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Proton Magnetic Resonance Spectra of Metal Ammine Complexes. VIII.* Hydrogen Isotopic Exchange in the $[Co(O)_2(N)_4]^+$ Complex Ions

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The rates of amine hydrogen isotopic exchange in the $[Co(O)_2(N)_4]^+$ complex ions, where $(O)_2$ represents carbonate, oxalate, or malonate ions, and $(N)_4$, tetraammine, bis(ethylenediamine), or bis(trimethylenediamine), were measured in D_2O at 35 °C by the PMR technique. It was found that: (1) the rates for *trans* (to oxygen) amines are faster than those for *cis* amines; (2) the rates, especially for *trans* amines, in the carbonato complexes are slower than those in the oxalato and malonato analogs, and (3) the difference between the rates for *cis* and *trans* amines is smaller in the bis(diamine) complexes than in the tetraammine complexes. These results are discussed in terms of the influence of the chelate geometry in the complex on the exchange reaction.

In our previous papers,$^{1)}$ it was reported that the *trans* amine hydrogen exchange in $[CoCN(NH_3)_5]^{2+}$, $[CoNO_2(NH_3)_5]^{2+}$, and *cis*-$[Co(CN)_2(en)_2]^+$ is unusually decelerated.** In general, coordinated ligand molecules are influenced by the electron-withdrawing effect of the positively charged metal ion. This effect leads to the decrease in the electron density on the nitrogen atom of the coordinated amine ligand and to a concomitant labilization of the hydrogen atom attached to this nitrogen. Therefore, if the Co–N bond is weakened, the electron density on the nitrogen atom will be restored and the amine ligand will approach its free state so that the hydrogen atom bound to this nitrogen atom becomes less labile. This is the reason for the deceleration in the above complexes. Thus, it was thought that the measurement of the rate of hydrogen exchange might serve as a convenient means of obtaining information on the chemical bonding in complexes.

On the other hand, it is known from the results of X-ray studies that the O–Co–O bond angles in the dicarboxylato complexes are *ca.* 70° for the carbonate ion,$^{2)}$ *ca.* 84° for the oxalate ion,$^{3)}$ and *ca.* 96° for the malonate ion.$^{4)}$ The effect of the deviation of these angles from the ideal octahedral value (90°) has been studied through the circular dichroism spectra of the dicarboxylatobis(ethylenediamine) complexes$^{5)}$ and the aquation reaction of the carbonato(N)$_4$ complexes.$^{6)}$ Douglas *et al.*$^{5)}$ reported that the T_{1g} rotatory strength decreases sharply, $CO_3^{2-} > ox^{2-} > mal^{2-}$, with an increase in the size of the carboxylato chelate ring. Dasgupta and Harris$^{6)}$ discussed the relationship between this deviation and the aquation kinetics. These studies interested us in the effect of this deviation on the rate of amine hydrogen exchange.

To investigate the influence of the geometry of the dicarboxylato chelate, the rates of amine hydrogen exchange in the $[Co(O)_2(N)_4]^+$ complex ions, where $(O)_2 = CO_3^{2-}$, ox^{2-}, or mal^{2-} and where $(N)_4 = (NH_3)_4$, $(en)_2$, or $(tn)_2$, have been determined by the PMR technique.

Experimental

Preparation. The $[CoCO_3(NH_3)_4]Cl \cdot 1/4H_2O$, $[CoCO_3(en)_2]Cl$, and $[Coox(tn)_2]Cl \cdot H_2O$$^{7)}$ complexes were prepared by the usual methods, and the number of molecules of the water of crystallization was determined by elemental analysis. $[Coox(NH_3)_4]Cl \cdot H_2O$, $[Comal(NH_3)_4]Cl \cdot 3/2H_2O$, and $[Coox(en)_2]Cl \cdot H_2O$ were obtained by adding an equimolar amount of oxalic and malonic acids to the corresponding carbonato complexes and then by heating the mixtures until the effervescence subsided. $[Comal(en)_2]Cl \cdot H_2O$ was obtained from the iodide salt$^{5)}$ by trituration with AgCl. $[CoCO_3(tn)_2]Cl \cdot H_2O$ was prepared by a method similar to that used for the bis(ethylenediamine) analog. *cis*-$[Co(CH_3CO_2)_2(NH_3)_4]ClO_4$ was prepared by Kuroda's procedure.$^{8)}$ All these complexes were recrystallized once or twice. The data of the spectrophotometric measurements are summarized in Table 1.

