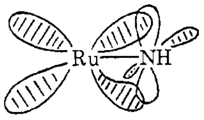
phile (eq 4 and 5). Thus the coordinated NH group in this complex reacts as a coordinated imido group, $-\overset{..}{\underset{..}{N}}H^{2-}$, and not as a coordinated nitrene, $-\ddot{N}H$. It should be noted that the imido and the nitrene formulations are, in fact, valence resonance structures, as shown by

$$\underset{\text{coordinated imido}}{[(NH_3)_5Ru^{IV}-\overset{..}{\underset{..}{N}}H]^{2+}} \longleftrightarrow \underset{\text{coordinated nitrene}}{[(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}}$$

These two structures show an electron pair localized either on the nitrogen (imido) or on the ruthenium (nitrene). The electron delocalization representation, with appropriate orbital overlap, is given by



This pictorial representation is preferable to the above valence bond designations, and suggests a structure somewhere between the extreme imido and nitrene forms. The experimental results show that this species reacts as a nucleophile, indicating that there is a fairly high electron density at the nitrogen atom of the intermediate. The electron delocalization stabilization of such a species may be responsible for the thermal reaction of certain azido metal complexes with acid,[4,5] as well as their photochemical reactions,[17] to yield molecular nitrogen.

Returning to the reaction scheme proposed (eq 2–5), the species involved can be represented in accordance with eq 3a–5a.

$$[(NH_3)_5Ru^{II}N_3H]^{2+} \longrightarrow [(NH_3)_5Ru^{IV}-\overset{..}{\underset{..}{N}}H]^{2+} + N_2 \quad (3a)$$

$$[(NH_3)_5Ru^{IV}-\overset{..}{\underset{..}{N}}H]^{2+} + H^+ \longrightarrow [(NH_3)_5Ru^{IV}-\ddot{N}H_2]^{3+} \quad (4a)$$

$$[(NH_3)_5Ru^{IV}-\ddot{N}H_2]^{3+} + [Ru^{II}(NH_3)_5H_2O]^{2+} + H^+ \longrightarrow [Ru^{III}(NH_3)_6]^{3+} + [Ru^{III}(NH_3)_5H_2O]^{3+} \quad (5a)$$

Under the conditions of the experiments in this investigation, the stoichiometry of the reaction was established to be that shown by eq 1. This means the proposed intermediate reacts (eq 4a) as the imido nucleophile and not as its valence resonance equivalent, the nitrene $[(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}$. It would be of interest to attempt this reaction in the presence of a high concentration of a strong nucleophile to determine if any of the nitrene behavior can be detected, but this was not done. However, the reactions[12] when oxygen is passed through a solution containing $[Ru(NH_3)_6]^{3+}$ and sulfur nucleophiles to produce $[Ru(NH_3)_5NHSO_3]^+$ may involve a nucleophilic attack on the nitrogen of the coordinated nitrene in the resonance system $[(NH_3)_5Ru^{IV}-\overset{..}{\underset{..}{N}}H]^{2+} \leftrightarrow [(NH_3)_5Ru^{II}-\ddot{N}H]^{2+}$. Additional studies are required to resolve the questions of reaction mechanisms in these systems, but it will be important in such investigations to keep in mind that the intermediate species may behave either as a nucleophile (imido) or an electrophile (nitrene).

Acknowledgment.—We thank Professor R. D. Gillard for helpful discussions and for the use of his laboratory to do the "last" experiment. We thank Professor R. G. Pearson for his help and we also thank Mr. T. R. Weaver for his help and Dr. L. Engelhardt for the magnetic measurement. The ruthenium used was loaned to us by the Matthey Bishop Co. and the project was supported by a grant from the National Science Foundation.

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[17] J. L. Reed, F. Wang, and F. Basolo, *J. Amer. Chem. Soc.*, in press.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Proton Nuclear Magnetic Resonance Determination of the Methanol Exchange Rate of the Monothiocyanate Complex of Cobalt(II)

BY JACK R. VRIESENGA

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Proton nmr was used to measure the methanol exchange rate from the cis and trans coordination sites of the $Co(CH_3OH)_5NCS^+$ ion by line-shape analysis of the methyl resonance of the coordinated methanol. The exchange contributions to the transverse relaxation times of the cis and trans methanols were found to be equal. The exchange contribution to the transverse relaxation time of the methyl resonance of the bulk methanol was measured and the result compared to the value predicted on the basis of the bound solvent relaxation data. From these measurements it was concluded that the methanol exchanged from each type of coordination site without internal rearrangement of the complex, and the cis and trans exchange rates were equal. The value for the solvent exchange rate constant per coordinated methanol molecule at 25° is 2.4×10^6 sec^{-1}. The corresponding values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 11.7 kcal mol^{-1} and 9.9 eu, respectively. Data describing the natural line widths and chemical shifts of the coordinated solvent are also included.

