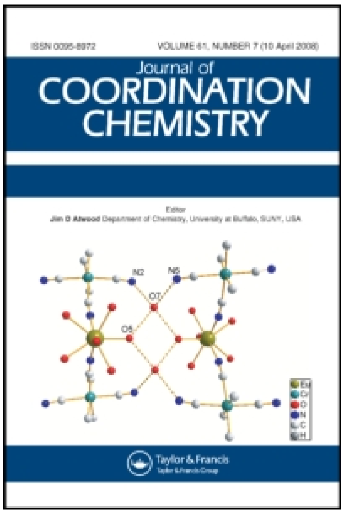

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LIGAND EXCHANGE KINETICS OF THE HEXAMETHANOLCOBALT(II) TETRAFLUOROBORATE COMPLEX

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The study of rates and mechanisms of ligand exchange reactions in coordination compounds has received a great deal of attention in the literature.[1,2] A volume of evidence has been accumulated to indicate that in the ligand substitution reactions of octahedral transition metal ion complexes, bond breaking is more important than bond formation in the determination of the reaction rate. Unfortunately, nearly all studies of this type carried out on octahedral complexes have been done in the free ligand as solvent.[2] Under these conditions there is no opportunity to study definitively the role of the free ligand in the exchange mechanism. Ideally, the study of the ligand exchange reaction should be carried out in an inert solvent so that the concentration of the free ligand can be varied with no fear of the solvent participating in the exchange reaction.

Previous to this work very few complexes have been studied in an inert solvent where the concentration of the reagents could be varied. In fact, until very recently all cases studied in this manner involved tetrahedral complexes of Co(II) and Ni(II).[3–5]

Several reports[6–9] have appeared in the literature on the ligand exchange kinetics of six coordinate Ni(II) and all but one of these was for a case with six equivalent ligands.[7–9] In this paper we investigate the ligand exchange kinetics of an octahedral Co(II) complex, $[Co(CH_3OH)_6](BF_4)_2$, under the above mentioned conditions by using NMR line-shape analysis, in an attempt to obtain information concerning the mechanism of the ligand exchange reaction.

EXPERIMENTAL

Reagents

In this set of experiments it is very important that all reagents be as dry as possible. Therefore, extreme care was taken in the purification and preparation of all reagents and compounds. All glassware was oven baked to insure dryness.

Absolute methanol (J. T. Baker Chemical Co.) was stirred over 3A molecular sieves for 24 hours, then fractionally distilled from magnesium and iodine and stored over 3A sieves.

Deuterochloroform was obtained from Diaprep Inc. and was dried over 3A sieves just prior to use.

The acidified methanol was prepared by the method of Meiboom[10] except that $AgBF_4$ was used to obtain an anhydrous solution of HBF_4 in methanol.

Preparation of Complex

$[Co(CH_3OH)_6](BF_4)_2$ was prepared by a previously reported method[11] using trimethyl-o-formate as the dehydrating agent and was recrystallized from methanol. *Anal.* Calcd.: C, 16.96; H, 5.65; Co, 13.86. Found: C, 16.78; H, 5.68; Co, 13.97.

Solutions

The kinetic experiments were carried out on deuterochloroform solutions of $[Co(CH_3OH)_6](BF_4)_2$ containing various amounts of methanol, which was 0.01 M in HBF_4. All sample preparations were carried out in a dry box, and all NMR samples were sealed.

It was necessary to acidify the methanol in order to collapse the spin-spin splitting between the –OH proton and the –CH_3 protons to produce a simple AB exchange system.

Five solutions were prepared where the complex concentration was held constant at 0.10 M, and the excess methanol concentration was varied systematically from 3.0 M to 8.0 M. It was not possible to use any lower concentration of methanol since the complex would not completely dissolve. A sixth solution was used where the complex concentration was increased to 0.15 M and the free ligand concentration was held constant at 5.99 M.

