Our data thus correspond to pseudo-first-order rate constants. $[Co(NO_2)(NH_3)_5]^{2+}$ gives only a single absorption line but separate rates for trans and cis protons can be obtained by fitting the data to an expression $[4\exp(-k_c t) + \exp(-k_t t)]$ (Fig. 2). Figure 2 clearly shows that trans ammine protons are less labile. Similarly, the result of cis-$[Co(CN)_2(en)_2]^+$ revealed that CN^- decelerates the exchange of trans ammine protons; $k_c = 3.2\times10^{-4}\,sec^{-1}$ and $k_t = 1.5\times10^{-4}\,sec^{-1}$ (Fig. 3).

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* Part IV; H. Yoneda, U. Sakaguchi, and Y. Nakashima, Bull. Chem. Soc. Japan, in press.

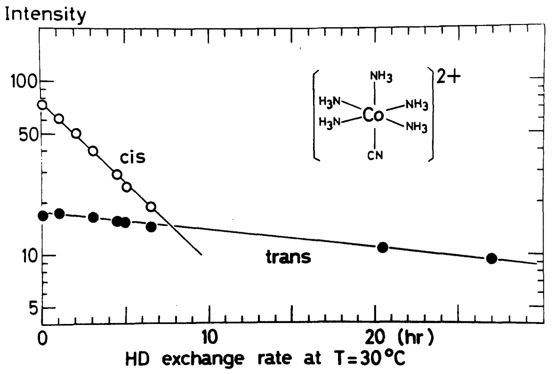

Fig. 1. The changes in ammine proton signal intensities of $[CoCN(NH_3)_5]^{2+}$ in D_2O.

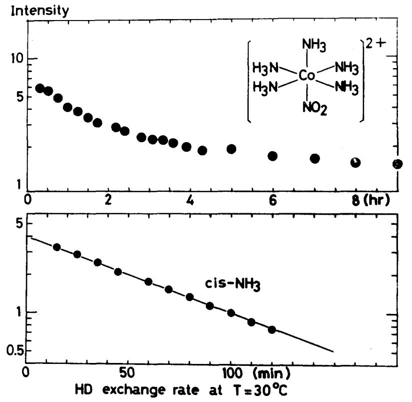

Fig. 2. HD exchange in $[Co(NO_2)(NH_3)_5]^{2+}$: (upper) experimental data; (lower) data analysed for cis ammine protons.

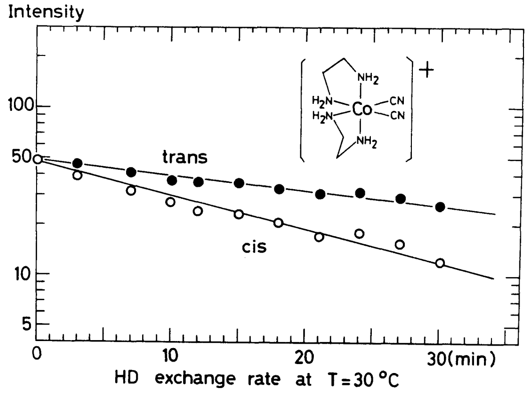

Fig. 3. The rate of hydrogen exchange in cis-$[Co(CN)_2(en)_2]^+$.

The implication of the present results may be twofold. First, the inductive effect of substituents could be detected as the rate of HD exchange. Thus, we obtain the following conclusion. The paramagnetic anisotropy of cobaltic ion determines the chemical shift of $[CoX(NH_3)_5]$, except the trans ammines of compounds with X = CN^- and NO_2^-. The discrepancies in X = CN^- and NO_2^- between the theory$^{1-3)}$ and observed values can be ascribed to the inductive effect of these ligands, which was not properly taken into account in the theory. In the case of cis-$[CoX_2(NH_3)_4]$ and cis-$[CoX_2(en)_2]$ excluding complexes with X = CN^-, the paramagnetic anisotropy of Co(III) is responsible for the chemical shift. In this case also, the large inductive effect of cyanide ion offsets the effect of magnetic anisotropy of the metal ion.

The second implication is that the rate of isotopic exchange is closely related to the trans-effect.$^{12-14)}$ Data of HD exchange rate reported for cobalt(III) ammines are rather limited.$^{4-11)}$ All these data seem to indicate that trans protons exchange faster than cis ones. The only example in which the separate rates were determined for trans and cis ammines was reported by Clifton and Pratt[9)] for fumaratopentaammine cobalt(III) ion. Basolo et al.[6-8)] measured the overall rates of hydrogen exchange in cis-$[Co(NO_2)_2(NH_3)_4]^+$ and cis-$[Co(NO_2)_2(en)_2]^+$ by following the change in absorption in the near infrared(1650nm due to OH^-). Basolo and Pearson, in their recent review,[12)] stated that it is not known whether the hydrogens exchanging faster are those trans to NO_2 or to NH_3, en. We solved this problem in previous papers[1-3)] by establishing a method of assigning NMR signals. Thus, all the data described in the literature can now be considered to have reported that trans ammine protons are more labile. Our present data offer another type of examples where trans ammine protons are <u>less</u> labile. This is especially noticed for CN^- and to a lesser extent for NO_2^-. Although the existence of the trans-effect in octahedral cobalt(III) complexes does not seem to be well established,[13)] it is clear that the rate of hydrogen exchange is a manifestation of this effect.

The trans decelerating ligands CN^- and NO_2^- both have vacant π orbitals available for metal-to-ligand π-bonding. Thus, in complexes containing these ligands back-donation might play a key role in determining the rate of hydrogen exchange. The simplest way of visualizing the situation may be such that these ligands weaken the trans Co-N bond via back-donation, resulting in the lengthening of this bond and hence in the deceleration of HD exchange. A similar trans-bond-lengthening effect has really been observed in $[Co(SO_3)(NH_3)_5]^+$.[15)] If we presume that the rate of exchange results at least partially from the ground state weakening of the trans Co-N bonds, it is highly probable that trans $Co-NH_3$ bonds in $[Co(CN)(NH_3)_5]^{2+}$ and $[Co(NO_2)(NH_3)_5]^{2+}$ are definitely longer than cis ones.

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