Introduction

Summaries of current theories concerning the mechanisms of substitution reactions of labile transition metal ions can be found in many recent reviews.[1] Detailed mechanistic information concerning substitution reactions of labile octahedral transition metal complexes has generally been limited to a few ions exhibiting comparatively slow reaction rates. For reactions involving substitution of coordinated solvent molecules, the reaction rate appears to be controlled by the rate of dissociation of the bound solvent molecule rather than by the rate of bond formation with the

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

incoming ligand. The key to resolving mechanistic questions concerning this particular type of substitution reaction appears to be in the understanding of the factors governing solvent exchange rates, such as total charge on the complex, the nature of the metal-ligand bond, and steric effects. In addition, information concerning the nature and rate of internal rearrangements, the exchange rate of nonequivalent solvent occupied sites, and whether or not so-called cis or trans effects are operative would be necessary to have a complete picture of the substitution process. Considerable progress has been made in understanding the influence of these factors for reactions of nonlabile complexes[2] but very little information of this kind is known for labile complexes.

This paper represents the first in a series of studies of the rate of methanol exchange of cobalt(II) complexes using nmr. The exchange rate is measured by studying the nuclear magnetic relaxation rate of the methyl protons of the coordinated methanol. The choice of cobalt(II) complexes was made for the following reasons. First, the methanol exchange rate of Co^{2+} is in a range convenient for nmr measurement.[3] Second, methanol is a liquid over a wide temperature range (65 to −97.8°), thereby granting considerable flexibility in adjusting the solvent exchange rate to a range amenable to nmr investigation by varying the temperature. Third, the methyl resonances of the coordinated methanol exhibit relatively narrow natural line widths, resulting from the rapid electronic relaxation rate of Co^{2+}. This facilitates the observation of the coordinated solvent resonances and permits the resolution of magnetically nonequivalent solvent occupied sites. Fourth, complexes of Co^{2+} exhibit pseudocontact shifts resulting in distinct, separate resonances for geometrically different coordination sites in the same complex. Consequently, the mean lifetime of a methanol molecule in the cis and trans sites of $Co(CH_3OH)_5X$, where X is a monodentate ligand, can be independently determined. Finally, since the resonances of the coordinated solvent for a particular complex are observed directly, the mean lifetime of a solvent molecule in a particular magnetic environment can be measured without a precise knowledge of the concentrations of the various species in solution.

The particular system of concern in this paper is the monothiocyanate complex of cobalt(II), $Co(CH_3OH)_5NCS^+$. The transverse relaxation rates and shifts of the methyl resonances of the methanols both cis and trans to the thiocyanate were measured as a function of temperature. The corresponding measurements were also made on the bulk solvent methyl resonance.

Experimental Section

Sample Preparation.—Anhydrous cobaltous perchlorate in methanol was prepared by dissolving cobaltous perchlorate in methanol and treating repeatedly with Linde 3A molecular seives. A minimum of three treatments of this type was required to reduce the water content to such a level that the methyl nmr resonance of the cis methanol in the $Co(CH_3OH)_5H_2O^{2+}$ ion could not be observed at −85°.[3] Experiments performed by adding successive small aliquots of water to a dry cobalt perchlorate solution indicate that this was a remarkably sensitive method for detecting water. The anhydrous cobalt solution was analyzed by an EDTA back titration with Zn^{2+} and Eriochrome Black T indicator.[4]