TABLE 1. FIRST ABSORPTION MAXIMA FOR THE $[Co(O)_2(N)_4]^+$ COMPLEX IONS (nm)

	CO_3	ox	mal	$(CH_3CO_2)_2$
$(NH_3)_4$	522	508	516	522
$(en)_2$	511	497	497	
$(tn)_2$	520	510		

Measurement. The rate of amine hydrogen exchange was determined by following the change in the PMR signal intensity with the time, which was measured at 35 °C with a Varian T-60 spectrometer. An adequate amount of the sample was dissolved in D_2O, and the pD was adjusted by HCl for the dicarboxylato chelate complexes and by $HClO_4$ for the diacetatotetraammine complex so that the exchange might be complete in an appropriate time. The PMR measurement was initiated a few minutes after the sample had dissolved, and the pD of the sample solution was measured at about 30 °C with a Hitachi Horiba Model F-7 pH meter using a microelectrode immediately after the PMR measurement. The absorption spectra were measured with a Shimadzu UV-200 double beam spectrophotometer.

The oxalato tetraammine complex is sparingly soluble in D_2O, and the *cis* and *trans* amine signals overlap.

The influence of counter ions on the rate seemed insignificant, because the change in the concentration of the complexes did not affect the rates, within the limits of experimental errors.

Results and Discussion

The PMR spectra of some samples in D_2O or HCl–D_2O are shown in Fig. 1. We have assigned the higher

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* Part VII: U. Sakaguchi, S. Yamazaki, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **49**, 402 (1976).

** In this paper, en, tn, ox, or mal represent ethylenediamine, trimethylenediamine, the oxalate ion, or the malonate ion respectively.

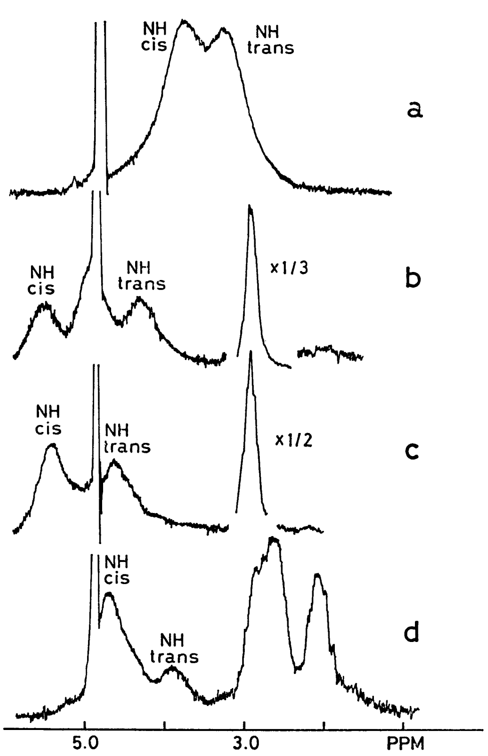

Fig. 1. The PMR spectra of (a) $[CoCO_3(NH_3)_4]^+$, (b) $[CoCO_3(en)_2]^+$, (c) $[Coox(en)_2]^+$, and (d) $[CoCO_3(tn)_2]^+$ in D_2O or $HCl-D_2O$.

field signal to the *trans* amine and the lower field signal to the *cis* amine based on the magnetic anisotropy of the cobalt ion.[9] In the tetraammine and bis(trimethylenediamine) complexes, both *trans* and *cis* amine proton signals appear at higher fields than the HDO signal, while the bis(ethylenediamine) complexes give the *trans* amine signal at a higher field, and the *cis* one at a lower field, than the HDO signal, except that $[Coox(NH_3)_4]^+$ has only one broad signal at a higher field than HDO.

Figure 2 shows the time change in the amine proton signal intensities for $[Comal(NH_3)_4]^+$ in D_2O. It may be noted in this figure that the *trans* amine signal disappears about ten minutes after dissolution, but the *cis* one remains almost unchanged. Therefore, the exchange rate for the *trans* amine hydrogens is much faster than that for the *cis* ones.