Line-Shape Calculations

The line-shape calculations were done as previously described in the literature by Zumdahl.[5] The procedure will not be discussed further here, except to mention the experimental parameters that are needed to carry out this calculation. These quantities are the chemical shifts for the two sites in the absence of exchange, and the transverse relaxation times in the two sites. A guessed value for the exchange rate $(1/\tau_m)$ is varied to fit the observed spectra. From this calculation the experimental $(1/\tau_m)$ values are obtained directly, where τ_m is the mean lifetime of a ligand in the primary coordination sphere of the metal ion.

NMR Spectra

The NMR spectra were run on a Jeolco C-60H High Resolution instrument using a VT-3 temperature controller which held the temperature constant to within ±2.0°C. Temperature was monitored by use of a Y.S.I. Model 42SL Thermistor Thermometer with an accuracy of ±0.5°C. TMS was used as an internal standard on all samples.

RESULTS AND DISCUSSION

For this study it was necessary to find a six coordinate Co(II) complex that would show simple AB exchange behavior in order to use our shape program and also one that would be sufficiently soluble in a mixture of an inert solvent and the free ligand. With these limitations in mind the $[Co(CH_3OH)_6](BF_4)_2$ complex was chosen. Luz and Meiboom have studied[10] the exchange kinetics of essentially the same complex, $[Co(CH_3OH)_6](ClO_4)_2$, in the free ligand (methanol) as solvent, and consequently were not able to obtain any mechanistic information on the exchange reaction. A comparison of the kinetic parameters obtained by Luz and Meiboom with those obtained here is made later.

In order to establish that the complex that is in solution is indeed the $[Co(CH_3OH)_6]^{++}$ moiety, the *d-d* electronic spectra were obtained for the solid complex, for the complex in pure methanol and for each of the solutions used for the kinetic study. The results were identical in all cases as indicated by Table I. Also, determination of the coordination number by integration of the NMR spectra was carried out for the solution containing the least amount of methanol and the solution containing the greatest amount of methanol from −25°C to −55°C. In all cases the coordination number was six, within experimental error, see Table II.

It was pointed out by Luz and Meiboom[10] that formation of the partially aquated species, $[Co(CH_3OH)_5(H_2O)]^{+2}$ and $[Co(CH_3OH)_4(H_2O)_2]^{+2}$, gives rise to additional peaks in the NMR spectrum. Repeated attempts to observe any additional peaks due to the aquated species proved negative.

On the basis of the above mentioned evidence, difficulty arising from the presence of some partially aquated species is not considered further, and it seems reasonable to state that over the temperature

TABLE I
Electronic spectral data for $[Co(CH_3OH)_6](BF_4)_2$

Solution		Values of λ max.	$(M\mu)^a$
0.1 M complex plus 2.99 M methanol in chloroform	475 sh	513 (6.0)	1,260 (1.5)
0.1 M complex in methanol	477 sh	513 (5.5)	1,255 (1.4)
solid complex in nujol mull	473 sh	508	1,215

[a] values in parenthesis are molar extinction coefficients.

TABLE II
Coordination numbers at various temperatures

Solution	−25°C	−40°C	−55°C
0.1 M $[Co(CH_3OH)_6](BF_4)_2$ plus 2.99 M methanol in chloroform	5.9 ± .3	6.0 ± .2	5.9 ± .2
0.1 M $[Co(CH_3OH)_6](BF_4)_2$ plus 5.99 M methanol in chloroform	6.1 ± .2	6.1 ± .2	6.0 ± .3

region studied we are dealing with the six coordinate methanol complex, $[Co(CH_3OH)_6]^{+2}$.