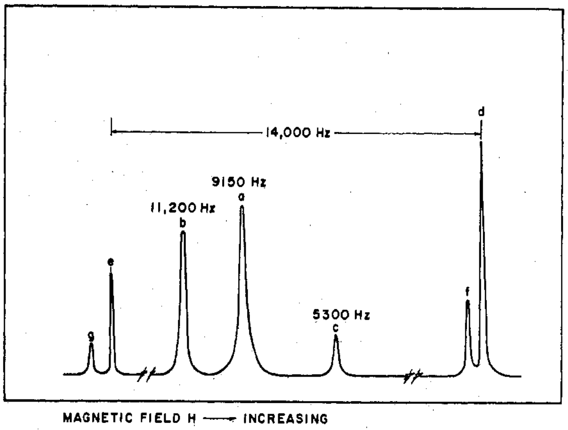

Figure 1.—A representation of a typical proton spectrum of the methyl resonances of methanol in a cobalt(II)-thiocyanate-methanol solution at −90°. Peak assignments are as follows: a, $Co(CH_3OH)_6^{2+}$; b, *cis*-$Co(CH_3OH)_5NCS^+$; c, *trans*-$Co(CH_3OH)_5NCS^+$. Resonances d, e and f, g are the respective first and second side bands of the bulk methyl and hydroxy resonances. The shifts are measured relative to d.

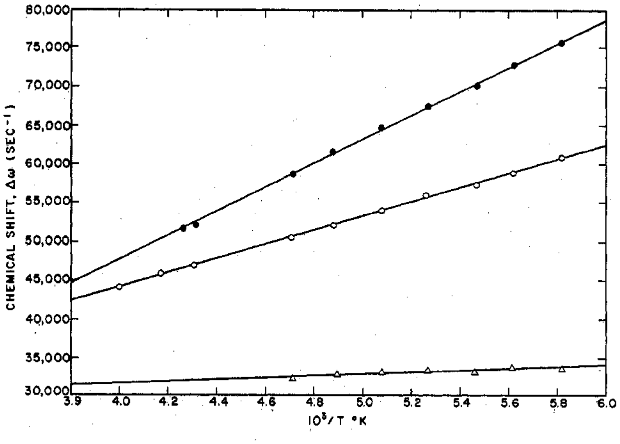

Figure 2.—Chemical shift of the methyl resonances of $Co(CH_3OH)_6^{2+}$ (○) and the cis (●) and trans (△) methyl resonances of $Co(CH_3OH)_5NCS^+$. All shifts are downfield relative to the bulk solvent methyl resonances.

The thiocyanate complex was prepared by introducing a weighed quantity of dried sodium thiocyanate (99.9% purity) into a flask which was stoppered with a serum cap. Dry nitrogen, introduced through syringe needles, was used to purge the air from the flask. A known volume of standardized anhydrous cobalt perchlorate solution was injected into the flask with a syringe. The resulting solution was then transferred to a 5-mm nmr tube using a syringe and under a constant flow of nitrogen. The nmr tube was quickly capped and sealed with silicone rubber cement. No evidence of water absorption was found and the samples were indefinitely stable to oxidation. The total cobalt(II) concentration ranged from 0.10 to 0.225 *M*; the thiocyanate concentration varied from *ca.* 0.05 to 0.17 *M*.

Instrumentation. All measurements were made on proton resonances at 100 MHz using a Jeolco 4H-100 spectrometer modified with an external variable frequency audio modulation source and power amplifier. Audio-phase detection of the resulting signals was effected with a Princeton Applied Research Model 121 lock-in amplifier. This method of detection was necessary in order to position side bands so that they would not overlap and interfere with analysis of the spectrum. The spectrum was simultaneously recorded in analog form on a recorder and in digital form as a 1000 data point representation

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[2] J. M. Pratt and R. G. Thorp, *Advan. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

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

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

TABLE I

SUMMARY OF PARAMETERS FOR EXCHANGE RATES AND CHEMICAL SHIFTS

	Activation parameters for exchange			Parameters defining chemical shift[a]	
	k, $\sec^{-1}$ (25°)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	M, °K $\sec^{-1}$	B, $\sec^{-1}$
$Co(CH_3OH)_5NCS^+$					
cis	2.4×10^6	11.7 ± 0.6	9.9 ± 1	1.57×10^7	−14,100
trans	2.4×10^6	11.7 ± 0.6	9.9 ± 1	1.26×10^6	26,400
$Co(CH_3OH)_6^{2+}$	2.1×10^4	13.2[b]	5.2[b]	9.42×10^6	6,590
	1.8×10^4 [b]	12.8	4.5		

[a] Shift $\Delta\omega$, $\sec^{-1}$, expressed as a linear equation $\Delta\omega = M(1/T°K) + B$. [b] Reference 1.

with a Jeolco JRA-5 Spectrum Computer. The spectrum was appropriately formated and labeled in the JRA-5 mini-computer and subsequently punched out on paper tape.

