

rapidly as shown in eq 21 and 22. The ring closure reactions (eq 23) are quite fast for cobalt(III) complexes but are in accord with other examples of this type.^{13,14}

It is often the case that hypohalous acids oxidize a particular substrate faster than the oxidation by the corresponding halogen.¹⁵⁻¹⁸ This effect is seen in the present study, where k_3/k_1 is 80 for $[\text{Co}^{\text{II}}\text{CyDTA}]^{2-}$ and 890 for $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$. Contrary to the prediction which is made on the basis of electrostatics, hypobromite ion oxidizes $[\text{Co}^{\text{II}}\text{L}]^{2-}$ faster than hypobromous acid. The ratio k_4/k_3 is 310 for the CyDTA complex and 31 for EDTA. This effect is probably due to the increased magnitude of K_4 over K_3 (eq 17 and 18). Hypobromite ion is almost as strong a Bronsted base as CN^- or NH_3 , and this can be expected to be reflected in Lewis basicity as well. Thus, the increased coordinating strength of OBr^- over HOBr overcomes the electrostatic disadvantage in forming the inner-sphere intermediate with $[\text{Co}^{\text{II}}\text{L}]^{2-}$.

The ratios of the rate constants for a given oxidant with

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the EDTA compared to the CyDTA complexes are 37, 49, and 41 for the reactions with Br_2 , Br_3^- , and OBr^- , respectively, but the same ratio is 410 for the HOBr reaction. A ratio of approximately 50 is typical for the relative stabilities of monodentate ligands with metal-EDTA compared to metal-CyDTA complexes,¹ so that the behavior of Br_2 , Br_3^- , and OBr^- is consistent with the proposed inner-sphere mechanism. The larger ratio for HOBr suggests that an additional factor such as a more favorable hydrogen-bonding interaction between the coordinating HOBr and an acetate segment of the EDTA enhances the rate relative to the CyDTA complex.

In conclusion, hypobromite ion reacts faster than molecular bromine with $[\text{Co}^{\text{II}}\text{L}]^{2-}$ by factors of 2.4×10^4 to 2.6×10^4 and the relative rate constants and products are consistent with a mechanism in which the oxidation step is subsequent to coordination of the bromine or hypobromite moiety to the cobalt(II) complex.

Registry No. $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$, 14931-83-0; Br_2 , 7726-95-6; $[\text{Co}^{\text{II}}\text{CyDTA}]^{2-}$, 28161-91-3; Br_3^- , 14522-80-6; HOBr , 13517-11-8; OBr^- , 14380-62-2.

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Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210

Kinetic Trans Effect Exhibited in the Methanol Exchange of the $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ Complex

K. PLOTKIN, J. COPEs, and J. R. VRIESENGA*

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Nuclear magnetic relaxation times, T_2 , were determined as a function of temperature from the line shape analysis of methyl pmr resonances of the methanol coordinated cis and trans to the pyridine in $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$. From the T_2 data the first-order solvent-exchange rate constants were determined for the cis and trans sites. T_2 and shifts of the bulk solvent methyl resonances were measured and compared to the coordinated solvent nmr data. From this it was concluded that no internal rearrangement was taking place during exchange. This system was found to exhibit a clear-cut example of the kinetic trans effect for a labile octahedral complex in that the trans site exchange rate constant per coordinated methanol molecule was 2.5-3.0 times that for the cis site. The rate constants at -30° are 410 and 1200 sec^{-1} for the cis and trans sites, respectively. The values of ΔH^\ddagger and ΔS^\ddagger are respectively 11.9 kcal mol^{-1} and 2.9 eu for the cis site and 11.2 kcal mol^{-1} and 2.2 eu for the trans site.

Introduction

Mechanistic inferences¹⁻³ concerning substitution reactions of the first-row transition metal ions are usually based on rate data for direct substitution reactions and a knowledge of the solvent-exchange rates of most of the fully solvated first-row transition metal ions. Unfortunately, the continued development and extension of our understanding of this type of reaction to substituted divalent metal ions has reached somewhat of an impasse for lack of the appropriate experimental solvent-exchange rate data. In an attempt to circumvent this impasse for at least one chemical system and thereby to establish a model system, efforts in this laboratory have been directed toward measuring the methanol-exchange rate of cobalt(II) complexes.^{4,5} The reasons for choosing this

system have been discussed in a previous publication.⁴

This paper reports the methanol-exchange rate data for the methanols cis and trans to pyridine (py) in $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$. Pyridine was chosen for this study because of the rather extensive evidence that it possesses π -acceptor properties when coordinated to Co^{2+} .⁶ The first exploratory steps in determining what effect a π -acceptor ligand has on the methanol-exchange rates of octahedral cobalt(II) complexes are reported here. Proton nmr was used to measure the line width of both the coordinated and bulk methanol methyl resonances as a function of temperature.

