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Monocomplex Formation Reactions of Hexaaquaruthenium(II): A Mechanistic Study

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The complex formation reactions between $[\mathrm{Ru(H_2O)_6}]^{2+}$ and a series of monodentate ligands have been followed by UV–visible or NMR spectroscopy. From variable-temperature experiments, the rate constants and activation enthalpies and entropies were determined. These are as follows for NMP$^+$ (*N*-methylpyrazinium cation), MeCN, DMSO, and 1,4-thioxane, respectively: $10^3\,k_f^{298}/m^{-1}\,s^{-1}$ = 0.73 ± 0.08, 2.07 ± 0.09, 1.31 ± 0.03, 2.2 ± 0.2; $\Delta H^{\ddagger}$/kJ mol^{-1} = 77.7 ± 3.0, 81.1 ± 2.4, 87.3 ± 1.4, 82.4 ± 3.7; $\Delta S^{\ddagger}$/J K^{-1} mol^{-1} = −44 ± 9; −24 ± 8, −7 ± 5, −2 ± 12. $k_f^{298}/m^{-1}\,s^{-1}$ = 2.4 ± 0.1 was obtained for tetrahydrothiophene. The similarity of the interchange rate constants, k_I, indicates that an interchange dissociative mechanism, I_d, operates. From the NMR and IR spectra, it has been concluded that DMSO binds via its sulfur atom.

Introduction

The substitution reaction mechanisms of the octahedral complexes of bi- or trivalent cations have been intensively studied for the first transition metal series.[1-3] A gradual changeover in substitution mechanism is observed, passing from an I_a mechanism for the elements at the beginning of the series to an I_d mechanism for the elements at the end of the series. These observations are explained by electronic and steric considerations. Such studies are more scarce for the octahedral aquo complexes of the second transition metal series. The water-exchange or complex formation studies on $[\mathrm{M(H_2O)_6}]^{n+}$, where M = Mo^{3+},[4] Ru^{3+},[5] Rh^{3+},[6] Cd^{2+},[7] or In^{3+},[8] seem to indicate a generally associative substitution behavior (I_a or A) for this series, due to their larger ionic radii. In the case of $[\mathrm{Ru(H_2O)_6}]^{2+}$, a different mechanism may be expected because of the particularly small ionic radius of Ru(II), 73 pm, caused by spin-pairing.

The mechanistic studies made on the substitution reactions of the aquaruthenium(II) ion present an apparent contradiction. It was shown that the rate constants and the enthalpies of activation for the anation of $[\mathrm{Ru(H_2O)_6}]^{2+}$ by Cl$^-$, Br$^-$, and I$^-$ are very similar,[9] indicating identical steps in each case to reach the transition state (i.e. dissociation of H$_2$O). More recently, variable-pressure studies on the water-exchange reaction gave an activation volume value near zero ($\Delta V^{\ddagger}$ = −0.4 cm^3 mol^{-1}),[5] suggesting an interchange (I) mechanism. Finally, in studies of the anation of the aquaruthenium(II) ion by the monoanion of oxalic acid,[10] it was pointed out that an attribution of the mechanism as I or I_d may lead to a restricted interpretation of the role played by the entering ligand in influencing the reaction pathway leading to the transition state.

In order to define more clearly the mechanism of substitution reactions of $[\mathrm{Ru(H_2O)_6}]^{2+}$, we have studied by UV–visible spectrophotometric and ^{1}H-NMR methods the monocomplex formation reaction (eq 1) for a series of neutral and positively charged ligands having either a nitrogen or a sulfur as donor atom.

$$[\mathrm{Ru(H_2O)_6}]^{2+} + \mathrm{L}^{n+} \xrightarrow{k_f} [\mathrm{Ru(H_2O)_5L}]^{(2+n)+} + \mathrm{H_2O} \qquad (1)$$

Experimental Section

Chemicals and Solutions. $[\mathrm{Ru(H_2O)_6}](\mathrm{tos})_2$ was prepared using the method described by Bernhard et al.[11] The product was recrystallized in an aqueous solution 1.2 M in *p*-toluenesulfonic acid. The *N*-methylpyrazinium tosylate (NMPtos) was synthesized according to Stoehr.[12] The other ligands, dimethyl sulfoxide (DMSO, Fluka, p.a.), acetonitrile (MeCN, Fluka, p.a.), 1,4-thioxane (Aldrich, 98%), and tetrahydrothiophene (4H-thiophene, Aldrich, 99%) were used as received without further purification.