A total line-shape analysis was carried out on the digitized spectrum using a Digital Data Corporation PDP-10 computer. A modified nonlinear regression program was used to analyze the data by fitting it to a series of Lorentzian lines. The fitting parameters consisted of resonance position, peak height, and half-width at half-height for each resonance, as well as a base-line and phase correction for the entire spectrum. This rather elaborate data processing system proved to be essential because the nmr resonances began to overlap as line broadening due to exchange processes occurred. Attempts to analyze such spectra by hand were highly sensitive to error due to extreme difficulty in judging proper phasing and neglect of the rather extensive "tails" on the Lorentzian-shaped resonances. A further advantage is the considerable economy in time since it is necessary to analyze several hundred spectra in a single study.

For the bound methanol resonance data, spectra were measured in the field scan mode, with careful attention paid to such factors as sweep calibration, filtering time constants, scan rates, and base-line stability. In all cases, slow passage and nonsaturation conditions were satisfied. For measurements on the bulk data the instrument was operated in the external lock mode, in which the magnetic field was locked to the resonance line of an external water sample in the probe. All shifts of bound solvent resonances were measured relative to the appropriate first side-band bulk signal.

Temperature was measured with a copper–constantan thermocouple immersed in a sample tube containing methanol of approximately the same volume as the sample. The thermocouple was positioned to measure temperature at the center of the detector coil. Temperature stability was found to be ±0.3°.

Data and Results

Figure 1 is a drawing representing the nmr spectrum of the bound methyl resonances of the $Co(CH_3OH)_6^{2+}$ and $Co(CH_3OH)_5NCS^+$ ions at −90°. The resonances d and e are the first and second side bands of the bulk solvent methyl groups, respectively; f and g are the corresponding hydroxy resonances. Resonance a corresponds to the methyl groups in $Co(CH_3OH)_6^{2+}$, and b and c are the respective cis and trans methyl resonances in $Co(CH_3OH)_5NCS^+$. The assignments of the cis and trans resonances were made on the basis of the constancy of the ratio of areas of b to c at 4.0 ± 0.2 over a wide concentration range. The measurements were made with the total Co^{2+} concentration maintained at 0.215 M and varying the NCS^- concentration from 0.00 to 0.173 M. Integrations were carried out numerically using the digitized data. Similar resonance assignments for $Co(CH_3OH)_5X^{n-}$ where X = Cl^- and H_2O have been reported.[3,5] Only resonances for the mono NCS^- complex were observed over the entire temperature and concentration range of this study.

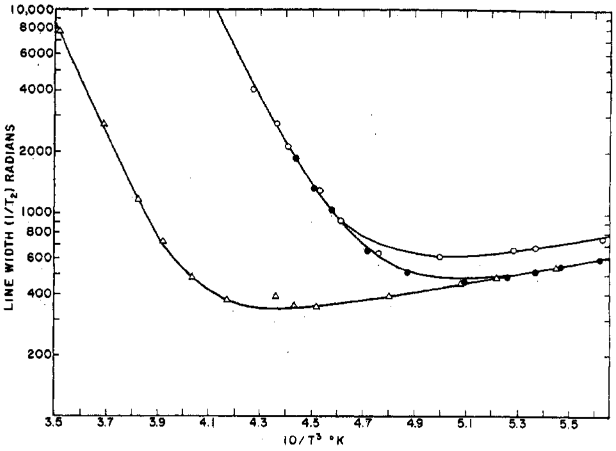

Figure 3.—The log of the observed methyl line width (radians) of the coordinated methanol in $Co(CH_3OH)_6^{2+}$ (△) and *cis*- (○) and *trans*-$Co(CH_3OH)_5NCS^+$ (●) as a function of the reciprocal of absolute temperature.