Experimental Section

Sample Preparation. An anhydrous methanol solution of cobaltous perchlorate was prepared by adding cobaltous perchlorate

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to methanol and treating repeatedly with Linde 3A molecular sieves. The solution was considered anhydrous when no coordinated methanol methyl resonance for the cis coordination site in $\text{Co}(\text{CH}_3\text{OH})_5\text{OH}_2^{2+}$ could be detected. The concentration of Co^{2+} was determined by an EDTA back-titration with Zn^{2+} using Eriochrome Black T as an indicator.⁷ The pyridine was weighed out in 5-ml volumetric flasks fitted with serum caps. Sufficient Co^{2+} solution containing approximately 2% TMS was introduced with a syringe into the flask to make a total of 5 ml of solution. A positive pressure of dry nitrogen was maintained in the flask during all solution-transfer operations. The sample was transferred to the nmr tube under a constant flow of dry nitrogen and the nmr tube was sealed with a pressure cap and coated over with silicone rubber cement. The samples appeared to be indefinitely stable to oxidation and uptake of water.

All the shift and relaxation data for the coordinated and bulk solvent resonances were made on samples having a total Co^{2+} concentration of 0.165 and 0.240 *M* with a total pyridine concentration of 0.0744 and 0.101 *M*, respectively.

Instrumentation and Measurements. All nmr measurements were made on a Jeolco 4H-100 100-MHz instrument. The spectrum was acquired as a 1000 data point digital representation in a minicomputer and was subsequently transferred to a PDP-10 where a total line shape analysis of the spectrum was carried out. A more complete description of the instrument, its modifications, the data acquisition system, and the data processing system is given elsewhere.⁴

The kinetic information is obtained from the nuclear magnetic relaxation times, T_2 , and shifts of the methanol methyl resonances of both the coordinated and bulk solvent. T_2 is obtained from line shape analysis of the nmr resonances, where the half-width at half-height, expressed in radians per second, is the reciprocal of T_2 . The equations relating the experimental data to the kinetic parameters are most conveniently expressed in terms of line widths, $1/T_2$; therefore, the subsequent presentation of data and its discussion will be expressed in terms of line widths rather than relaxation times. Digital techniques for data acquisition and processing are necessary to obtain accurate values of T_2 and relative integrated intensities of overlapping resonances. Numerical data processing techniques are a necessary adjunct in obtaining accurate shifts of bulk solvent resonances because the maximum of the observed line is a sensitive function of the phasing of the signal (*i.e.*, the amount of dispersion in the signal). The computer programs for processing the data take into account the necessary phasing corrections.

All measurements were carried out under conditions of slow passage and nonsaturation. The temperature was maintained to within $\pm 0.2^\circ$.

Data and Results

At sufficiently low temperatures (-50 to -100°) the various proton nmr resonances of methanol and pyridine coordinated to cobalt(II) can be observed. It was observed from these measurements that if the total cobalt concentration is in sufficient excess (0.1 *M* or greater) over the total pyridine concentration, only $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ and $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ exist in appreciable concentrations. If this condition was not satisfied, resonances of higher complexes were observed. The ring proton resonances of the coordinated pyridine were identified by the line widths, the behavior of the line widths as a function of temperature, and comparison to spectra using pyridine-*d*₆. At -53° the 2 and 6 ring protons and the 3 and 5 ring protons had resonances at 11,000 and 3800 Hz downfield, respectively. These assignments are in substantial agreement with those reported for cobalt(II)-pyridine complexes in water-acetone mixtures.⁸ It was also noted that the amplitude of the ring proton resonances of the higher complexes diminished relative to the resonances of the mono complex without broadening when the temperature was increased, thus indicating a decreasing stability of the higher complexes relative to the mono complex with increasing temperature.