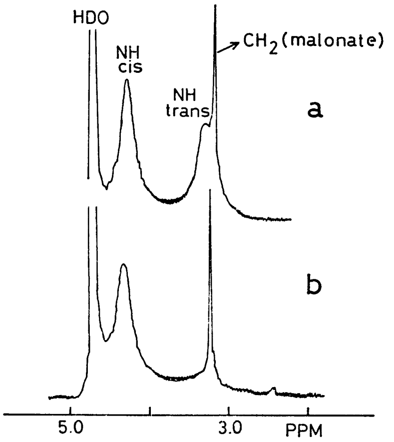

Fig. 2. The PMR spectra of $[Comal(NH_3)_4]^+$ in D_2O (a) immediately after dissolution, and (b) about ten minutes after dissolution.

The rate constant for the exchange is given by

$$\ln h_t = -kt + c$$

where h_t and k refer to the peak height of an amine proton signal at time t and the rate constant respectively, and where c is a constant. As is shown in Fig. 3, plots of log h_t against the time gave straight lines. The rate constants for hydrogen exchange were obtained from the slopes of these plots. It is known[10] that the pseudo-first-order rate constant is directly proportional to the concentration of OD^- ions:

$$k_{obsd} = k_0[OD^-]$$

where k_{obsd} and k_0 refer to the observed and the second-order rate constant respectively.

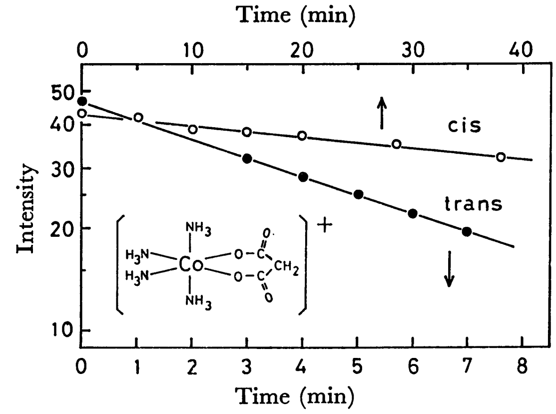

Fig. 3. Plots of log h_t vs. t. ●: *trans*, ○: *cis*.
Trans and *cis* amines correspond to the downward and upward scales respectively.

The rate-constant data obtained in this manner are collected in Table 2. The data are also plotted in Fig. 4. A comparison of these data indicates that: (1) *trans* amine protons are more labile than *cis* ones; (2) the

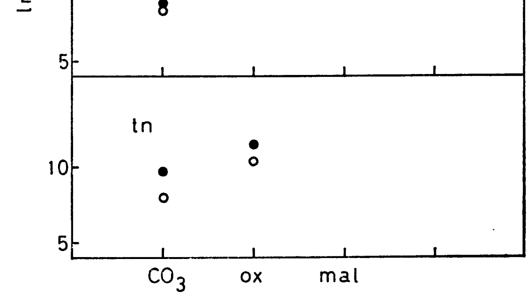

Fig. 4. Plots of ln k_0.
●: *trans*, ○: *cis*, ◐: not assigned.

Table 2. Rate constants for hydrogen exchange in $[Co(O)_2(N)_4]^+$ at 35 °C

k_{obsd}: observed rate constant ($s^{-1} \times 10^3$), k_0: second-order rate constant ($M^{-1} s^{-1} \times 10^{-4}$).

		CO_3			ox			mal			$(CH_3CO_2)_2$		
		pD[a]	k_{obsd}	k_0	pD	k_{obsd}	k_0	pD	k_{obsd}	k_0	pD	k_{obsd}	k_0
$(NH_3)_4$	*cis*	7.93	1.3	0.15	6.02	0.18	1.7[b]	6.41	0.14	0.54	6.75	0.34	0.60
	trans	7.93	2.2	0.26				6.41	2.1	8.2	6.75	4.6	8.2
$(en)_2$	*cis*	7.77	2.6	0.44	6.66	0.81	1.8	6.86	1.5	2.1			
	trans	7.77	4.1	0.70	6.66	4.0	8.8	6.86	5.4	7.5			
$(tn)_2$	*cis*	7.26	0.53	0.29	5.10	0.041	3.3						
	trans	7.26	3.0	1.7	5.10	0.13	9.9						

a) The pD was calculated using the formula pD=pH+0.4, in which pH is a value measured with a usual pH meter in D_2O. b) Not assigned to *cis* or *trans*.

rates for the carbonato complexes are slower than those for the oxalato and malonato analogs; (3) the difference between the rates for the *cis* and *trans* amines is much smaller in the carbonato complexes, and (4) this difference seems to be smaller in the complexes with chelated amines.