Data summarizing the bound methyl resonance shifts, $\Delta\omega$, measured relative to the bulk solvent methyl resonance are given in Figure 2. All shifts were downfield and gave a good straight line when plotted *vs.* the reciprocal of absolute temperature. The parameters describing these lines are given in Table I. The shifts did not exhibit a temperature dependence characteristic of isotropic contact shifts in that the intercepts at infinite temperature were not zero. This is probably a consequence of dipolar shifts resulting from the electronically degenerate ground state of Co^{2+}.[6]

The results of the bound methanol methyl line width measurements (in radians) for $Co(CH_3OH)_6^{2+}$ and *cis*- and *trans*-$Co(CH_3OH)_5NCS^+$ are summarized in Figure 3, where the log of the observed half-width at half-height, $1/T_2$, in radians, *i.e.*, $\sec^{-1}$, is plotted *vs.* the reciprocal of temperature. T_2 is the observed transverse relaxation time. The theoretical expressions relating the line width to the mean lifetime of a solvent molecule in a specific magnetic environment used in this work were developed by Swift and Connick.[7]

At low temperature, where the exchange rate was slow, the observed line width was the natural line width, $(1/T_2^0)$. For the system studied the natural line width could be empirically described by the expression

$$(1/T_2^0) = Ae^{-E_a/RT} \qquad (1)$$

where A is the preexponential factor; E_a, the activation energy; R, the gas constant; and T, the absolute temperature. The appropriate constants for eq 1 corresponding to natural line widths of the methyl resonances of $Co(CH_3OH)_6^{2+}$ and *cis*- and *trans*-$Co(CH_3OH)_5NCS^+$ are A 32.4, 60.7, and 30.0 $\sec^{-1}$ and E_a −1.0, −0.9, and −1.0 kcal, respectively.

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(5) Z. Luz, *J. Chem. Phys.*, **41**, 1748 (1964).

(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).

A very sharp increase in line width of the resonances of the NCS^- complex was observed as the temperature increased above −60°. The increased relaxation was ascribed to methanol exchange with different magnetic environments. The exchange contribution to the line width, $(1/T_2)_{ex}$, is defined by the expression

$$(1/T_2)_{ex} = 1/T_2 - 1/T_2^0 \qquad (2)$$

$(1/T_2)_{ex}$ is related to the mean lifetime, τ_{ex}, of a nucleus in a particular magnetic environment by the relationship[7]

$$(1/T_2)_{ex} = 1/\tau_{ex} \qquad (3)$$

It is necessary to question whether $(1/T_2)_{ex}$ is a result of exchange with the bulk solvent, internal rearrangement, or both. In principle this question could be answered by measuring the exchange contribution, $1/T_{2p}$, of the bulk (noncoordinated) methyl resonance, and comparing the observed value with that predicted from the bound solvent relaxation data. Equation 4 defines $1/T_{2p}$.

$$1/T_{2p} = (1/T_2)_{bulk} - (1/T_2^0)_{bulk} \qquad (4)$$

where $(1/T_2)_{bulk}$ is the observed half-width at half-height (in radians) for the bulk solvent methyl resonance, $(1/T_2^0)_{bulk}$ is the natural line width when the Co^{2+} complex is present but without the effect of exchange, and where $(T_2)_{bulk}$ and $(T_2^0)_{bulk}$ are the corresponding transverse relaxation times. At low temperatures, where $1/T_{2p}$ was zero, the natural line width $(1/T_2^0)_{bulk}$ was found to be a function only of the total Co^{2+} concentration and independent of the amount of Co^{2+} complexed by NCS^-. Since $Co(CH_3OH)_6^{2+}$ makes no contribution to the exchange broadening of the bulk methyl resonance in the temperature region of concern, the natural line width, $(1/T_2^0)_{bulk}$, of the exchange broadened resonance was taken to be the same as a sample containing the same total Co^{2+} concentration without NCS^-.

Bulk line width measurements were carried out over the temperature range of −90 to −28° on a sample having a total Co^{2+} concentration of 0.225 *M* and NCS^- concentration of 0.137 *M*. Exchange broadening became apparent at about −40°; however, only at the two highest temperatures, −28 and −32°, was there sufficient exchange broadening to obtain a reasonably accurate value for $1/T_{2p}$. The observed line widths were 195 and 126 sec^{-1}, respectively. Calculation of the predicted value for $1/T_{2p}$ was carried out using the expression[7]