The exchange rate data were obtained by observing the transverse relaxation times, T_2 , of the methyl protons of the

coordinated methanol. The observed shifts for these resonances are a result of both the isotropic contact⁹ and dipolar¹⁰ (pseudocontact) interactions. The experimentally measured shifts, ω_1 (sec^{-1}), are summarized in terms of the empirical equation

$$\omega_1 = a_i(1/T) + b_i \quad (1)$$

where the subscript *i* indicates to which resonance the associated parameters correspond, and *T* is absolute temperature. The experimentally determined parameters, a_i and b_i , are given in Table I.

Methanol exchange of the appropriate rate between two or more different magnetic environments can provide a mechanism for transverse relaxation, T_2 , which is physically manifested as line broadening. The observed line width of the coordinated solvent resonances can be expressed as the following limiting form of the equations developed by Swift and Connick¹¹

$$(1/T_{2i})_c = (1/T_{2i}^0)_c + 1/\tau_i \quad (2)$$

where $(1/T_{2i})_c$ and $(1/T_{2i}^0)_c$ are the observed line width and the line width in the absence of exchange (natural line width) of the *i*th coordinated solvent resonance, and τ_i is the mean lifetime of a methanol molecule in the *i*th magnetic environment. At low temperatures, where $1/\tau_i$ is approximately zero, the observed line width is equal to the natural line width. It has been found that the natural line width can be adequately described by the function^{2,3}

$$(1/T_{2i}^0)_c = A_i \exp(-E_i/RT) \quad (3)$$

where A_i and E_i are determined from the observed line width data in the appropriate temperature range. The values of A_i and B_i are given in Table I. The line width data for the $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ and *cis*- and *trans*- $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ resonances for all temperatures studied are summarized in Table II. $1/\tau_{\text{cis}}$ can then be determined by subtracting the computed value of the natural line width from the observed line width. Figure 1 shows the relationship of $1/\tau_{\text{cis}}$ and $1/\tau_{\text{trans}}$ to the observed line width data. Probably the most salient feature of these data is that the mean lifetime of a methanol molecule in the *trans* environment is only 0.4 of that in the *cis*. The only other report of this type of behavior has been for the $\text{Co}(\text{CH}_3\text{OH})_5\text{Cl}^{2+}$ complex.¹²

It is possible that the observed values of τ_i for the *cis* and *trans* resonances are not exclusively a function of exchange with bulk solvent (solvent exchange), but rather a composite result of exchange with the bulk and exchange between the *cis* and *trans* sites (internal rearrangement). This can be expressed algebraically as

$$1/\tau_i = 1/\tau_i^{\text{ex}} + 1/\tau_i^{\text{int}} \quad (4)$$

where τ_i^{ex} and τ_i^{int} are the mean lifetimes with respect to exchange and internal rearrangement, respectively.

The magnitude of τ_i^{int} can be obtained by measuring the overall solvent-exchange rate constant for the pyridine complex from bulk solvent relaxation data. Swift and Connick¹¹ have derived an equation from which the bulk solvent methyl line widths and shifts can be calculated in terms of ω_1 , τ_i^{ex} , τ_i^{int} , and the natural line widths. This equation assumes that the population of methanol molecules in the bulk environ-

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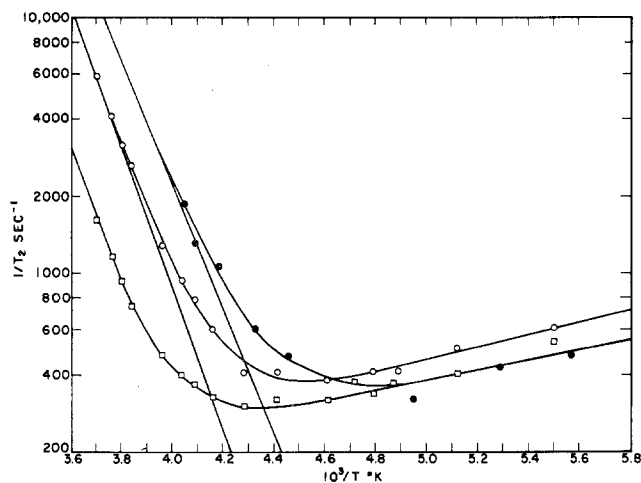
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Table I. Parameters Describing the Temperature Dependence of the Coordinated Methanol Methyl Resonance Shifts and Natural Line Widths of $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ and *cis*- and *trans*- $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$

