to those of the binary molecules as illustrated in Table III.

Registry No. I_2, 7553-56-2; Cl_2, 7782-50-5; IBr, 7789-33-5; $SbCl_5$, 7647-18-9; $(I_2Cl)SbCl_6$, 38656-79-0; $(BrICl)SbCl_6$, 38656-80-3; $(ICl_2)SbCl_6$, 38656-81-4.

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Proton Nuclear Magnetic Resonance Determination of the Cis and Trans Methanol Exchange Rates of $Co(CH_3OH)_5OH_2{}^{2+}$

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The methanol-exchange rate constants per coordinated solvent molecule for the methanols cis and trans to H_2O in $Co(CH_3OH)_5OH_2{}^{2+}$ were determined by direct observation of the methyl proton resonances of the coordinated methanol. The composition of the sample as a function of temperature was obtained by measuring the relative integrated intensities of the cis aquo complex resonance and that corresponding to $Co(CH_3OH)_6{}^{2+}$. With this information it was possible to interpret the exchange-induced relaxation and shifts of the bulk methanol methyl resonance in terms of an overall solvent-exchange rate constant. Comparison of the exchange data from the coordinated and bulk resonances indicated there was no exchange-induced rearrangement taking place in the aquo complex. The cis and trans sites were found to have equal exchange rate constants *per coordinated methanol* (609 sec^{-1} at $-30°$). The enthalpy and entropy of activation were 12.8 kcal mol^{-1} and 6.9_6 eu, respectively.

It is well established that the measurement and understanding of solvent-exchange rates is, in general, an important key to understanding the kinetics of substitution reactions for labile octahedral complexes.[1] Studies of the methanol-exchange rates of a number of $Co(CH_3OH)_5X^n$ complexes are being undertaken in this laboratory in an attempt to correlate the observed exchange kinetics with the properties of the monodentate ligands X (where n is the charge on the complex).[2] The reasons for studying the $Co(CH_3OH)_5OH_2{}^{2+}$ complex are twofold. First, significant differences between the kinetic parameters observed in this laboratory and those of a previous study were found.[3] Second, water is a common "impurity" in the cobalt(II)-methanol system and for that reason it is desirable to have a firm understanding of its effect on the methanol-exchange rates.

Variable-temperature studies of the transverse relaxation times and shifts of both the coordinated and bulk methanol methyl resonances are reported in this paper. A much more complete study of the bulk solvent resonance than in the previous study[2] was made and yielded more definitive results concerning the kinetic trans effect and internal rearrangements in the aquo complex.

Experimental Section

Sample Preparation. An anhydrous methanol solution of cobaltous perchlorate was prepared by adding cobaltous perchlorate to methanol and treating repeatedly with Linde 3A molecular sieves. The solution was considered sufficiently anhydrous when no coordinated methanol methyl resonance for the cis coordination site in $Co(CH_3OH)_5OH_2{}^{2+}$ 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.[4] The water was introduced into the sample with a microliter syringe fitted with a device for reproducible ejection of aliquots, and the size of the aliquot was calibrated with mercury. All the shift and relaxation data for the coordinated and bulk solvent resonances were made on samples having a total Co^{2+} concentration of 0.216 M and a total water concentration of 0.470 M. All samples were prepared in a glove bag under dry nitrogen.

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.[2]

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 their 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 ±0.2°.

Data and Results

For the reagent concentrations used in this study, the only nmr resonances observed were for the $Co(CH_3OH)_6{}^{2+}$ and $Co(CH_3OH)_5OH_2{}^{2+}$ complexes. The two most intense resonances observed were, of course, those of the bulk methanol hydroxyl and methyl protons. Three much less intense resonances located downfield relative to the bulk methyl resonance were identified as the methyl resonances of the meth-

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[1] (a) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970); (b) A. McAuly and J. Hill, *Quart. Rev., Chem. Soc.*, **23**, 18 (1969).

[2] J. R. Vriesenga, *Inorg. Chem.*, in press.

[3] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 40, 1058 (1964).

[4] F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," Van Nostrand, Princeton, N. J., 1958.

anol coordinated to $Co(CH_3OH)_6{}^{2+}$ and of the methanol cis and trans to H_2O in $Co(CH_3OH)_5OH_2{}^{2+}$. The downfield shifts at −73° relative to the bulk methyl resonance are 8450, 7200, and 11,100 Hz, respectively. Procedures for identifying the resonances were the same as those reported previously.[2,3] The observed shifts are a result of both the isotropic contact[5] and dipolar[6] (pseudocontact) interactions. The experimentally measured shifts, ω_i (sec^{-1}), are summarized in terms of the empirical equation

$$\omega_i = a_i(1/T) + b_i \tag{1}$$

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

Methanol exchange at the appropriate rate between two or more different magnetic environments can provide an additional mechanism for transverse relaxation, T_2, 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 Connick[7]

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

where $(1/T_{2i})_c$ and $(1/T^0{}_{2i})_c$ are the observed line width and the line width in the absence of exchange (natural line width) of the ith coordinated solvent resonance and τ_i is the mean lifetime of a methanol molecule in the ith magnetic envirronment. 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]

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

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 $Co(CH_3OH)_6{}^{2+}$ and *cis*- and *trans*-$Co(CH_3OH)_5OH^{2+}$ resonances are summarized in Table II. $1/\tau_i$ 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 $1/\tau_{cis}$ and $1/\tau_{trans}$ to the observed line width data.