$$1/T_{2p} = \sum_i \frac{P_i(\tau_i/(T_{2i}^0)^2 + 1/T_{2i}^0 + \tau_i \Delta\omega_i^2}{(1 + \tau_i/T_2^0)^2 + \tau_i^2 \Delta\omega_i^2} \qquad (5)$$

where P_i is the mole ratio of the methanol coordinated in the *ith* magnetic environment to the bulk methanol; τ_i is the mean lifetime of a solvent molecule in the *i*th environment with respect to exchange with the bulk solvent. The subscript *i* indicates either a cis or trans magnetic environment. By noting that $1/\tau_i^0$ is just the first-order rate constant, k_i^0, for the exchange with the bulk, the temperature dependence of τ_i can be expressed in terms of the equation

$$\tau_i = (h/k_B T)e^{-\Delta S^\ddagger/r} e^{\Delta H^\ddagger/RT} \qquad (6)$$

where *h* is Planck's constant, k_B is Boltzmann's constant, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ the enthalpy and entropy of activation, respectively. A pseudo-first-order rate constant for exchange of a given solvent molecule in the *i*th environment, k_i^0, is defined in terms of the corresponding mean lifetime as follows

$$k_i^0 \equiv \frac{1}{\tau_i} \qquad (7)$$

A fundamental problem in correlating the bound and bulk relaxation data is to establish the value of P_i. To compute P_i one must know quantitatively the composition of the solution at each temperature. Estimates of sample composition as a function of temperature were made by measuring the relative areas under the bound $Co(CH_3OH)_6^{2+}$ and *cis*-$Co(CH_3OH)_5NCS^+$ methyl resonances as a function of temperature for a sample of known total Co^{2+} concentration.

Measurements of the ratio of areas were carried out on the same samples on which the bulk line-width measurements were made. At low temperatures the ratio of areas indicated that nearly all the NCS^- was complexed. Dissociation of the complex increased as the temperature was increased, and it was found that about 80% of the NCS^- was complexed at −41.2°. Extrapolation of the ratio of areas indicated that at −30° about 70% of the NCS^- was complexed. This figure was used to compute P_i at −28 and −32°. If one assumes that $(1/T_2)_{ex}$ for the cis and trans resonances is due solely to exchange with the bulk, then $(1/T_2)_{ex}$ gives τ_i^0 directly. On substituting the calculated value for P_i and the extrapolated values found for $1/T_{2i}$, τ_i^0, and $\Delta\omega_i$ into eq 4, the values of line widths were determined to be 207 and 132 sec^{-1} for −28 and −32°, respectively. These compare very favorably with the observed values of 195 and 126 sec^{-1}.

A measure of the reliability of these results can be ascertained by considering the experimental errors associated with the measurements. First the measurement of the ratio of areas showed an average scatter of ±7%. Collectively, the ratio of areas as a function of temperature definitely indicated dissociation of the complex with rising temperature. The low-temperature ratio measurement on relatively sharp, well resolved lines gave a scatter of only ±2%, and indicated that the NCS^- was 95–100% complexed. The high-temperature measurements obtained at −41.2° indicated that about 75–85% of the NCS^- was complexed, while subsequent extrapolation to −30° indicated 65–75% of the NCS^- complexed. A second major source of uncertainty is encountered in the extrapolation of τ_i to approximately −30°. The accuracy of this extrapolation depends on the accuracy of the value of $\Delta H^\ddagger$ which was reliable to ±0.7 kcal. Considering that any experimental error in measuring the bulk line width is negligible compared to the errors already mentioned, it seems reasonable to conclude that the predicted and observed values of $1/T_{2p}$ are equal within the limits of experimental error; namely, ±10%.

From the fact that the exchange contribution to the bulk relaxation rate can be adequately predicted from the bound relaxation data, it can be concluded that the hypothesized reaction mechanism on which the calculations were based was adequate to explain the experimentally observed facts. Additional support for this supposition is the observation that exchange contributions to both the cis and trans relaxation rates are identical. If one postulates mechanisms requiring cis and trans effects and internal rearrangements to explain the relaxation data, it would be necessary to postulate very specific relationships between the processes to account for the equality of $(1/T_2)_{ex}$. It is felt that the existence of such relationships is improbable.