Complex (i)	Shift parameters (see eq 1)		Natural line width parameters (see eq 3)	
	a_i	b_i	A_i	B_i
$\text{Co}(\text{CH}_3\text{OH})_6^{2+}$				
Cis	1.61×10^7	-11,100	26.1	-1140
Trans	-4.40×10^6	38,800	21.3	-1140
$\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$	9.24×10^6	7,270	21.9	-1140

Table II. Line Widths^a of Coordinated Methanol Methyl Resonances of *cis*- and *trans*- $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ and $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$

Part A			Part B	
Temp, °C	<i>cis</i> - $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$	$\text{Co}(\text{CH}_3\text{OH})_6^{2+}$	Temp, °C	<i>trans</i> - $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$
-2.7	5900	1608	-25.9	1846
-7.0	4180	1080	-28.5	1256
-9.9	3170	936	-33.6	1049
-12.6	3680	735	-42.2	609
-20.4	1290	484	-49.0	477
-25.5	942	408	-61.1	371
-28.7	791	377	-71.1	320
-32.5	609	333	-84.1	427
-39.5	408	301	-93.4	471
-46.3	408	320		
-55.0	377	327		
-64.4	414	329		
-67.7	408	377		
-77.5	509	414		
-91.2	603	559		

^a Units sec^{-1} .**Figure 1.** The log of the observed line width, $(1/T_2)_c$, of the coordinated methanol resonances for $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ (\square) and *cis*- (\circ) and *trans*- (\bullet) $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ plotted vs. the reciprocal of absolute temperature, $1/T$. The corresponding straight lines are the log of $1/\tau_{\text{cis}}$ and $1/\tau_{\text{trans}}$ plotted vs. $1/T$.

ment is much greater than that in the coordinated environment. The sample concentrations used in this work satisfied this condition. It can be shown using numerical evaluation of the Swift and Connick expression for three-site exchange that the bulk line widths and shifts are to a very good approximation independent of the *cis-trans* exchange, τ_1^{int} , over the entire relevant temperature range, encompassing both the exchange- and relaxation-controlled regions. Consequently, only τ_1^{ex} will affect the line width of the bulk solvent resonance. Thus, from comparison of τ_1^{ex} computed from the bulk solvent relaxation data and τ_1 obtained from direct observation of the coordinated solvent resonances one can gain information on the rate of internal rearrangement. By setting $1/\tau_1^{\text{int}} = 0$ one can derive the expressions 5-7 for

the line widths and shift of the bulk solvent from the more general expression of Swift and Connick.¹¹ The advantage of these equations over the much more complex expression involving τ_1^{int} is that the individual contributions of each type of magnetic environment to the bulk line width and shift can be clearly identified. $(1/T_2)_B$ and $(1/T_2^0)_B$ are the

$$(1/T_2)_B = (1/T_2^0)_B + \sum (1/T_{2i}^{\text{ex}})_B \quad (5)$$

$$(1/T_{2i}^{\text{ex}})_B = P_i \frac{(1/T_{2i}^0)_c^2 \tau_i^{\text{ex}} + (1/T_{2i}^0)_c + \tau_i^{\text{ex}} \omega_i^2}{(1 + (1/T_{2i}^0)_c \tau_i^{\text{ex}})^2 + (\tau_i^{\text{ex}} \omega_i)^2} \quad (6)$$

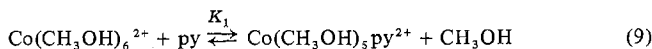
$$\Delta\omega_B = \Delta\omega_B^0 + \sum_i \frac{P_i \omega_i}{(1 + (1/T_{2i}^0)_c \tau_i^{\text{ex}})^2 + (\tau_i^{\text{ex}} \omega_i)^2} \quad (7)$$

methanol methyl line widths of the bulk solvent in the presence and in the absence of exchange (natural line width), respectively. $(1/T_{2i}^{\text{ex}})_B$ is the contribution to the bulk solvent line width due to exchange with the *i*th coordination site to the number of moles in the bulk solvent, and $\Delta\omega_B$ and $\Delta\omega_B^0$ are the bulk solvent shifts relative to TMS in the presence and absence of exchange, respectively. All other terms have their previously defined meaning. The temperature dependence of $(1/T_2^0)_B$ can be described by a function analogous to eq 3 having the experimentally determined parameters A_B and E_B of 6.2 sec^{-1} and $0.8 \text{ kcal mol}^{-1}$ (for the sample $0.165 M$ in Co^{2+}). These parameters were determined in a manner analogous to those for the natural line widths of coordinated solvent resonances. The observed bulk solvent line widths and shifts are given in Table III. $1/\tau_i^{\text{ex}}$ is equal to a pseudo-first-order rate constant, k_i , for the exchange of a solvent molecule from the *i*th coordination site. The temperature dependence can be expressed as

$$\tau_i^{\text{ex}} = 1/k_i = h/kT \exp((\Delta H^\ddagger - T\Delta S^\ddagger)/RT) \quad (8)$$

where ΔH^\ddagger and ΔS^\ddagger are the enthalpy and entropy of activation, respectively, and the other constants have their usual meaning.