All solutions were prepared at ambient temperature in a drybox (oxygen content <2 ppm), the oxygen content of the solvent water was eliminated with an argon stream before use, and all kinetic runs were performed under inert atmosphere. All concentrations were determined by weighing and are consequently given in molality (mol (kg of solvent)$^{-1}$). In all solutions, *p*-toluenesulfonic acid (Htos, Fluka, puriss. p.a.) was added (C_{Htos} = 0.1 *m*) to prevent a hydrolytic pathway for the monocomplex formation reaction. For the reaction with NMP$^+$, doubly distilled water and 10% oxygen-17 enriched water (Yeda) were used as the solvents for the spectrophotometric and NMR measurements, respectively. The solvent for the reactions with the other ligands was 99.95% deuterated water.

Kinetic Studies. The monocomplex formation reaction between $[\mathrm{Ru(H_2O)_6}]^{2+}$ and NMP$^+$ (Figure 1) was studied by UV–visible spectrophotometry between 350 and 650 nm using a Perkin-Elmer Lambda 5 spectrophotometer with thermostated cells. To limit the absorbance at a maximum value of 2 and consequently prevent a deviation from the Lambert–Beer law, different lengths of cells were used (1.0, 0.5, and 0.2 cm). Runs were followed over 1–52-h periods between 298 and 328 K. The initial Ru(II) ion concentrations (C_{Ru}) and initial ligand concentrations ($C_{\mathrm{NMP^+}}$) were between 0.008 and 0.047 *m* and between 0.000 10 and 0.000 38 *m*, respectively (ionic strength *I* = 0.13–0.24 *m*).

To check the kinetic data obtained by spectrophotometry, the reaction rate of Ru(II) (0.098 *m*, in excess) with NMP$^+$ (0.063 *m*, *I* = 0.46 *m*) was also measured at 308.2 K by 200-MHz ^{1}H-NMR spectroscopy on a Bruker AC-200 (4.7 T) spectrometer. The nature of the product of this reaction was identified by both 200-MHz ^{1}H-NMR and 27.13-MHz

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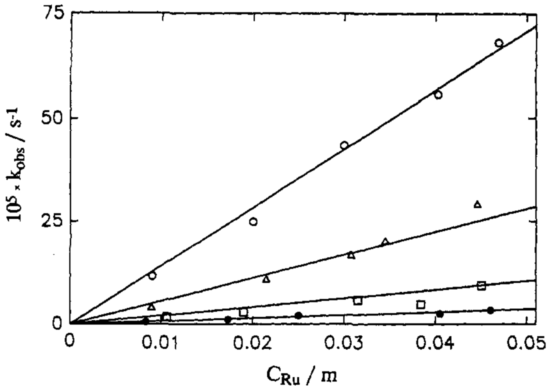

Figure 1. Reaction of $[Ru(H_2O)_6]^{2+}$ with NMP^+: observed pseudo-first-order rate constant, k_{obs}, for the monocomplex formation reaction as a function of C_{Ru} at four different temperatures. T = 298.2 K (●), 308.2 K (□), 318.2 K (△), 328.2 K (○).

^{17}O-NMR spectroscopy on the same apparatus. For the NMR measurements, $[Ru(H_2O)_6](tos)_2$ was first enriched with oxygen-17 by leaving the complex in enriched water at ambient temperature for 0.5 h ($k_{ex}^{H_2O}$ = 0.018 s^{-1} at 298 K).[5] NMP^+ and tosylic acid, dissolved in enriched water, were then added at ambient temperature to the Ru(II) ion solution, and the mixture was transferred into the NMR probe thermostated at 308.2 K for the measurements. The monocomplex formation was monitored by recording alternatively ^1H-NMR and ^{17}O-NMR spectra. The NMR parameters for ^1H (^{17}O) spectra were 16K (2K) data points, 2000-Hz (12 500-Hz) frequency range, 0.3-μs (40-μs) pulse width, and 16 (3500) transients summed.