It is possible that the observed value 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

$$1/\tau_i = 1/\tau_i{}^{ex} + 1/\tau_i{}^{int} \tag{4}$$

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

The magnitude of $\tau_i{}^{int}$ can be obtained by measuring the overall solvent-exchange rate constant for the aquo complex from bulk solvent relaxation data. Swift and Connick[7] have derived an equation from which the bulk solvent methyl line widths and shifts can be calculated in terms of ω_i, $\tau_i{}^{ex}$, $\tau_i{}^{int}$, and the natural line widths. This equation assumes that the population of methanol molecules in the bulk environment 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, that the bulk line widths and shifts are to a very good approximation independent of the value of $\tau_i{}^{int}$ over the entire relevant temperature range, encompassing both the exchange- and relaxation-controlled regions. Consequently only $\tau_i{}^{ex}$ will affect the line width of the bulk solvent resonance. Thus, from comparison of $\tau_i{}^{ex}$ computed from the bulk solvent relaxation rate and τ_i obtained from direct observation of the coordinated solvent resonances one can gain information on the rate of internal rearrangement. The following expressions for the line widths and shift of the bulk solvent have been derived by Swift and Connick for the case $1/\tau_i{}^{int} = 0$.[7] The advantage of these equations over the much more complex expression involving $\tau_i{}^{int}$ is that the individual contributions of each

Table I. Parameters Describing the Temperature Dependence of the Coordinated Methanol Methyl Resonance Shifts and Natural Line Widths of $Co(CH_3OH)_6{}^{2+}$ and *cis*- and *trans*-$Co(CH_3OH)_5OH_2{}^{2+}$

Complex (i)	Shift parameters (see eq 1)		Natural line width parameters (see eq 3)	
	a_i	b_i	A_i	E_i
$Co(CH_3OH)_5OH_2{}^{2+}$				
Cis	6.26×10^6	14,300	58.2	−805
Trans	1.54×10^7	−7,220	88.8	−710
$Co(CH_3OH)_6{}^{2+}$	8.63×10^6	9,830	58.2	−805

Table II. Line Widths[a] of Coordinated Methanol Methyl Resonances of *cis*- and *trans*-$Co(CH_3OH)_5OH_2{}^{2+}$ and $Co(CH_3OH)_6{}^{2+}$

	$Co(CH_3OH)_5OH_2{}^{2+}$		
Temp, °C	Cis	Trans	$Co(CH_3OH)_6{}^{2+}$
−23.2	1162	1269	448
−27.0		1062	
−28.7	816	1017	395
−30.9	684	830	340
−32.5	659		379
−35.0	605	650	366
−37.6	494	615	385
−40.8	471	567	367
−45.6		502	
−50.1	404	472	387
−57.3		516	
−70.2	425	496	425
−80.0		515	
−85.6	519	710	519
−91.3		645	

[a] Units of sec^{-1}.

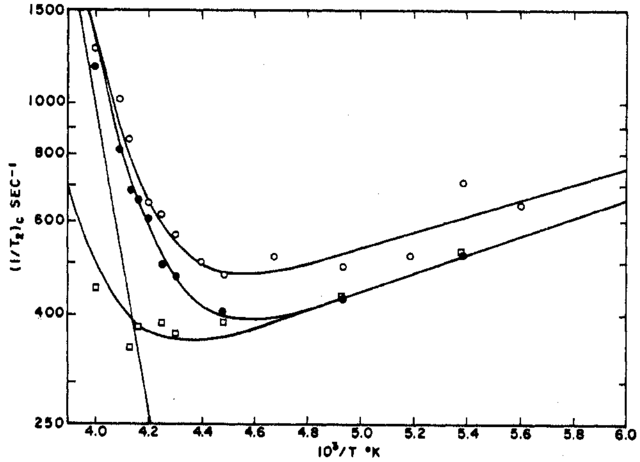

Figure 1. The log of the observed line width, $(1/T_2)_c$, of the coordinated methanol methyl resonances for $Co(CH_3OH)_6{}^{2+}$ (□) and the cis (●) and trans (○) isomers of $Co(CH_3OH)_5OH_2{}^{2+}$ plotted *vs.* the reciprocal of absolute temperature, $1/T$. The straight line is the log of $1/\tau_{cis}$ and $1/\tau_{trans}$ plotted *vs.* $1/T$.