ω_i and the various coordinated solvent natural line widths needed in eq 5-7 to compute bulk solvent line widths and shifts were obtained directly from the coordinated solvent nmr measurements. In order to calculate P_i at various temperatures, it is necessary to know the concentration of each species in solution. These concentrations are determined from the relative areas under coordinated methanol methyl resonance of the *cis* pyridine complex and $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$. These measurements were made on the same sample as were the bulk solvent measurements. The ratios of concentrations of $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ to $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$, Q , as a function of temperature are shown in Figure 2. In order to make the desired calculations, P_i must be known for higher temperatures than can be obtained by direct observation of the coordinated solvent resonances; thus, Q must be extrapolated to higher temperatures. This extrapolation is also shown in Figure 2. The straight-line extrapolation of the observed values of $\log Q$ assumes that ΔH of the following equilibrium is small



To test these assumptions the formation constant, K_1 , was determined as a function of temperature. The procedures and data will be presented in a separate publication.¹³ The assumptions were found to be very good since ΔH was measured to be only $-2.6 \text{ kcal mol}^{-1}$ and K_1 was 530 at -30° .¹⁴

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(14) $K_1 = [\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}][\text{CH}_3\text{OH}]/[\text{Co}(\text{CH}_3\text{OH})_6^{2+}][\text{py}]$.

Table III. Observed and Computed Line Widths and Shifts of the Bulk Methanol Methyl Resonance

A. Line Widths ^a						
Temp, °C	Total line widths, $(1/T_2)_B$		Natural line, width, $(1/T_2)_B$	Predicted contributions of $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$		$(1/T_{2i})_B$ of $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$
	Obsd	Calcd		Cis	Trans	
[Co ²⁺] _{total} = 0.165 M, [py] _{total} = 0.0744 M						
11.3	339	324	24	117	20	161
5.6	245	230	26	83	22	99
-0.5	151	158	27	53	21	57
-6.5	94	110	28	33	17	32
-12.8	73	76	29	19	11	17
-27.1	35	44	32	5	3	4
[Co ²⁺] _{total} = 0.240 M, [py] _{total} = 0.101 M						
11.3	490	453	36	159	27	231
5.6	351	327	37	113	30	147
-27.1	51	59	43	7	4	5

B. Shifts^b

Temp, °C	Exchange contribution to shifts, $c \Delta\omega_B - \Delta\omega_B$		Predicted contributions		
	Obsd	Calcd	$\text{Co}(\text{CH}_3\text{OH})\text{py}^{2+}$		$\text{Co}(\text{CH}_3\text{OH})_6^{2+}$
			Cis	Trans	
11.3	90	101	46	33	22
5.6	41	53	20	25	8
-0.5	25	25	8	15	2
-6.5	13	11	3	7	1
-12.8	6	4	1	3	0
-21.3	0				
-27.1	0				

^a All line widths are in sec^{-1} . ^b All shifts are in sec^{-1} and measured relative to TMS. ^c $\Delta\omega_B$ was taken to be 2173 sec^{-1} .

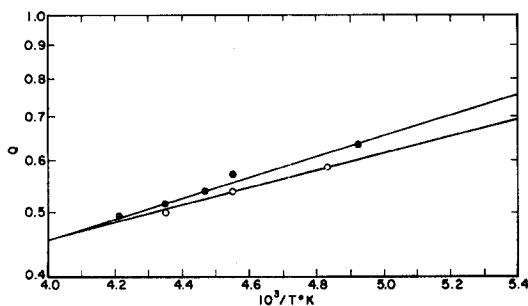


Figure 2. The ratio of areas, Q , of the cis methanol methyl resonance of $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ to the coordinated solvent methyl resonance of $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ vs. the reciprocal of absolute temperature, $1/T$: ●, 0.165 M Co^{2+} and 0.0744 M pyridine; ○, 0.240 M Co^{2+} and 0.101 M pyridine.