The monocomplex formation reactions between $[Ru(H_2O)_6]^{2+}$ and the ligands DMSO, MeCN, 1,4-thioxane, and tetrahydrothiophene (I = 0.40 m) were followed by 200-MHz ^1H-NMR spectroscopy on a Bruker CXP-200 (4.7 T) spectrometer with the following parameters: 16K data points, 1700-Hz frequency range, 2-μs pulse width, and 16 transients summed. The complex formation reactions were followed at different temperatures between 278 and 317 K. The NMR temperatures were measured by a substitution technique using a 100-Ω Pt resistor.[13] The chemical shifts are referenced to TMS and measured with respect to the methyl protons of the tosylate anion (δ = 2.38 ppm).

The typical estimated precisions of the individual rate constants are 0.5–1% for UV–visible spectroscopic determinations and 1–2% for the NMR measurements.

Results

The monocomplex formation reaction between $[Ru(H_2O)_6]^{2+}$ and NMP^+ was followed by UV–visible spectroscopy (eq 1a). A

$$[Ru(H_2O)_6]^{2+} + NMP^+ \xrightarrow{k_f} [Ru(H_2O)_5NMP]^{3+} + H_2O \quad (1a)$$

large excess metal concentration was used for every experiment (between 30- and 350-fold), and under these conditions the reaction rate is pseudo-first-order and only the monocomplex is formed. The rate constants for the monocomplex formation were calculated from the absorbance values at 524 nm. Under pseudo-first-order conditions, the variation of the absorbance as a function of time, A_t, can be expressed by eq 2, where A_0 and A_∞ are the

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t) \quad (2)$$

absorbances at the beginning and the end of the reaction, respectively, k_{obs} is the pseudo-first-order rate constant, and t is the time. The calculation of k_{obs} was made with a nonlinear-least-squares fitting program using eq 2 with A_0, A_∞, and k_{obs} as adjustable parameters. The variation of k_{obs} as a function of initial metal concentration, C_{Ru}, is shown in Figure 1 at four different temperatures. In each case, within experimental errors, there is a linear variation of the observed rate constant with C_{Ru}. Therefore, the second-order rate constant for the monocomplex formation, k_f, can be obtained from the slopes (eq 3).

$$k_{obs} = k_f C_{Ru} \quad (3)$$

The enthalpy of activation, ΔH_f^*, and the entropy of activation, ΔS_f^*, for the monocomplex formation reaction (Table I) were calculated by fitting simultaneously all the measured rate constants with eq 4. The error given for the rate constant in

$$k_{obs} = C_{Ru}(k_B T/h)\exp(-\Delta H_f^*/RT + \Delta S_f^*/R) \quad (4)$$

Table I was obtained by repeating the fit with k_f^{298} and ΔH_f^* as adjustables. The lines in Figure 1 were calculated using the ΔH_f^* and the ΔS_f^* values.

The same reaction was followed by ^1H-NMR and ^{17}O-NMR at 308.2 K. The kinetics of the reaction was followed in the proton spectra by monitoring the increase of the intensity of the bound NMP^+ methyl signal at 3.50 ppm (the free NMP^+ peak was hidden by the bulk water signal). The signal of the methyl protons of the tosylate anion, whose concentration, C_{tos}, is known and was constant throughout the experiment, was used as an internal intensity reference, I_{tos}. The monocomplex concentration as a function of time, $[RuNMP^{3+}]$, was calculated from the peak integrals (eq 5). The values obtained were fitted with eq 6, which

$$[RuNMP^{3+}] = C_{tos}I_{RuL}/I_{tos} \quad (5)$$

$$[RuNMP^{3+}] = (C_{Ru}C_{NMP^+}(E-1))/(EC_{NMP^+} - C_{Ru}) \quad (6)$$

$$E = \exp((C_{NMP^+} - C_{Ru})k_f(t - t_0))$$

is the integrated form of a second-order rate law, with k_f and t_0 as adjustable parameters.[14] The rate constant found by ^1H-NMR, $k_f = (1.93 \pm 0.09) \times 10^{-3}\ m^{-1}\ s^{-1}$ at 308.2 K, is in good agreement with the value, $k_f = (2.1 \pm 0.1) \times 10^{-3}\ m^{-1}\ s^{-1}$ at 308.2 K, calculated above from the activation parameters obtained by UV–visible measurements.