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(5) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).

(6) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, 2, 286 (1970).

(7) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

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

A. Line Widths[a]

	Total line widths, $(1/T_2)_B$		Natural line width,	Predicted contributions of $Co(CH_3OH)_5OH_2{}^{2+}$		$(1/T_{2i}{}^{ex})_B$ of
Temp, °C	Obsd	Calcd	$(1/T^0{}_2)_B$	Cis	Trans	$Co(CH_3OH)_6{}^{2+}$
6.3	409	421	30	217	59	115
4.0	360	364	31	189	50	93
−2.3	235	232	32	118	30	52
−6.8	176	166	33	80	20	34
−13.5	104	104	34	42	10	17
−19.5	60	73	35	23	6	9
−30.0	37	50	38	7	2	3
−50.3	46	44	44			
−71.3	52	53	53			

B. Shifts

	Obsd shift,	Exchange contribution to shifts,[c] $\Delta\omega_B - \Delta\omega^0{}_B$		Predicted contributions		
				$Co(CH_3OH)_6OH_2{}^{2+}$		
Temp, °C	$\Delta\omega_B$[b]	Obsd	Calcd	Cis	Trans	$Co(CH_3OH)_6{}^{2+}$
6.3	2342	142	132	101	21	10
4.0	2292	91	93	72	14	7
−2.3	2248	43	32	25	5	2
−6.8	2217	10	14	11	2	1
−13.5	2210					
−19.3	2213					
−30.0	2214					
−50.3	2227					
−71.3	2258					

[a] All line widths are in sec^{-1}. [b] All shifts are in sec^{-1} and measured relative to TMS. [c] $\Delta\omega^0{}_B$ exhibits a slight temperature dependence and can be expressed as $\Delta\omega^0{}_B = 2069 \exp(34.0/RT)$.

type of magnetic environment to the bulk line width and shift can be clearly identified.

$$(1/T_2)_B = (1/T^0{}_2)_B + \sum_i (1/T_{2i}{}^{ex})_B \tag{5}$$

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

$$\Delta\omega_B = \Delta\omega^0{}_B + \sum_i \frac{P_i\omega_i}{(1 + (1/T^0{}_{2i})_c \tau_i{}^{ex})^2 + (\tau_i\omega_i)^2} \tag{7}$$

$(1/T_2)_B$ and $(1/T^0{}_2)_B$ are the methanol methyl line widths of the bulk solvent in the presence and in the absence of exchange (natural line width), respectively. $(1/T_{2i}{}^{ex})_B$ is the contribution to the bulk solvent line width due to exchange with the ith coordination site, P_i is the ratio of the number of moles of methanol in the ith coordination site to the number of moles in the bulk solvent, and $\Delta\omega_B$ and $\Delta\omega^0{}_B$ are the bulk solvent shifts relative to TMS in the presences and absences of exchange, respectively. All other terms have their previously defined meaning. The temperature dependence of $(1/T^0{}_2)_B$ can be described by a function analogous to eq 3 having the experimentally determined parameters A_B and E_B of 7.24 sec^{-1} and 798 cal mol^{-1}. 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. $1/\tau_i{}^{ex}$ is equal to a pseudo-first-order rate constant, k_i, for the exchange of a solvent molecule from the ith coordination site. Its temperature dependence can be expressed as

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

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ 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 were determined from the relative areas under the *cis*-$Co(CH_3OH)_5OH_2{}^{2+}$ and $Co(CH_3OH)_6{}^{2+}$ resonances. These measurements were made on the same sample as were the bulk solvent measurements. The ratio of concentrations of $Co(CH_3OH)_5OH_2{}^{2+}$ to $Co(CH_3OH)_6{}^{2+}$, Q, as a function of temperature is given 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 shown in Figure 2. The straight line drawn through the observed values of Q assumes that the concentrations of uncoordinated water changes only negligibly as a function of temperature and that the heat capacity, ΔC_p, for the following equilibrium is small

$$Co(CH_3OH)_6{}^{2+} + H_2O \overset{K_1}{\rightleftharpoons} Co(CH_3OH)_5OH_2{}^{2+} + CH_3OH \tag{9}$$

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.[8] The assumptions were found to be very good since ΔH was measured to be only 0.3 kcal mol^{-1} and K_1 was 48.8 at −31°.[9]

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, $1/\tau_i{}^{int} = 0$. The predicted contribution of each type of coordination site to the bulk line width and shift as well as the total predicted contribution is given in Table III. The good agreement of the line width data extended into the temperature region where the bulk solvent relaxation rate is a function of both

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(8) J. R. Vriesenga, to be submitted for publication.