Excellent agreement between the predicted and observed line width and shift data is obtained if one assumes that no internal rearrangement is taking place, namely, $1/\tau_1^{\text{int}} = 0$. The predicted contributions of each type of coordination site to the bulk line width and shift as well as the observed and total predicted contributions are given in Table III. The good agreement for the line width data extended into the temperature region where the bulk solvent relaxation rate is a function of both exchange and the so-called $\Delta\omega$ mechanism.¹¹ Both the shifts and line widths are a function of the same parameters, namely, P_1 , ω_1 , τ_1^{ex} , and $(1/T_{2i})_B$, but they have different functional dependencies on these parameters. For example, in the exchange-controlled region (slow exchange region) the shifts are related to $(\tau_1^{\text{ex}})^{-2}$ and the line widths are related $(\tau_1^{\text{ex}})^{-1}$. The fact that there is good agreement between the predicted and observed results, even when they are expressed by very different functional relationships, indicates the internal consistency of the coordinated and bulk data line width and shift data and that the temperature-

dependent composition of the solution has been accurately assessed.

The good agreement between the observed and predicted line width and shift data for the bulk solvent indicates that there is no appreciable contribution to the coordinated solvent line width by internal rearrangement. Therefore, a kinetic trans effect is observed where the rate of trans methanol exchange is approximately 2.5–3.0 times that of the cis (per coordinated solvent molecule). At -30° k_{cis} and k_{trans} are 405 and 1200 sec^{-1} , respectively. The corresponding activation parameters, ΔH^\ddagger and ΔS^\ddagger , are 11.9 and $11.3 \text{ kcal mol}^{-1}$ and 2.9 and 2.2 eu, respectively. The values of k , ΔH^\ddagger , and ΔS^\ddagger for $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$ are 95 sec^{-1} (-30°), $13.0 \text{ kcal mol}^{-1}$, and 4.2 eu, which are in good agreement with previously reported values.^{4,5,15}

Discussion

It is generally observed that complexation of a transition metal ion results in the enhancement of the solvent-exchange rate of the remaining coordinated solvent relative to the fully solvated ion. The $\text{Co}(\text{CH}_3\text{OH})_5\text{py}^{2+}$ complex is no exception. At -30° the cis and trans exchange rate constants are respectively 4 and 12 times that for $\text{Co}(\text{CH}_3\text{OH})_6^{2+}$. The only other monosubstituted cobalt(II) complex having a 2+ charge for which the methanol exchange rate constants are known is $\text{Co}(\text{CH}_3\text{OH})_5\text{OH}_2^{2+}$ ($k_{\text{cis}} = k_{\text{trans}} = 610 \text{ sec}^{-1}$).⁵ There are a number of differences between the aquo and pyridine complexes which may possibly account for the differences in methanol-exchange rates. There is in the literature substantial evidence to indicate that appreciable π -bonding interactions exist in cobalt(II)-pyridine complexes.⁶ Such bonding would not be possible in the aquo complex. A second difference is that pyridine is a stronger base than water and, therefore, may result in stronger σ bonding. Strengths of σ bonding have been used to rationalize various kinetic effects in $\text{Pt}(\text{II})$ ^{16,17} and $\text{Co}(\text{III})$ ¹⁸ complexes. For methanol exchange of cobalt(II) complexes there is as yet too little experimental information to make correlations and draw conclusions about such effects.

It is of interest to note that the comparison of the solvent-exchange rate data for aquo and pyridine complexes provides a clear example of the added information obtained when solvent-exchange rates are measured using both coordinated solvent and bulk solvent relaxation times. For the pyridine complex the coordinated solvent shifts and exchange rate constants are such that if only bulk solvent relaxation data were measured, an average exchange rate constant very near that for the aquo complex would be obtained. Yet, the overall kinetics of the two systems are quite different.