The nature of the product of the reaction was checked by comparing the ^1H-NMR and ^{17}O-NMR measurements. The oxygen-17 spectra consist of the signal of bulk water fixed at 0 ppm as a reference, the signal of $[Ru(H_2O)_6]^{2+}$ at −196 ppm,[5] and a third signal at −149 ppm. At any time during the complex formation reaction, the concentrations of $[Ru(H_2O)_6]^{2+}$ and $[RuNMP(H_2O\text{-eq})_4(H_2O\text{-ax})]^{3+}$ are known from the ^1H-NMR kinetic data. The ratios of the integrals of the ^{17}O-NMR signal from the waters in the hexaaqua ion and of the third ^{17}O-NMR signal, measured simultaneously, indicate that the signal at −149 ppm corresponds to the four equatorial water molecules coordinated to one Ru(II) in a monocomplex (the signal of the axial water molecule is probably hidden by bulk water, as can be inferred from previous studies on other complexes).[15,16]

The reactions of $[Ru(H_2O)_6]^{2+}$ with DMSO, MeCN, 1,4-thioxane, and tetrahydrothiophene were followed by 200-MHz ^1H-NMR. For each reaction, a small excess metal concentration was used (between 1.1- and 1.9-fold) to prevent biscomplex formation. The typical time evolution of a monocomplex

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Table I. Rate Constants and Activation Parameters for the Monocomplex Formation Reactions of $[Ru(H_2O)_6]^{2+}$ with Different Ligands L in Aqueous Solutions

L	$10^3k_f^{298}/m^{-1}\ s^{-1}$	ΔH_f^*/kJ mol^{-1}	ΔS_f^*/J K^{-1} mol^{-1}	$K_{os}{}^a/m^{-1}$	$10^3k_I^{298\ b}/s^{-1}$	I/m	ref
Cl^-	8.5^c	84.4	−2	1	9	0.3	9
Br^-	10.2^c	82.8	−5	1	10	0.3	9
I^-	9.8^c	81.5	−10	1	10	0.3	9
(oxalate)H$^-$	26^c	101.1	+65	2	13	1.0	10
H_2O		88	+9		18^d	1.0	5
MeCN^e	2.07 ± 0.09	81.1 ± 2	−24 ± 8	0.16	13	0.2–0.4	this work
DMSO^e	1.31 ± 0.03	87.3 ± 2	−7 ± 5	0.16	8	0.4	this work
1,4-thioxane^e	2.2 ± 0.2	82.4 ± 4	−2 ± 12	0.16	14	0.4	this work
4H-thiophene^e	2.4 ± 0.1^f			0.16	15	0.4	this work
maleic acid^e	2.18^c	84	−15	0.16	14	0.7	17
fumaric acid^e	1.72^c	128	+133	0.16	11	0.6	17
2,5-dihydrofuran^e	1.06^c	126	+120	0.16	7	1.0	17
NMP$^+$	0.73 ± 0.08	77.7 ± 3	−44 ± 9	0.02^g	40	0.1–0.2	this work

[a] K_{os} calculated using the Eigen–Fuoss relation for the reaction of $[Ni(H_2O)_6]^{2+}$ with similar ligands.[18] [b] Calculated with the relation $k_f^{298} = K_{os}k_I^{298}$. [c] dm^3 mol^{-1} s^{-1}. [d] Rate constant for the exchange of a particular water molecule[19] as obtained from ^{17}O isotopic labeling NMR kinetic experiments. [e] In D_2O. [f] Estimation from the value at 302.0 K, $k_f^{302.0} = 3.79 \pm 0.04\ m^{-1}\ s^{-1}$, with $\Delta H_f^* = 82.4$ kJ mol^{-1} (see 1,4-thioxane). [g] According to a reviewer, it could be questioned whether the "ion-pair model" is still useful with an association constant calculated to be 0.02 m^{-1}. This K_{os} value should therefore not be given too much importance.