For this system, the slow exchange region (the region where separate resonances are observed for the free and the coordinated ligand) begins at approximately −15°C and exchange is stopped at approximately −40°C. Exchange data was obtained in the slow exchange region where the line-width, $\Delta\nu_{1/2}$, is simply related to the transverse relaxation time, T_2, ($\pi\Delta\nu_{1/2} = 1/T_2$). The spectrum of each solution was obtained from −15°C to −65°C and the $(1/\tau_m)$ values were calculated by the complete lineshape method. The values of $(1/\tau_m)$ were determined at 2–3°C intervals from −20°C to −36°C. Over the concentration range studied no change within experimental error in the $(1/\tau_m)$ value was obtained for a given temperature.

Since $1/\tau_m$ is independent of the methanol concentration at any temperature, it can be said that over the concentration range and temperature range studied the $[Co(CH_3OH)_6](BF_4)_2$ complex undergoes ligand exchange by the same mechanism as that in the pure methanol. It also appears that this octahedral Co(II) exchange reaction follows a rate law of the type

$$\text{rate} = nk\ [\text{complex}]$$

where n represents the coordination number of the exchanging ligands. This is in agreement with the rate law expressed recently by Zumdahl[7] for octahedral Ni(II) complexes.

An analysis of the kinetic data was carried out using the following expression for k, the rate constant,

$$k = 1/\tau_m = k'T/h \exp\left[-(\Delta H^{++} - T\Delta S^{++})/RT\right].$$

A summary of the kinetic data obtained in this work and that obtained by Luz and Meiboom[10] is presented in Table III for ease of comparison. As can be seen, the results agree extremely well even though the solvent employed is quite different. This very close agreement for the two systems may to some degree depend on the large methanol concentrations employed and can be used to rule out any participation of the anion in the exchange mechanism in chloroform since one might expect more significant differences in these parameters if the anions did participate in the mechanism.

It is impossible to conclude from these experiments which of the following mechanisms governs the exchange of methanol with the cobalt(II) complex:

Mechanism 1: S_N1(lim) or D-type

$$Co(MeOH)_6^{+2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(MeOH)_5^{+2} + MeOH \quad \text{slow}$$

$$Co(MeOH)_5^{+2} + MeOH^* \xrightarrow{k_2} Co(MeOH)_5(MeOH^*)^{+2} \quad \text{fast}$$

for which the rate law is

$$\text{Rate} = k_1\,[Co(MeOH)_6^{+2}]$$

Mechanism 2: S_N(IP) or I_d

$$Co(MeOH)_6^{+2} + MeOH^* \overset{K_{OS}}{\rightleftharpoons} \{Co(MeOH)_6^{+2}\}\{MeOH^*\} \quad \text{fast}$$

$$\{Co(MeOH)_6^{+2}\}\{MeOH^*\} \xrightarrow{k_1} Co(MeOH)_5(MeOH^*) + MeOH \quad \text{slow}$$

which has the rate law

$$\text{Rate} = \frac{k_1 K_{OS}[Co]_T[MeOH]}{K_{OS}[MeOH] + 1}$$

where

$$[Co]_T = [Co(MeOH)_6^{+2}] + [\{Co(MeOH)_6^{+2}\}\{MeOH^*\}$$

TABLE III
Summary of Kinetic Data for $[Co(CH_3OH)_6]^{+2}$

	ΔH^{++} (Kcal/mole)	ΔS^{++}(e.u.)	$1/\tau_m$ at 25°C
$[Co(CH_3OH)_6](BF_4)_2$ in deuterochloroform plus methanol	13.3	+6.1	$2.4 \times 10^{+4}$
$[Co(CH_3OH)_6](ClO_4)_2$ in methanol as solvent	13.8[a]	+7.2[a]	$1.8 \times 10^{+4}$[a]

[a] Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

If the first mechanism were operative, first-order exchange kinetics would be observed regardless of concentration conditions. However, the kinetics observed for the second mechanism would depend upon the relative magnitudes of the terms in the denominator of the rate expression. When $K_{OS}[\text{MeOH}] \gg 1$, the rate law reduces to a form identical to that for Mechanism 1. Under these conditions, it is impossible to distinguish between the two mechanisms since both would be consistent with the same rate law. If it were possible, however, to decrease the methanol concentration to a small enough value (depending upon the value of K_{OS}), eventually the situation would be reached where $1 \gg K_{OS}[\text{MeOH}]$ and second-order kinetics would be observed if Mechanism 2 were correct. There would then be sufficient evidence for distinguishing between Mechanisms 1 and 2.