Probably the most significant result of this study is the clear-cut demonstration of the kinetic trans effect operative in a labile octahedral complex. Relaxation data reported for the methyl resonance of the coordinated methanol in $\text{Co}(\text{CH}_3\text{OH})_5\text{Cl}^+$ indicate that the kinetic trans effect could also be operative in this system.¹² Unfortunately, very poor correlation between the bulk and coordinated solvent nmr measurements was found,¹⁹ thus leaving the interpretation of the coordinated solvent relaxation data unresolved. There is much evidence for the existence of the kinetic trans effect

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in less labile octahedral transition metal complexes.^{16,17} For the most part, this evidence tends to be inconclusive because of the existence of complicating side reactions having about the same rate and activation energy as the kinetic process being studied. This is especially true for Co(III) and Pt(IV) complexes where spontaneous and catalyzed internal rearrangements cloud the interpretation of the kinetic data.¹⁶⁻¹⁸

The measurement of methanol exchange of cobalt(II) complexes is not hindered by side reactions and should, therefore, provide a very useful system for studying kinetic *cis* and *trans* effects in octahedral complexes. Poe and coworkers have measured the effect of various ligands on the substitution rates of the *trans* sites in Rh(III) complexes but have not established whether this is a general labilization effect or a result of a specific *trans*-directing effect of the ligand.²⁰

Finally, this study does provide some insight into the nature of the intermediates or activated complexes for the exchange process. There is a considerable body of information in the

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literature which tends to indicate that the substitution mechanisms of the first-row transition metal ions are primarily dissociative in nature.^{1-3,21} This study and previous work in this laboratory^{1,5} indicate that no internal rearrangement takes place when methanol exchanges with monosubstituted cobalt(II) complexes. Taking these two observations into account, it is most likely that the reaction does not proceed by a five-coordinate trigonal-bipyramidal intermediate or activated complex.

Measurements of the methanol-exchange rates of a variety of other Co²⁺ complexes are presently under way in this laboratory.

Registry No. Co(CH₃OH)₅py²⁺, 39208-17-8; Co(CH₃-OH)₆²⁺, 15276-50-3.

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Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

Stereochemical Studies of Metal Chelates. X.¹ Preparation and Stereochemistry of Diacidocobalt(III) Complexes Coordinated with (4*R*,5*S*)-Dimethyl-3,6-diaza-1,8-diaminooctane and Its Optically Active Derivatives

MASAFUMI GOTO, HAJIME MATSUSHITA, MASAHIKO SABURI, and SADA O YOSHIKAWA*

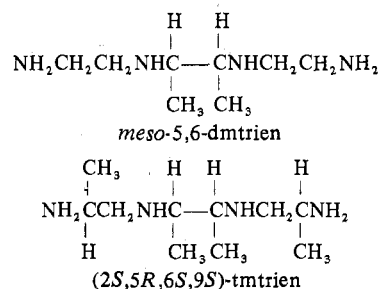
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The preparation and characterization of isomers of dichloro- and dinitrocobalt(III) complexes containing (4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane (abbreviated as *meso*-5,6-dmtrien) and (5*R*,6*S*)-dimethyl-4,7-diaza-(2*S*,9*S*)-diaminodecane [abbreviated as (2*S*,5*R*,6*S*,9*S*)-tmtrien] are reported. One type of *cis*- β isomer and one type of *trans* isomer were isolated, and another *trans* form was detected for the complexes of *meso*-5,6-dmtrien. The stereochemistry of these complexes was studied in detail by means of proton magnetic resonance (pmr) and circular dichroism (CD). The absolute configurations of the coordinated secondary nitrogen atoms were antimeric (*R* and *S*) for the *cis*- β isomers. The isolated *trans* isomer had the *meso*-*trans* structure, in which the conformation of the central chelate ring was an envelope form. The complexes prepared in this study showed some behaviors in reactivities different from those of triethylenetetramine complexes, owing to the difference in the coordination mode of the secondary amine groups of the ligands.

A number of publications have described cobalt(III) complexes containing tetradentate ligands, especially tetramines. It has been observed that several specific geometrical isomers are preferably obtained when the ligands having asymmetric substituents at the carbon atoms of triethylenetetramine (trien) are employed.¹⁻⁶ The structures of these complexes have been explained in relation to the configurations and position of the substituents in the trien skeleton. For all the methyl-substituted triens, the methyl group(s) adopted pre-

ferentially the equatorial orientation with respect to the *gauche* five-membered chelate ring.

The ligands prepared in the present study, (4*R*,5*S*)-dimethyl-3,6-diaza-1,8-diaminooctane (*meso*-5,6-dmtrien) and (5*R*,6*S*)-dimethyl-3,7-diaza-(2*S*,9*S*)-diaminodecane [abbreviated as (2*S*,5*R*,6*S*,9*S*)-tmtrien], have two methyl groups derived from *meso*-butane-2,3-diamine (*meso*-bn) in the central chelate ring. The *meso*-bn linkage may coordinate to a



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