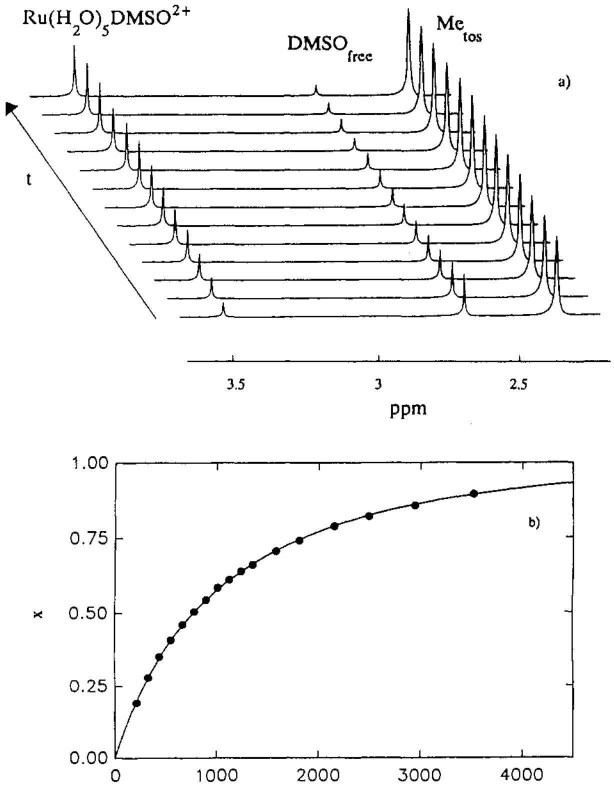

Figure 2. (a) Stacked plot of the 200-MHz ^{1}H-NMR spectra showing the evolution as a function of time, at 317.1 K, of the reaction taking place in a deuterated water solution containing initially 0.097 *m* $[Ru(H_2O)_6]^{2+}$, 0.063 *m* DMSO, and 0.101 *m* *p*-toluenesulfonic acid. The time interval between two spectra is 228 s. (b) Mole fraction of bound DMSO as a function of time for the system described in (a).

formation reaction with the progressive disappearance of the free-ligand signal and appearance of the bound-ligand signal is shown in Figure 2a. For the four ligands used, the signal of the bound species always appears at a lower field than the signal of the free species. The chemical shifts, measured with respect to the methyl protons of the tosylate anion, were 3.55 and 2.97 ppm for the singlets of bound DMSO and bound MeCN, respectively, 2.98 and 4.27 ppm for the two multiplets of bound 1,4-thioxane, and 2.16 and 3.03 ppm for the two multiplets of bound tetrahydrothiophene.

The mole fraction of bound ligand, x_{RuL}, was calculated throughout an experiment from the integrals of the signals (eq 7). The ratio of the sum of the integrals of the bound and free signals compared to the integral of the signal of the methyl protons of the tosylate anion was found to be constant throughout each experiment, within experimental errors. Thus, there was no

$$x_{RuL} = I_{RuL}/(I_{RuL} + I_L) \qquad (7)$$

evidence of biscomplex formation or side reactions. For a small excess metal concentration, the kinetics of the reaction follow a second-order rate law (eq 8), where [Ru], [L], and [RuL] are

$$d[RuL]/dt = k_f[Ru][L] \qquad (8)$$

the concentrations as a function of time of Ru(II), of the ligand, and of the monocomplex, respectively. The time evolution of the reactant concentrations can be described by the integral of eq 8 (eq 9) as a function of initial Ru(II) concentration, C_{Ru}, and

$$(1/(C_L - C_{Ru}))\ \ln(C_{Ru}[L]/C_L[Ru]) = k_f t \qquad (9)$$

initial ligand concentration, C_L. Since the monocomplex is the only significant product of the reaction, eqs 10 and 11 apply.

$$C_L = [L] + [RuL] \qquad (10)$$

$$C_{Ru} = [Ru] + [RuL] \qquad (11)$$

Combination of eqs 9–11 gives the evolution of the molar fraction of bound ligand (eq 12). The experimental data obtained from

$$x_{RuL} = [RuL]/C_L = C_{Ru}(E - 1)/(EC_L - C_{Ru}) \qquad (12)$$

$$E = \exp(k_f(t - t_0)(C_L - C_{Ru}))$$

eq 7 were analysed with a nonlinear-least-squares fitting program using eq 12 with k_f and t_0 as adjustable parameters.[14] An example fit is shown in Figure 2b. From variable-temperature studies, the enthalpies of activation (ΔH_f^*) and the entropies of activation (ΔS_f^*) were calculated using Eyring's equation (eq 13). The fits

$$\ln(k_f/T) = \ln(k_B/h) + (-\Delta H_f^*/RT + \Delta S_f^*/R) \qquad (13)$$

are presented in Figure 3. The different kinetic parameters measured are reported in Table I. As for the reaction with NMP$^+$, the errors for the rate constants are obtained by repeating the fit with k_f^{298} and ΔH_f^* as adjustable parameters.