Studies in aqueous solution with charged reactant species usually give values of K_{OS} between 0.1 and 20.[1,2] In chloroform, a low dielectric constant solvent with smaller hydrogen-bonding ability than water, one would expect values of K_{OS} to be substantially larger. Assuming a reasonable lower limit of 1 for this system, changing the [MeOH] from 3 to 8 M, as done here, would increase the rate constant by about 10%. Experimental error would make this small change very difficult to detect. A larger value of K_{OS} would make the respective rate constants even more similar. For this reason, we cannot distinguish between the two mechanisms described above for the system reported here.

NMR exchange studies performed by other workers[7–9] using varying concentrations of exchanging ligand in non-coordinating solvents, such as chloroform, nitromethane, methylene chloride, and acetone, have all shown strictly first-order kinetics. On the basis of this kinetic data, these workers have concluded that Mechanism 1 is operative. We feel that although the conclusions drawn by these workers are probably correct, their data do not necessarily substantiate their conclusions. In all instances, charged complexes were employed. In non-coordinating, low-dielectric-constant solvents like those used, association of the polar excess ligand with the charged complex would be expected to be much more extensive than in aqueous solution; i.e., values of K_{OS} would be much larger in chloroform, say, than in water. Therefore, unless the concentration of free exchanging ligand were made very small (0.1 M or less if $K_{OS} \cong 10$), first-order kinetics would still be observed, according to the rate law for Mechanism 2. As an example, consider the study performed on the exchange of bulk DMF with $\text{Ni(DMF)}_6{}^{2+}$ in nitromethane solvent, using concentrations of DMF ranging from 1 M to 12.9 M.[8] Rate constants were observed ranging from 6×10^3 to 6.75×10^3 over this concentration range. The claim is made that the invariance of k with DMF concentration supports Mechanism 1 because the reported values of k are the same within experimental error, even though these values do increase regularly with increasing [DMF]. However, the critical point is that if Mechanism 2 were operative, a value for K_{OS} of $\geqslant 5$ would lead to a change in observed rate constant of only about 12% or less over the concentration range studied. Considering the usual precision of rate constants obtained from line width measurements (5–15%), such a small relative change in rate constant would be difficult of detection. Preferential solvation of $\text{Ni(DMF)}_6{}^{+2}$ by nitromethane would certainly decrease the expected value of K_{OS} for formation of an outer sphere complex between $\text{Ni(DMF)}_6{}^{+2}$ and DMF. Such preferential solvation is one possible explanation for the stopped-exchange line width data reported in Ref. 8. The interpretation of this data in terms of preferential solvation necessitates assuming that T_{2_s}, the transverse relaxation time of the formyl proton of DMF in the second coordination sphere of the metal ion, is independent of solvent composition. It seems that the possibility that T_{2_s} is inherently different in the two solvent compositions should not be ruled out.

The fact that the DMF line width is narrower in CD_3NO_2 indicates that K_{OS} is less in CD_3NO_2 than in DMF, but does not necessarily mean that the K for formation of a 1:1 outersphere complex is smaller than 5 in the former solvent. This must be shown before pure dissociative activation can be conclusively proved. Until then, the data presented in Ref. 8 do not provide a convincing distinction between the two possible mechanisms. In order to truly test the I_d mechanism in non-aqueous solvents, it will be necessary to study a system in which the free ligand concentration can be made sufficiently low that $1 \gg K_{OS}$ [L]. It is only under these conditions that the second-order characteristics of the I_d mechanism will become evident.

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