As has been mentioned before, the O–Co–O bond angle increases with an increase in the size of the dicarboxylato chelate ring. The deviation of the O–Co–O bond angle from the ideal octahedral value (90°) is greatest in the carbonato complex, and the coplanar N–Co–N bond angle is enlarged in comparison with the octahedral value. This effect will make the Co–N bond less stable, and the hydrogen exchange for *trans* amines will be decelerated. This is considered to be the reason why the rates for *trans* amines in the carbonato complexes are much slower than in the oxalato and malonato analogs. The rates for *trans* amines in the $[Coox(en)_2]^+$ and $[Comal(en)_2]^+$ ions are similar to each other, probably because the deviation of the O–Co–O bond angle is smaller in these complexes. Therefore, the difference in the steric effect between the oxalato and malonato ligands does not seem to be apparent in the hydrogen exchange, though this effect may play an important role in the base hydrolysis of these complex ions.[11]

If *cis* amines are not so much influenced by the carbonato chelate, the difference in the rates for *trans* and *cis* amines necessarily becomes smaller in the carbonato complexes. This seems to be the case with the tetraammine and bis(ethylenediamine) complexes.

The remarkable deceleration of the hydrogen exchange for *cis* amines in $[CoCO_3(tn)_2]^+$ is not clearly explicable. It may be due to the internal hydrogen bonding, as suggested by a study of the carbonate exchange in a basic medium.[12]

The difference between the rates for *trans* and *cis* amine protons is appreciably smaller in the bis(ethylenediamine) and bis(trimethylenediamine) complexes than in the tetraammine analogs. Though the origin of this difference is not known, it is probable that the alkyl bridge links the *cis* to the *trans* amine and imparts a similar bonding property to both amines. Therefore, the rate for *cis* amines will be more similar to the rate for *trans* amines in the chelate amine complexes than in the complexes with no chelated amines.

Factors other than steric ones which affect the rate of hydrogen exchange, will now be examined. The maxima of the first absorption bands are nearly equal. They are positioned at 522, 508, and 516 nm in, for example, the tetraammine complexes of the carbonate, oxalate, and malonate ions respectively, as is shown in Table 1; therefore, the ligand field effect seems insignificant. The ligand field of the carbonato ligand, however, is slightly weaker than that of the others, and one may think that the peculiarity of the rate for the carbonato complex is due to this slight difference in ligand field strength. To make it clear, the rate of amine hydrogen exchange in *cis*-$[Co(CH_3CO_2)_2(NH_3)_4]^+$ was measured, for which λ_{max} is almost equal to that for the corresponding carbonato complex, as is shown in Table 1. In contrast to this similarity in the ligand field strength, the rate for *cis*-$[Co(CH_3CO_2)_2(NH_3)_4]^+$ is much more analogous to that for the malonato complex than for the corresponding carbonato complex. This result supports our expectation that the ligand field effect is less important for the rate of amine hydrogen exchange.

Thus, it can be concluded that the difference in the rate of amine hydrogen exchange arises from the steric source and not from the ligand field effect, and that the peculiarity of the carbonato complexes probably originates from the remarkably strained chelate geometry, where the O–Co–O bond angle is *ca.* 70°. Then, this peculiarity leads us to expect that the *trans*-bond-weakening effect is larger in the carbonato complex than in the oxalato and malonato analogs, although this effect on the Co–N bond length is not clearly apparent in the reported crystal structures.[2] It was also found that the difference in the rate for *trans* and *cis* amines is smaller in the chelate amine complexes than in the complexes with no chelated amines. This suggests that the effect of a dicarboxylato ligand on *trans* and *cis* amines is averaged to some extent through the alkyl bridge of the amine chelate.

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