Discussion

The different rate constants and activation parameters available for monocomplex formation reactions of $[Ru(H_2O)_6]^{2+}$ are

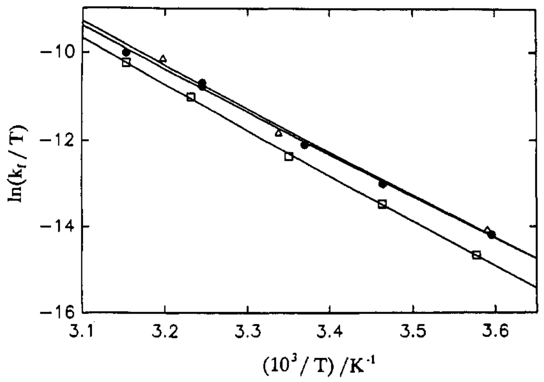

Figure 3. Eyring plots of the forward rate constant, k_f, for the formation of $[Ru(H_2O)_5L]^{2+}$. L = DMSO (□), MeCN (●), 1,4-thioxane (▲).

summarized in Table I. It can be seen that, for identically charged ligands, the second-order rate constants are quite similar even though the ligands are very different. This seems to indicate that the entering group has little influence on the transition state. However, the charge of the ligands seems to influence the rate of the reaction. This effect can be rationalized with the Eigen–Wilkins model[20] where the reaction of the ligand proceeds via the formation of an outer-sphere complex. The rate constant of the rate-limiting step (i.e. the ligand-interchange process), k_I, can be expressed by eq 14, where K_{os} is the equilibrium constant of the

$$k_f^{298} = K_{os}k_I^{298} \tag{14}$$

outer-sphere complex formation. This equilibrium constant has already been calculated using the Fuoss equation[21] for complex formation reactions of $[Ni(H_2O)_6]^{2+}$.[22] As Ni(II) and Ru(II) have similar ionic radii and identical charge, the K_{os} values should not differ widely for the two cations, and so, in Table I, we report the values calculated for the reactions with Ni(II) and the resulting k_I values. Since the values of the rate constants for the interchange process, k_I, are seen to be very similar and the small differences observed can be explained by the uncertainty of the calculated K_{os} values (these values are usually considered to be known within a factor of 2–4),[23] we can assign a dissociative interchange mechanism, I_d. This assignment is in contradiction with the conclusion of a previous study of the pressure dependence of the water-exchange rate of $[Ru(H_2O)_6]^{2+}$,[5] where an interchange, I, mechanism was inferred from the volume of activation for the exchange reaction ($\Delta V^{\ddagger} = -0.4 \pm 0.6$ cm^3 mol^{-1}). In a study of the aquation reactions of $[Co(NH_3)_5L]^{n+}$ (n = +1, +2, +3),[24] the authors measured the activation volumes of these reactions and estimated the difference between the molar volume of the hexaammine complex and the pentaammine intermediate ($V_c([Co(NH_3)_6]^{3+}) - V_c([Co(NH_3)_5]^{3+})$) to be equal to 17-20 cm^3 mol^{-1}. If we suppose for our case a dissociative mechanism, D, the activation volume of the water-exchange reaction may be written as

$$\Delta V^{\ddagger} = V_c([Ru(H_2O)_5]^{2+}) + V_c(H_2O) - V_c([Ru(H_2O)_6]^{2+}) \tag{15}$$

If we have for eq 15 the same volume difference between the hexacoordinated and the pentacoordinated species as for the cobalt reactions, knowing that the molar volume of water is equal to 18 cm^3 mol^{-1}, we can obtain an activation volume value near zero. Thus, the zero value of the activation volume may be supposed to be due to the compensation between a positive contribution (the loss of a water molecule) and a negative one (the contraction of the complex at the transition state). This explanation is still valid for an I_d mechanism, but in this case the $V_c(H_2O)$ value is smaller than for a dissociative process, since a part of the molecule remains in the environment of the metal cation. The value can be approximated to 15 cm^3 mol^{-1}.[24] The volume difference between hexaaquaruthenium(II) and the intermediate cation is also smaller for an I_d than for the D mechanism since, at the transition state, the complex has not enough time to reorganize. Therefore, a zero value for the activation volume is also plausible for the I_d mechanism.[25]