The rate constant and activation parameters summarized in Table I are based on the above mechanism. Included in Table I and in Figure 3 are the data for the line widths and methanol exchange rate of $Co(CH_3OH)_6^{2+}$. These data indicate that NCS^- exchanges very slowly compared to the methanol exchange rate of $Co(CH_3OH)_5NCS^+$. If this were not the case, appreciable line broadening for the $Co(CH_3OH)_6^{2+}$ resonance would have been observed, and one would be forced to consider the exchange of NCS^- as providing an additional relaxation mechanism for the $Co(CH_3OH)_5NCS^+$ resonances.

Discussion

The simplest mechanistic interpretation of the coordinated methanol relaxation data appears to require that exchange occurs exclusively between the bulk and bound environments, and that no appreciable rearrangement in either the activated complex or an intermediate occurs. These results are markedly different from those previously reported for similar systems. Earlier studies of methanol exchange of $Co(CH_3OH)_5OH_2^{2+}$[3] and $Co(CH_3OH)_5Cl^+$[5] indicate that the mean lifetime of a methanol molecule in the trans site is 0.59 times that for the cis. To account for this difference in relaxation rates one must postulate a mechanism implying either a cis effect, a trans effect, internal rearrangement, or some combination of these processes. The results for the NCS^- system indicate that neither internal rearrangement nor kinetic cis or trans effects are operative. Thus, there is retention of configuration on exchange, whereas for the H_2O and Cl^- systems this is unclear.

It is a well documented fact, especially for Ni^{2+}, that substitution into the first coordination sphere by some nonsolvent ligand enhances the rate of exchange of the remaining coordinated solvent molecules. This was observed in the present work, as well as previously reported for cobalt(II) complexes in methanol.[3,5] The reasons for the rate increase, however, are not clear.

One could speculate on the role total charge plays in determining the solvent exchange rates and point out differences between water and methanol exchange rates for analogous complexes. But, in fact, there has as yet been an insufficient number and variety of systems studied to provide a basis to judge the generality of such conclusions. A systematic investigation of the methanol exchange rates of a wide variety of cobalt(II) complexes is presently underway in this laboratory in an attempt to assemble sufficient information to draw correlations between exchange rates and various possible factors influencing them.

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Unusual Solvent Effect on the Paramagnetic Proton Chemical Shift of a Cobalt(II) Complex

BY TIM W. McGAUGHY AND B. M. FUNG*

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The proton nmr of hydrotris(1,2,4-triazol-1-yl)boratocobalt(II) was studied in solutions of varying D_2O–D_2SO_4 content. In dilute acid solutions ($D_2O/D_2SO_4 > 150$), there are three sets of proton peaks for the protons in the ligand. One set is due to the dissociated ligand. The second set is due to the normal paramagnetic complex. The third set, which has smaller paramagnetic shifts, is due to a species in which water replaces one (or more) triazole unit in the ligands. The positions of the paramagnetic peaks change significantly with an increase in acid content; this phenomenon is explained by a change in the geometry of the complexes. In concentrated acid solutions ($D_2O/D_2SO_4 < 1.2$), the two sets of paramagnetic signals merge into one set of three peaks, indicating fast chemical exchange. The change of chemical shifts with solvent composition in this range is dominated by the shift in equilibrium between the two species.

Introduction

Nuclear magnetic resonance (nmr) studies on the second coordination sphere of transition metal complexes have been reported in several experiments.[1–7] The solvent-induced changes in the proton chemical shifts of the ligands in several cobalt(III) complexes illustrate the formation of the second coordination sphere through hydrogen bonding.[1,2] Complex formation between the tris(ethylenediamine)cobalt(III) ion and the phosphate ion decouples the ^{59}Co–^{1}H spin–spin coupling because of more effective ^{59}Co quadrupole relaxation.[3,4] The formation of outer-sphere complexes

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(1) B. M. Fung, *J. Amer. Chem. Soc.*, **89**, 5788 (1967).

(2) B. M. Fung and I. H. Wang, *Inorg. Chem.*, **8**, 1867 (1969).

(3) J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

(4) L. R. Froebe and B. E. Douglas, *Inorg. Chem.*, **9**, 1513 (1970).

(5) D. R. Eaton, *Can. J. Chem.*, **47**, 2645 (1969).

(6) L. S. Frankel, *J. Phys. Chem.*, **73**, 3897 (1969).

(7) L. S. Frankel, C. H. Langford, and T. R. Stengle, *ibid.*, **74**, 1376 (1970).