(9) $K_1 = [Co(CH_3OH)_5OH_2{}^{2+}][CH_3OH]/[Co(CH_3OH)_6{}^{2+}][H_2O]$.

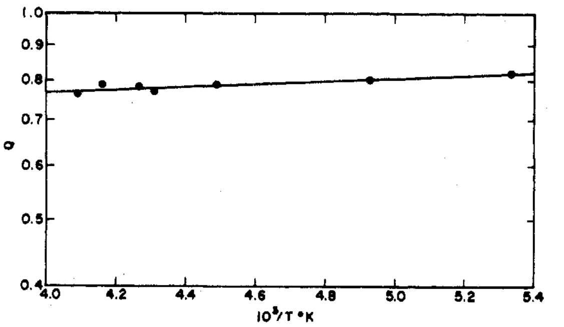

Figure 2. The ratio (Q) of the area of the cis methanol methyl resonance of $Co(CH_3OH)_5OH_2{}^{2+}$ to that of the coordinated solvent methyl resonance of $Co(CH_3OH)_6{}^{2+}$ *vs.* the reciprocal of absolute temperature, $1/T$.

exchange and so-called $\Delta\omega$ mechanism.[7] Both the shifts and line widths are a function of the same parameters, namely, P_i, ω_i, τ_i^{ex}, and $(1/T^0{}_{2i})_c$, but they have different functional dependencies on these parameters. For example, in the exchange-controlled region (slow-exchange region) the shifts are related to $(\tau_i^{ex})^{-2}$ and the line widths are related $(\tau_i^{ex})^{-1}$. The fact that there is excellent 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.

If internal rearrangement were taking place, the observed values of the shifts and line widths would be consistently less than those predicted from the coordinated solvent data. Thus it is concluded that no evidence for internal rearrangement was found and that the exchange rate constants per coordinated solvent molecule for the cis and trans sites are equal. The exchange rate constants at $-30°$ are 609 sec^{-1}, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 12.8 kcal mol^{-1} and 6.9_6 eu, respectively.

Discussion

The rate constants obtained in this study agree with the value for the cis site previously reported[3] (assuming no internal rearrangement). These values are 609 and 600 sec^{-1} at $-30°$, respectively. It was also reported[3] that the exchange contribution to the trans line width was 1.7 times that for the cis site. This implied either that the trans site exchanged more rapidly than the cis (kinetic trans effect) or that part of the line broadening was due to internal rearrangement of the methanol between the cis and trans environments. The present study indicates that the exchange contributions to the cis and trans line widths are equal. In addition it was found that the trans resonance natural line width was about 12% greater than the cis. This fact probably accounts for some of the differences in the interpretation of the trans data. In addition, the increased sensitivity and resolution of a 100-MHz nmr plus increased accuracy by using digital techniques would most likely account for the remaining differences.

A much more extensive investigation of the bulk solvent shifts and line widths was made in this study than in the past. Whereas no definite conclusion about exchange-induced internal rearrangement rates could be reached previously, this work clearly indicates that it does not take place and that there is no kinetic trans effect in this case. Analogous results have been obtained from the methanol-exchange rate of $Co(CH_3OH)_5NCS^{2+}$.[2] In the case of the $Co(CH_3OH)_5Cl^+$ complex, τ_{cis} is reported to be shorter than τ_{trans} implying that the exchange rates are different or that internal rearrangement is taking place.[10]

In fact that there was no exchange-induced rearrangement implies that there is retention of configuration in the activated complex and in any intermediate that may be formed. Because the methanol-exchange rate constants are for pseudo-first-order reaction conditions, it is not possible to establish the molecularity of the reaction; consequently, it is not possible to establish whether the reaction proceeds by primarily a concerted or a dissociative mechanism. Regardless of which of these mechanisms predominates, these results for the $Co(CH_3OH)_5OH_2{}^{2+}$ complex place restrictions on the nature of any postulated activated complex. The structure of the activated complex or intermediate must be such that the incoming methanol molecule will occupy a site of the same type as the leaving molecule.

As frequently observed in previous investigations, it was observed that substitution of Co^{2+} by some nonsolvent molecule labilizes the remaining coordinated solvent. The solvent-exchange rate per coordinated methanol molecule is approximately 6 times faster for the aquo complex relative to $Co(CH_3OH)_6{}^{2+}$ at $-30°$. The factors governing the magnitude of this rate enhancement are not well understood and are the subject of further investigation in this laboratory.

Registry No. $Co(CH_3OH)_5OH_2{}^{2+}$, 15726-51-4; $Co(CH_3OH)_6{}^{2+}$, 15276-50-3.

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[10] X. Luz, *J. Chem. Phys.*, 41, 1756 (1964).