The mechanism proposed is the same as for substitution reactions of pentaammineaquaruthenium(II).[26] The observed second-order rate constant is about 1 order of magnitude lower for substitution reactions of the hexaaqua complex. The reactivity difference between the two species explains why dinitrogen was fixed to pentaammineaquaruthenium(II) a long time ago[27] while (dinitrogen)aquaruthenium(II) was prepared only very recently.[15] For a dinitrogen solubility of 6.57×10^{-4} M at 1 atm and 25 °C[28] and a $[Ru(H_2O)_6]^{2+}$ concentration of 0.1 M, the half-life of the reaction is several days. Consequently, it is necessary to have a high dinitrogen pressure to prepare the $[Ru(H_2O)_5N_2]^{2+}$ species.

The binding mode of the ligands in Table I needs further discussion. Maleic acid, fumaric acid, and 2,5-dihydrofuran are η^2-coordinated to ruthenium with their π-bonds.[17] Water is bound via the oxygen atom, MeCN and NMP^+ are bound via a nitrogen atom, and tetrahydrothiophene is bound via the sulfur atom. The case of DMSO is ambiguous, since it can bind via the sulfur or the oxygen atom. Both cases have already been encountered for complexes of ruthenium(II) and DMSO[29,30] although the S-bonded form is the rule. NMR and IR spectrometry can usually be used to distinguish between the two possibilities.[31] In the NMR spectra, the difference of 0.84 ppm observed between the singlets of bound and free DMSO (3.55 and 2.71 ppm, respectively) can be attributed to the S-bonded species (for the O-bonded species the methyl resonance is scarcely shifted).[31] In the IR spectrum of $[Ru(H_2O)_5(DMSO\text{-}d_6)](tos)_2$, the absorption observed at 1054 cm^{-1} due to the S=O stretching cannot be used alone for the attribution of the binding atom, but combining this with the NMR measurements, one can conclude that the DMSO ligand is bound to Ru(II) most probably via its sulfur atom.[31,32] In the case of 1,4-thioxane, in order to determine whether it is bound via the oxygen or the sulfur atom, we have tried to perform a complex formation reaction between $[Ru(H_2O)_6]^{2+}$ and dioxane. After 1 day at ambient temperature, no bound dioxane was detectable in the NMR spectra. From this, we conclude that 1,4-thioxane binds via the sulfur atom.

This kinetic study was performed with an excess metal concentration. Trials with an excess ligand concentration led to two situations. With dimethyl sulfoxide, a 3-fold excess ligand concentration did not produce further complexation after 3 days at ambient temperature. With acetonitrile, a 4-fold excess ligand concentration led to the formation of many different species. In the NMR spectra, we see the appearance of several peaks showing

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a decrease in the chemical shifts with an increase of the number of bound MeCN molecules (all the signals appeared between the signal of the monocomplex, $\delta = 2.37$ ppm, and the signal of free acetonitrile, $\delta = 2.06$ ppm). The difference in behavior between DMSO and MeCN may result from the greater steric hindrance of the former and better π-accepting capability of the latter.

In conclusion, the large diversity of the ligands in Table I should be stressed. First, there are the negatively charged ligands, the halides. Second, the binding sites of the neutral ligands are very different: the nitrogen of a nitrile group (MeCN), the sulfur of a sulfoxide (DMSO), the sulfur of a sulfide (1,4-thioxane, tetrahydrothiophene), the oxygen of the water molecule, and the π-bond of some unsaturated molecules. Moreover, the reaction was also performed between two positively charged entities ($[Ru(H_2O)_6]^{2+}$ and the cyclic amine ligand NMP^+). This variety of incoming groups lends support to our use of the similarity of the interchange rate constants, k_I, as a criterion for the determination of the mechanism of the substitution reactions of $[Ru(H_2O)_6]^{2+}$ which can be assigned as I_d.

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Supplementary Material Available: Initial reactant concentrations, ionic strengths, and rate constants as a function of temperature for the reactions of $[Ru(H_2O)_6]^{2+}$ with NMP^+, MeCN, DMSO, 1,4-thioxane, and tetrahydrothiophene (Tables SI–SV) (3 pages). Ordering information is given on any current masthead page.